# Syntheses of Nonracemic Ortho-Mercurated and Ortho-Ruthenated Complexes of 2-[Tricarbonyl($\eta^6$-phenyl)chromium]pyridine

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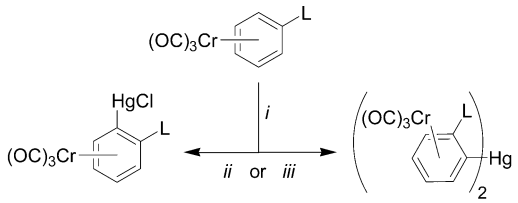
The reaction of racemic orthomercurated ($\eta^6$-arene)tricarbonylchromium complexes with bis[($\eta^6$-cymene)ruthenium(II)dichloride] affords the corresponding dinuclear (Cr,Ru) products with moderate yields, which have been satisfactorily characterized by X-ray diffraction analysis. The synthesis of nonracemic orthomercurated ($\eta^6$-arene)tricarbonylchromium complexes has been attempted starting from enantio-enriched homo- and heteroleptic Pd(II) bischelated complexes. Both enantiomers of ortho-mercurated 2-[tricarbonyl($\eta^6$-phenyl)chromium]pyridine have been synthesized by reaction of a heteroleptic Pd(II) bischelated with $HgCl_2$. The two mercury(II) complexes were also submitted to a transmetalation reaction with bis[($\eta^6$-cymene)ruthenium(II)dichloride] and yielded the corresponding nonracemic (Cr,Ru) products, with enantiomeric excesses ranging from 82 to 89% as suggested by $^1$H NMR analyses in the presence of BINPHAT anion.



## Introduction

The deprotonation−lithiation of ($\eta^6$-arene)tricarbonylchromium complexes can be achieved with great enantioselectivity, as demonstrated by many authors in the recent past,[1] to afford valuable planar-chiral lithio($\eta^6$-arene)tricarbonylchromium intermediates. To the best of our knowledge, however, there have been no extensive reports on the use of such enantio-enriched reactive species in preparative transmetalation reactions, although many examples of such reactions are known in the racemic series.[2] Recently, it was reported that the ortho mercuration of tricarbonyl($\eta^6$-arene)chromium complexes was readily achievable with a series of substrates by a reaction with mercury(II) acetate in technical grade absolute alcohol at moderately high temperatures (Scheme 1);[3] the resulting ortho-mercurated compounds are convenient substrates for the preparation of a large variety of ortho-metalated complexes by transmetalation.[4] Although the mercuration of ($\eta^6$-arene)tricarbonylchromium complexes offers the advantage of providing rather air-resistant substrates, the versatility and the ability of the corresponding mercurated complexes to exchange the Hg(II) center for transition metals different from Pd(II) still have to be further investigated.

**Scheme 1**




*i*: $Hg(OAc)_2$, EtOH, 50 °C. *ii*: $CaCl_2$, EtOH. *iii*: KI excess, EtOH

In parallel, several reports have emphasized the high enantioselectivities achievable in organic transformations with Lewis-acidic catalysts based on planar-chiral palladated aromatics.[5] This upsurge of interest for nonracemic metalated metallocenic or half-sandwich

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10.1021/om0494667 CCC: $27.50 
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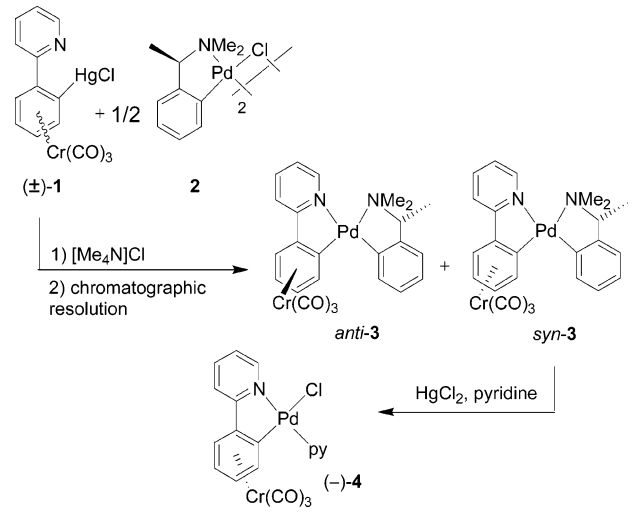
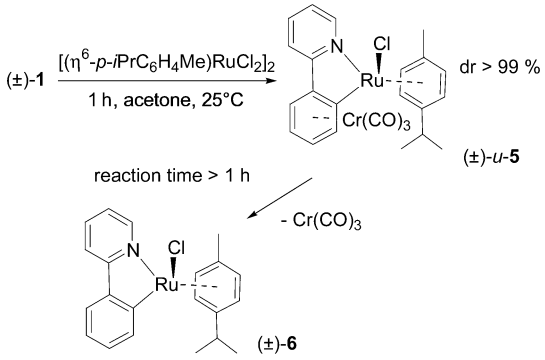
**Scheme 2**




**Scheme 3**




complexes raises the challenge of establishing efficient synthetic methods. This has motivated our quest for reliable procedures of preparation of nonracemic planar-chiral transition metal chelates (e.g., **4**, Scheme 2) starting from readily available and air-stable ortho-chloromercurated ($\eta^6$-arene)$Cr(CO)_3$ complexes (e.g., **1**, Scheme 2), via enantiopure diastereomeric intermediates, such as **3** (Scheme 2).[6] As the main difficulty in the preparation of nonracemic ortho-metalated complexes is the resolution step, we decided to combine chemical and chromatographic resolution methods using chiral hetero-bischelated Pd(II) complexes as key intermediates. Herein, we disclose a series of results on the reactivity of ortho-mercurated ($\eta^6$-arene)tricarbonylchromium complexes toward bis[($\eta^6$-cymene)ruthenium(II)dichloride]. We also describe the synthesis of nonracemic ortho-mercurated ($\eta^6$-arene)tricarbonylchromium complexes and their application to the synthesis of enantio-enriched cycloruthenated complexes.

## Results and Discussion

**Replacement of "HgCl" by "[($\eta^6$-*p*-*i*$PrC_6H_4Me$)RuCl]" in the Racemic Series.** Direct ortho-ruthenation by C−H bond activation with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in basic conditions in the presence of potassium hexafluorophosphate is the most direct way to introduce efficiently a Ru(II) center on dimethylbenzylamine derivatives.[7] Unfortunately, in our hands, application of this method to 2-phenylpyridine moieties afforded cycloruthenation products only in moderate yields after 20 h of reaction.[7b] Furthermore, the use of acetonitrile as a solvent caused the loss of the $\eta^6$-bonded arene ligand.

We also found that the direct ruthenation of either 2-[tricarbonyl($\eta^6$-phenyl)chromium]pyridine or [tricarbonyl($\eta^6$-*N*,*N*-dimethylbenzylamine)chromium] by C−H activation in basic conditions afforded only decomposition of the starting chromium complexes and intractable greenish insoluble residues. This led us to look for an alternative synthetic procedure. Much better results were obtained by transmetalation starting from **1** (Scheme 3).[8]

The reaction time had to be limited to ca. 1 h in order to minimize the extent of decomposition and preserve an optimal yield of ca. 70% in "metal-exchange" product **5**. In this case, the main decomposition process in acetone was the loss of the $Cr(CO)_3$ moiety and the formation of **6**. This was readily observed when the reaction medium was left to react overnight at room temperature. The peculiar chemical instability of **5**, which was also observed in other solvents such as $CH_2Cl_2$ and $Et_2O$ and also in the absence of light, implied that its purification be carried out by flash chromatography at low temperature and by swift recrystallization. Of course, it was verified experimentally that compound **6** could also be synthesized starting from **7**.[9] Depending on whether $[Me_4N]Cl$ was present in the medium or not (Scheme 4), the transmetalation gave two slightly different products.

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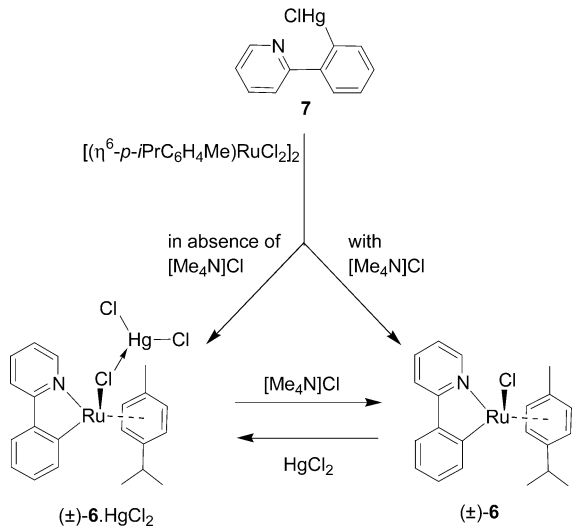
**Scheme 4**




When the reaction was carried out in the absence of chloride salt, the main product was the adduct **6**·$HgCl_2$. In the presence of chloride the only product obtained was compound **6**. Consistently, adduct **6**·$HgCl_2$ could readily be either dismantled by treatment with excess of $[Me_4N]Cl$ or formed upon stoichiometric reaction of **6** with $HgCl_2$. It is known that chloride ion enables the trapping of $HgCl_2$ and the subsequent formation of its insoluble conjugated Lewis-base, e.g., $HgCl_3^-$, also formulated as $Hg_2Cl_6^{2-}$.[10] Recrystallization of both complexes **6** and **6**·$HgCl_2$ provided crystals, which were analyzed by X-ray diffraction. ORTEP diagrams of the latter two Ru(II) complexes are displayed in Figures 1 and 2. Relevant acquisition and refinement parameters are listed in Table 1. Analyzing these structures, it is clear that in **6**·$HgCl_2$ the interaction of mercuric chloride with the chloro ligand induces only a slight increase of the Cl−Ru distance of about 0.02 Å and a decrease of the $C_{ipso}$−Ru distance of about 0.01 Å as compared to **6**. In the adduct, the mercury center sits in a distorted trigonal planar environment surrounded by three Cl atoms, among which two are ca. 2.35 Å from the mercury center. The third chloro group, also bonded to

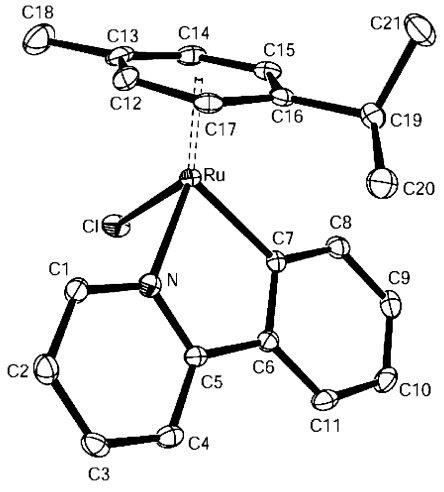



**Figure 1.** ORTEP diagram for complex **6**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angle (deg): Ru−C(7), 2.062(2); Ru−Cl, 2.4154(7); C(7)−Ru−N, 77.66(9); C(6)−C(7)−C(8), 117.3(2).

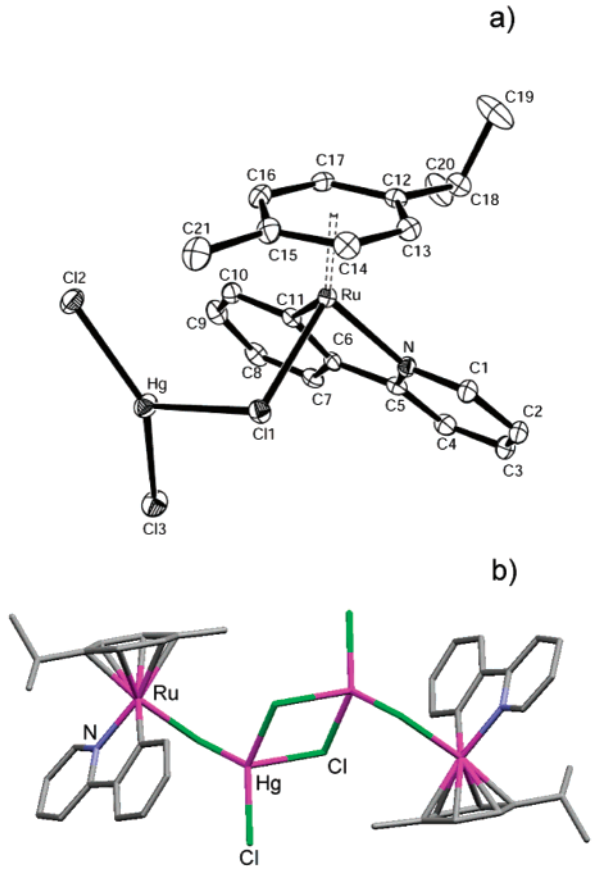
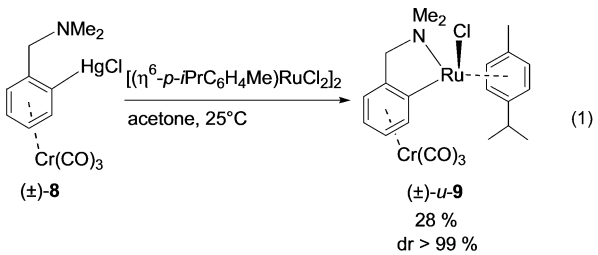



**Figure 2.** Upper view (a): ORTEP diagram for complex **6**·$HgCl_2$. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms and molecules of solvent have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ru−C(11), 2.051(3); Ru−Cl(1), 2.4396(9); Hg−Cl(1), 2.6088(3); Hg−Cl(2), 2.3751(3); Hg−Cl(3), 2.3375(3); C(11)−Ru−N, 77.9(1); Cl(2)−Hg−Cl(3), 142.63(1); C(10)−C(11)−C(6), 116.9(3). Lower view (b): CSD *Mercury* "capped sticks" view of the inversion-related dimer [**6**·$HgCl_2$]$_2$: blue, nitrogen; green, chlorine; gray, carbon; pink, metals

ruthenium, is ca. 2.61 Å from mercury. In the crystal cell, two independent molecules are related by an inversion center located in the vicinity of the quasi trigonal $HgCl_3$ fragment. Two neutral $HgCl_3$ fragments interact in a way similar to that of the $HgCl_3^-$ anion in its related dimer $Hg_2Cl_6^{2-}$.[10] In the inversion-related dimer [**6**·$HgCl_2$]$_2$, the "bridging" Hg−Cl distance amounts to about 3 Å, which is longer than in dianionic $Hg_2Cl_6^{2-}$ by only ca. 0.2−0.5 Å.[11]




Worthy of note, the reaction of **1** with [(η⁶-*p*-*i*PrC$_6$H$_4$Me)RuCl$_2$]$_2$ did not lead to the formation of an adduct with $HgCl_2$ probably as a result of the strong electron-

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**Table 1. Acquisition and Refinement Data for the X-ray Diffraction Analyses of 5, 6, 6·$HgCl_2$, 9, 10, and (p*S*)-1**

| | *u*-**5** | **6** | **6**·$HgCl_2$ |
|---|---|---|---|
| formula | $2(C_{24}H_{22}ClCrNO_3Ru)\cdot CH_2Cl_2$ | $C_{21}H_{22}ClNRu$ | $C_{21}H_{22}Cl_3HgNRu\cdot CH_2Cl_2$ |
| mol wt | 1206.87 | 424.94 | 781.37 |
| cryst syst | triclinic | monoclinic | triclinic |
| space group | $P\bar{1}$ | $P2_1/c$ | $P\bar{1}$ |
| *a* (Å) | 10.7708(4) | 16.5286(2) | 9.3773(2) |
| *b* (Å) | 11.0259(5) | 7.8387(2) | 11.4892(2) |
| *c* (Å) | 11.2497(7) | 15.0003(4) | 11.7871(3) |
| α (deg) | 85.299(5) | | 92.349(5) |
| *β* (deg) | 80.929(5) | 111.215(5) | 94.701(5) |
| *γ* (deg) | 65.830(5) | | 96.020(5) |
| *V* (Å$^3$) | 1203.4(1) | 1811.77(7) | 1257.09(5) |
| *Z* | 1 | 4 | 2 |
| color | orange | orange | orange |
| cryst dimens (mm) | 0.16 × 0.12 × 0.08 | 0.18 × 0.12 × 0.08 | 0.20 × 0.18 × 0.12 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.67 | 1.56 | 2.06 |
| $F_{000}$ | 606 | 864 | 744 |
| *μ* (mm$^{-1}$) | 1.328 | 1.014 | 7.242 |
| transmn min. and max. | 0.9627/1.0000 | 0.9738/1.0000 | 0.250/0.419 |
| *hkl* limits | −13,10/−14,9/−14,14 | −19,19/−10,8/−21,21 | −12,12/−15,15/−16,12 |
| *θ* limits (deg) | 2.5/27.44 | 2.5/27.49 | 2.5/29.12 |
| no. of data measd | 6739 | 7663 | 9045 |
| no. of data with $I > 3\sigma(I)$ | 3522 | 3136 | 5094 |
| no. of variables | 304 | 217 | 271 |
| *R* | 0.041 | 0.025 | 0.027 |
| $R_w$ | 0.055 | 0.032 | 0.031 |
| GOF | 1.091 | 1.159 | 1.027 |
| largest peak in final diff (e Å$^{-3}$) | 1.114 | 0.622 | 0.842 |

| | *u*-**9** | **10** | (p*S*)-**1** |
|---|---|---|---|
| formula | $C_{22}H_{26}ClCrNO_3Ru$ | $C_{22}H_{25}Cl_2CrHgNO_3Ru\cdot 2CH_2Cl_2$ | $C_{14}H_8ClCrHgNO_3$ |
| mol wt | 540.98 | 945.88 | 526.26 |
| cryst syst | orthorhombic | triclinic | monoclinic |
| space group | $P2_1\,2_1\,2_1$ | $P\bar{1}$ | $P2_1$ |
| *a* (Å) | 6.8552(1) | 10.5002(2) | 7.4678(3) |
| *b* (Å) | 12.8758(2) | 11.8848(2) | 7.4018(4) |
| *c* (Å) | 24.8345(5) | 13.7371(2) | 13.1418(5) |
| α (deg) | | 78.926(5) | |
| *β* (deg) | | 67.892(5) | 98.381(5) |
| *γ* (deg) | | 71.869(5) | |
| *V* (Å$^3$) | 2192.05(6) | 1503.90(4) | 718.66(6) |
| *Z* | 4 | 2 | 2 |
| color | orange | dark red | yellow |
| cryst dimens (mm) | 0.20 × 0.06 × 0.04 | 0.14 × 0.11 × 0.09 | 0.08 × 0.06 × 0.06 |
| $\rho_{calc}$ (g cm$^{-3}$) | 1.64 | 2.09 | 2.43 |
| $F_{000}$ | 1096 | 908 | 488 |
| *μ* (mm$^{-1}$) | 1.329 | 6.503 | 11.616 |
| transmn min. and max. | 0.909/0.948 | 0.9798/1.0000 | 0.438/0.498 |
| *hkl* limits | −9,9/−18,18/−34,34 | −13,13/−15,15/−17,17 | −10,10/−9,10/−18,18 |
| *θ* limits (deg) | 2.5/30.03 | 2.5/27.48 | 2.5/29.98 |
| no. of data measd | 6351 | 9840 | 3460 |
| no. of data with $I > 3\sigma(I)$ | 3060 | 6122 | 3088 |
| no. of variables | 262 | 334 | 189 |
| *R* | 0.026 | 0.030 | 0.027 |
| $R_w$ | 0.033 | 0.061 | 0.033 |
| GOF | 1.058 | 1.225 | 1.077 |
| largest peak in final diff (e Å$^{-3}$) | 0.360 | 1.441 | 1.537 |

withdrawing effect of $Cr(CO)_3$, which strengthens the Ru−Cl bond and makes less electron density available for an interaction with the mercury(II) center. Similarly to **1**, complex **8** reacted with $[(\eta^6\text{-}p\text{-}i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}_2]_2$ to afford a single product **9** in about 28% yield after chromatographic purification (eq 1).

The relative stereochemistry of the stereogenic elements contained in both **5** and **9** was firmly established through X-ray diffraction analyses of their respective crystals. Figures 3 and 4 display the ORTEP diagrams for complexes **5** and **9**, respectively. In both cases the chloro ligand attached to the ruthenium atom is located anti with respect to the $Cr(CO)_3$ moiety, thus conferring to both complexes a relative "*u*" stereochemistry.[12] Other possible "*l*" diastereomers with the Ru-bound chloro ligand in a syn relationship with respect to the $Cr(CO)_3$ moiety of either **5** or **9** were not detected by $^1$H NMR spectroscopy. Although at this stage one cannot rule out their existence in solution as a consequence of a possible swift inversion of configuration at the ruthenium center, their formation is unlikely or at least thermodynamically disfavored due to the strong steric interactions that would arise between the chloro ligand and the $Cr(CO)_3$ group.

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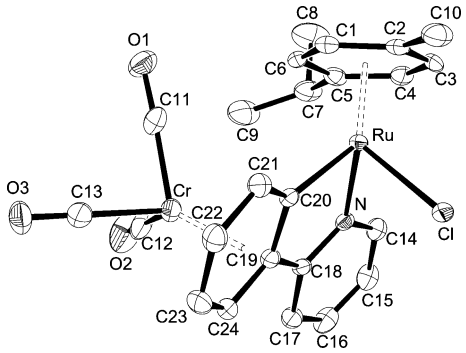



**Figure 3.** ORTEP diagram for complex (*rel*)-*u*-**5**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms and molecules of solvent have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ru−C(20), 2.048(5); Ru−Cl, 2.416(1); Cr−C(20), 2.328(5); N−Ru−C(20), 78.4(2); C(21)−C(20)−C(19), 116.1(4).

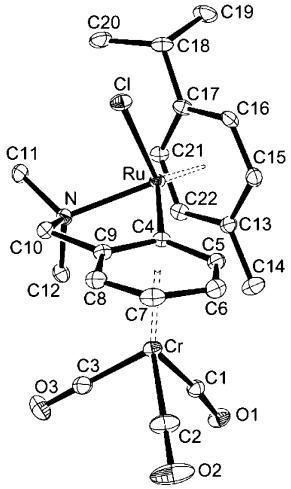



**Figure 4.** ORTEP diagram for complex (*rel*)-*u*-**9** (Flack's parameter $x = 0.45(4)$). Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ru−C(4), 2.078(4); Ru−Cl, 2.4327(9); Cr−C(4), 2.397(3); C(4)−Cl, 3.039(4); C(9)−C(4)−C(5), 116.0(3); N−Ru−C(4), 84.50(9).

The configurational lability of the ruthenium center in similar half-sandwich complexes has been thoroughly studied[13] and firmly established with less entangled chelates of the benzylamine series.[14] However, information is still lacking for similar C,N-heterochelates of the 2-phenylpyridine series.

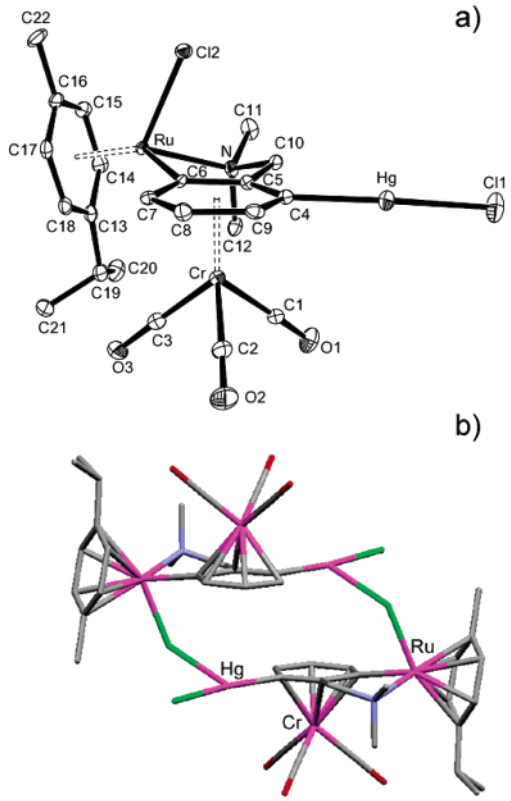
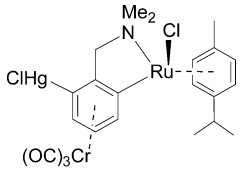



**Figure 5.** (a) ORTEP diagram for complex **10**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms and molecules of solvent have been omitted for clarity. Selected interatomic distances (Å) and angles (deg): Ru−C(6), 2.074(4); Ru−Cl, 2.433(1); Cr−C(6), 2.322(4); Cr−C(4), 2.230(5); C(7)−C(6)−C(5), 117.1(4); C(5)−C(4)−C(9), 119.2(4); N−Ru−C(6), 78.5(2); C(4)−Hg, 2.076(5); Hg−Cl(1), 2.311(5). (b) CSD *Mercury* "capped sticks" view of the inversion-related dimer [**10**]$_2$: blue, nitrogen; green, chlorine; gray, carbon; pink, metals

Noteworthy, while sorting a batch of crystals of complex **9** for X-ray analysis, a set of homomorphic darker crystals representing ca. 1−2% of the overall mass were noticed. The identity of the latter was established by X-ray diffraction analysis as being that of hetero-trinuclear complex *u*-**10** (Figure 5). The chemical purity of complex **8**, originating from **11** (eq 2) was promptly investigated by $^{13}C$ and $^{199}Hg$ NMR spectroscopy, and a slight contamination by a second mercurated compound, putatively **12**, the possible precursor of **10**, was revealed.

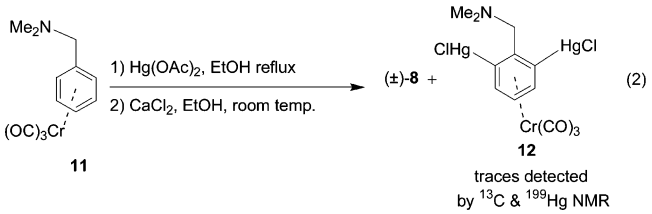



(±)-*u*-**10**

(12) (a) Throughout this article, the stereodescriptor "*l*" (like) is used for diastereomers with two stereogenic centers of identical configurations (either both "*R*" or both "*S*"). With diastereomers possessing combined "p*R*" and "$R_{Ru}$" or "p*S*" and "$S_{Ru}$" configurations, "*l*" is also used. The antonym "*u*" (unlike) is used whenever the configurations of the two stereogenic centers are different. For references: Eliel, E. L.; Wilen, S. H. In *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994. (b) Configurations at the ruthenium, in complexes such as **5**, are obtained by applying the so-called Cahn−Ingold−Prelog rule extended to half-sandwich complexes, considering the hapto-6 bonded cymene ligand as having priority order 1. In complex **5**, the priority order around the Ru(II) center is for instance (1) cymene; (2) Cl; (3) $N_{py}$; (4) $C_{ipso-Cr}$. Further reading: *IUPAC*, *Nomenclature of Inorganic Chemistry*, *Recommendations 1990*; Leigh, G. J., Ed.; Blackwell Scientific Publications: Oxford, UK, 1991.

(13) (a) Brunner, H.; Oeschley, R.; Nuber, B. *Inorg. Chem.* **1995**, *34*, 3349−3351. (b) Brunner, H. *Angew. Chem.* **1999**, *111*, 1248−1263; *Angew. Chem., Int. Ed.* **1999**, *38*, 1194−1208. (c) Brunner, H.; Klankermayer, J.; Zabel, M. *Organometallics* **2002**, *21*, 5746−5756. (d) Brunner, H.; Zwack, T.; Zabel, M.; Beck, W.; Böhm, A. *Organometallics* **2003**, *22*, 1741−1750. (e) Faller, J. W.; Parr, J.; Lavoie, A. R. *New J. Chem.* **2003**, *27*, 899−901.

(14) (a) Brunner, H.; Zwack, T. *Organometallics* **2000**, *19*, 2423−2426. (b) Pfeffer, M. *Organometallics* **2000**, *19*, 2427. (c) Ritleng, V.; Bertani, P.; Pfeffer, M.; Sirlin, C.; Hirschinger, J. *Inorg. Chem.* **2001**, *40*, 5117−5122. (d) Robitzer, M.; Ritleng, V.; Sirlin, C.; Dedieu, A.; Pfeffer, M. *C. R. Chimie* **2002**, *5*, 467−472.



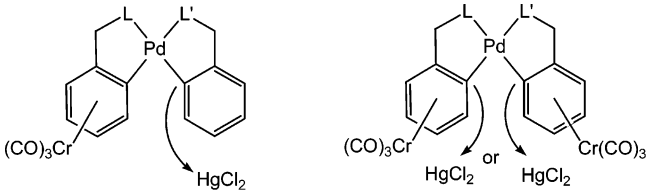

A series of low-intensity signals in the $^{13}C$ NMR spectrum (measured in $d_6$-acetone) of **8** were detected but not assigned with certainty, as they were partly hidden in the baseline's noise. However, a signal plausibly arising from the $Cr(CO)_3$ moiety of **12** at 232.7 ppm was detected nearby a stronger signal generated by **8** at 235.2 ppm. In addition, the analysis of our batch of **8** by $^{199}Hg$ NMR spectroscopy (in $d_6$-acetone) revealed a weak signal at $\delta$ −958 ppm near the intense singlet produced by **8** at $\delta$ −963 ppm. Unfortunately, all attempts to prepare **12** in sufficient amounts failed, which undermined its full characterization.

**Molecular Structures of Complexes 5, 9, and 10.** The coordination of a $Cr(CO)_3$ moiety to the aryl fragment bonded to the ruthenium does not affect significantly the $C_{ipso}$−Ru bond. For instance the latter interatomic distance in **5** is only 0.02 Å shorter than in **6**. With **9**, we have a similar trend, with the $C_{ipso}$−Ru bond being roughly as long as in the structure of a parent $Cr(CO)_3$-free complex reported elsewhere.[8] Larger differences are observed however for the bite angle N−Ru−$C_{Ar}$ of **9**, which amounts to 84.5° and only 74° in a $Cr(CO)_3$-free analogue. The same angle in **10** amounts to only 78°. No important distortions of the $\pi$-coordinated arene are noticed, although the $Cr(CO)_3$ fragment is in most cases slightly tilted away from the substituted position of the arene ligand (cf. Supporting Information). Interestingly, in the unit cell of the analyzed crystal of **10**, two molecules are related by an inversion center located at equal distance from the mercury-substituted arene carbon atom C(4) of inversion-related molecules. In fact, **10** can be considered as a true molecular dimer in the chemical sense, in which chloro-to-mercury Hg−Cl(2) distances of ca. 2.99 Å are similar to those observed with **6**·$HgCl_2$ and thus suggest a stabilizing bonding interaction.

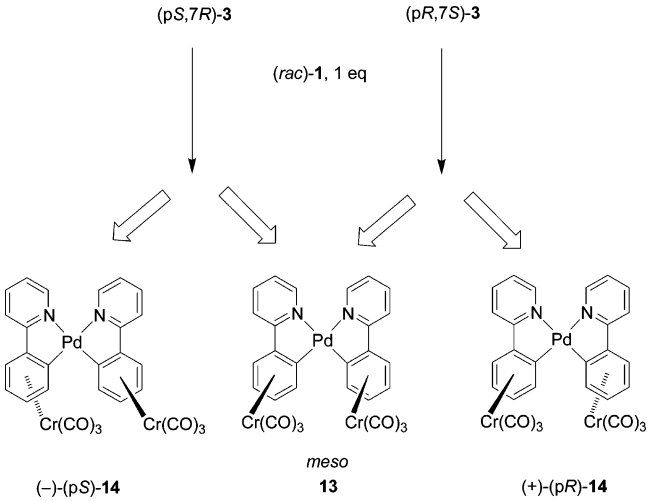
**Syntheses of (*ent*)-1 and (*ent*)-5.** The physical separation of diastereomers allows in principle a concomitant access to pairs of separated enantiomers upon release of a chiral auxiliary. A recent report detailed the preparation of (+) and (−) enantiomers of monomeric complexes **4** by the reaction of $HgCl_2$ with chromatographically separated enantiopure diastereomers of dinuclear hetero cis-bischelated Pd(II) precursors 2-phenylpyridine, **3** (Scheme 2).[6] The chemo- and regioselectivity of the electrophilic attack of $HgCl_2$ to the "less electron poor" arene carbon bonded to the Pd(II) atom was a new example of the tremendous electronic effects exerted by the electron-withdrawing $Cr(CO)_3$ moiety through the arene ligand. It was therefore obvious that the formation of compound (*ent*)-**1** could only be favored by canceling the electronic unbalance between the two aryl groups bonded to the Pd(II) center (Scheme 5). This was verified by using bis[(aryl)$Cr(CO)_3$]-Pd(II) complexes as shown below.

**1. Homoleptic and Homochiral Bischelated Pd(II) Complexes.** In a previous article we reported the

**Scheme 5**




**Scheme 6**




synthesis of complexes **13** and (*rac*)-**14** by a reaction of a heteroleptic bischelated substrate with (*rac*)-**1**.[6b] It was expected, in a first approach, that $C_2$-symmetric (*ent*)-**14** could be a suitable source of (*ent*)-**1**, provided that the former bischelated Pd(II) compound exhibited enough reactivity to react in a typical ligand exchange reaction with $HgCl_2$ with retention of planar configuration.

The synthesis of homochiral (*ent*)-**14** was undertaken by a reaction of enantiopure diastereomers of **3** with racemic **1** expecting the formation of two products, namely, (+)- or (−)-**14** and the *meso* diastereomer **13** (Scheme 6).

The readily available diastereomers (p*S*,7*R*)-**3** and (p*R*,7*S*)-**3**, whose synthesis has been detailed elsewhere, were selected as the most convenient substrates.[6] In a typical experiment, a sample of **3** was set to react with a slight excess of (*rac*)-**1** for about 12 h in acetone at room temperature. In one case, the main products of the reaction, **13** and **14**, were recovered as an admixture with 79% yield after a first chromatographic workup. The main difficulty arose during the second chromatographic separation, whose aim was to obtain pure **13** and **14**. Despite the lower polarity of **14** as compared to that of **13**, only a small fraction of **14** could be obtained pure, immediately followed by a mixture of **14** and **13**. This practical problem was particularly acute when the chromatographic resolution was carried out with an amount of admixture of **14** and **13** higher than 200 mg.

Nonetheless, the two samples of (+)-**14** and (−)-**14** that were obtained afforded reciprocal CD spectra with Cotton effects of similar absolute intensity (Figure 6). Unfortunately these two complexes displayed no diastereomeric $^1H$ NMR splitting in the presence of either TRISPHAT or BINPHAT anions,[15] which precluded a direct determination of their respective enantiomeric excesses. The sequential reaction of (*ent*)-**14** with

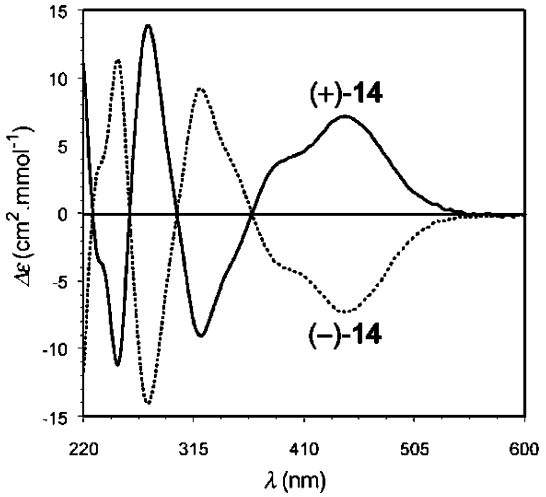



**Figure 6.** CD spectra of compounds(+)-**14** and (−)-**14** in $CH_2Cl_2$ at room temperature.

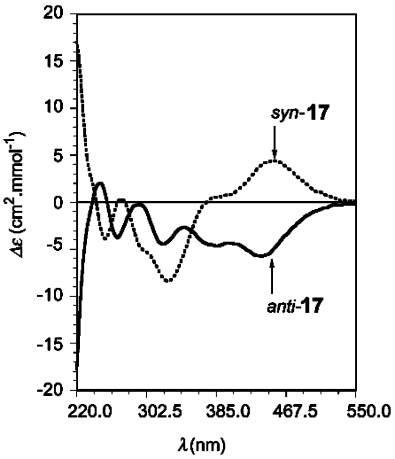



**Figure 7.** CD spectra of heteroleptic complexes *anti*-**17** and *syn*-**17** in $CH_2Cl_2$ at room temperature.

$(PhCN)_2PdCl_2$ and pyridine in order to obtain (*ent*)-**4** unfortunately failed. This would have allowed the indirect determination of the enantiomeric excess of (*ent*)-**14** since **4**, the expected product, is known to undergo diastereomeric $^1H$ NMR splitting in the presence of TRISPHAT.[6] All attempts resulted in decomposition and massive formation of black material, putatively containing Pd(0). This failure to determine the enantiomeric purity of **14** led us to opt for an alternative route to (*ent*)-**1** (vide infra).

**2. Syntheses of Enantio-enriched Complexes 1 and 5 from Heteroleptic 17.** As a second approach to the synthesis of (*ent*)-**1**, chiral heteroleptic bis[(η⁶-aryl)-tricarbonylchromium]palladium (II) complexes **17**, which exist as neutral and separable (*l*)-*anti*-facial and (*u*)-*syn*-facial diastereoisomers, appeared as the ultimate alternative substrates (Figure 7).

It was reported previously[6b] that the latter could be synthesized as a 3:2 mixture of *anti*-**17** and *syn*-**17** isomers by a ligand exchange reaction between racemic **15** and chiral auxiliary **16** (Scheme 7, path i).

The reaction of $HgCl_2$ with both syn and anti isomers of **17** occurred without distinction at the two palladated

**Scheme 7**

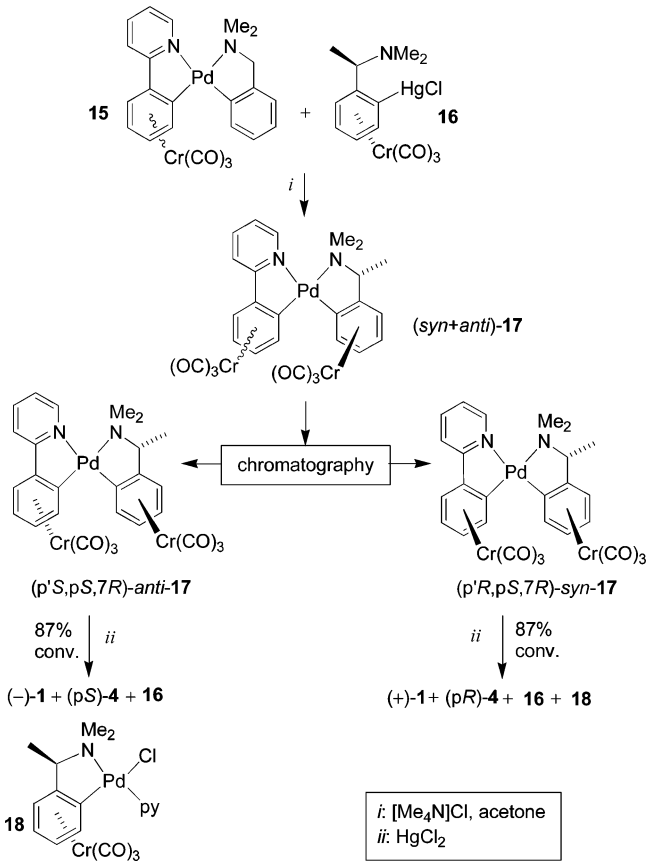



**Table 2. Distribution of Products in the Reactions Affording Nonracemic Complex 1 from Heteroleptic Bis[(η⁶-aryl)Cr(CO)₃] Pd(II) Substrates 17**

| substrate | products (% yield) | | | |
|---|---|---|---|---|
| *syn*-**17** | (+)-**1** (28) | **18** (12) | **16** (21) | (+)-**4** (26) |
| *anti*-**17** | (−)-**1** (50) | **18** (8) | **16** (13) | (−)-**4** (16) |

arene positions of each trinuclear substrate, thus yielding a mixture of products with an overall conversion of 87% (Scheme 7, path ii). In each case, complexes (+)-**1** and (−)-**1** were separated from the remaining components by low-temperature chromatography. Compounds **18** and (+)-**4**/(−)-**4** were recovered as admixtures. Table 2 lists the individual yields in products for the respective reactions of *syn*-**17** and *anti*-**17** with $HgCl_2$, upon chromatographic separation. With *syn*-**17**, the attack of $C_{Ar}$−Pd bonds[16] by $HgCl_2$ made no discrimination between the two aryl substituents of the Pd(II) center, giving rise to an almost equal amount of (+)-**1** and (+)-**4**, whereas with *anti*-**17**, the formation of (−)-**1** was largely favored.

The enantio-purity of (+)-**1** and (−)-**1**, which produced reciprocal CD spectrograms with an intense Cotton effect at 305 nm (Figure 8, $\Delta\epsilon = -7.5$ for (+)-**1** and +7.5 for (−)-**1**), could not be determined directly by $^1H$ NMR spectroscopy due to the absence of enantio-differentiation in the presence of either TRISPHAT[17] or BINPHAT[18] salts.

The determination of the ee's of byproducts (+)-**4** (mainly (p*R*)-**4**, ee 85% ± 2%) and (−)-**4** (mainly (p*S*)-**4**,

(15) For a review see: Lacour, J.; Hebbe-Viton, V. *Chem. Soc. Rev.* **2003**, *32*, 373−382.

(16) van der Ploeg, A. F. M. J.; van Koten, G.; Vrees, K. *J. Organomet. Chem.* **1981**, *222*, 155−174.

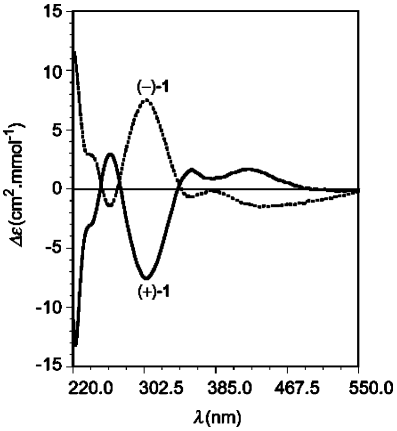



**Figure 8.** CD spectra of nonracemic (+)-**1** and (−)-**1** in $CH_2Cl_2$ at room temperature.

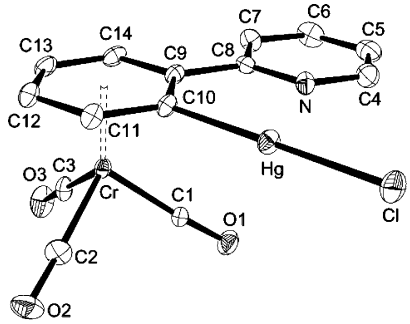



**Figure 9.** ORTEP diagram for complex (p*S*)-**1**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. The geometrical features were found identical to those reported previously for (±)-**1** (see ref 3). The absolute structure was refined against Flack's parameter ($x = 0.00(3)$) (see ref 19).

ee 89% ± 2%) by using [*n*-$Bu_3$NH][Λ-TRISPHAT] as chiral shift reagent gave us a first indirect estimation of the enantiopurity of (+)-**1** and (−)-**1**.[6] Fortunately, the absolute configuration of the major enantiomer in (−)-**1** could be assigned by X-ray diffraction analysis (Figure 9).[19] The CD spectrum of the analyzed crystal dissolved in $CH_2Cl_2$, whose molecular structure is displayed in Figure 9, matched the one measured for (−)-**1**, confirming unambiguously that the levogyric major enantiomer in (−)-**1** possesses a p*S* configuration (Figure 10). This result also indicates that the replacement of Pd(II) by Hg(II) in (p*S*,p*S*,7*R*)-*anti*-**17** occurred with retention of the planar-chiral configuration at the 2-phenylenepyridine fragment.

The estimated enantiopurities of the latter two samples of (*ent*)-**1** from the data obtained for (+)-**4** and (−)-**4** were corroborated by reacting compounds (+)-**1** and (−)-**1** with $[(\eta^6\text{-}p\text{-}i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}_2]_2$ and by analyzing the resulting products, (+)-*u*-**5** and (−)-*u*-**5**, respectively, by $^1$H NMR spectroscopy (Scheme 8).[20] These two com-

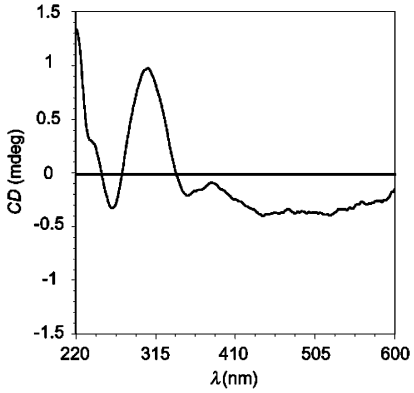
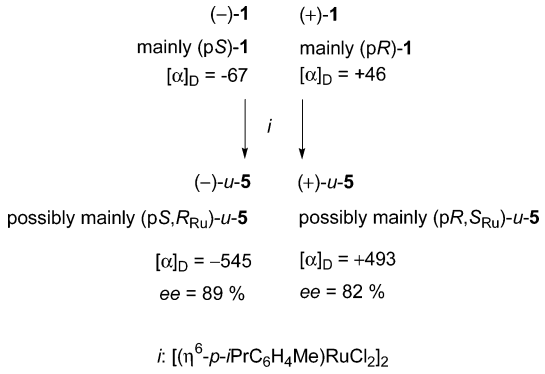



**Figure 10.** CD spectrum of the crystal of (p*S*)-**1** analyzed previously by X-ray diffraction and dissolved in $CH_2Cl_2$ in a 1 mm optical path quartz cell at room temperature. The raw ellipticity (mdeg) is plotted against wavelength (nm).

**Scheme 8**




plexes, which are chiral at the Ru[13,21] atom and at the chelate, displayed almost reciprocal CD spectrograms with Cotton effects identical in shape at similar wavelength but opposite in signs (Figure 11). Again, the $^1$H NMR spectra of both (+)-*u*-**5** and (−)-*u*-**5** proved to be insensitive to the presence of either Δ or Λ-TRISPHAT anions in solution. In turn, Δ-BINPHAT anion induced a weak albeit sufficient peak splitting for all the discernible signals belonging to (+)-*u*-**5** or (−)-*u*-**5** (Figure 11). The largest split in the presence of Δ-BINPHAT anion ($\Delta\delta = 0.065$ ppm) was observed for the

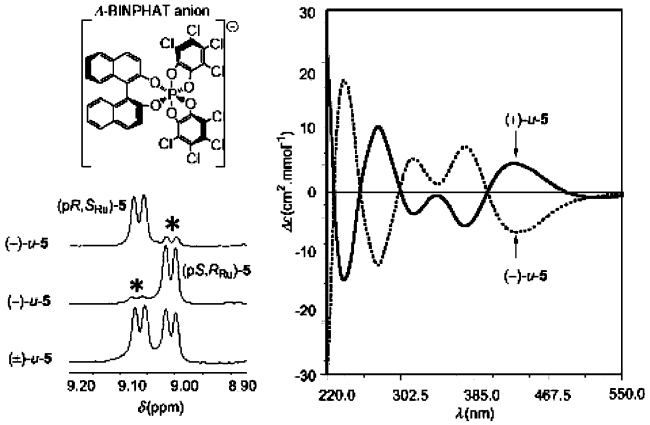



**Figure 11.** Left: $^1$H NMR (300 MHz, 293 K) stacked spectra of (+)-*u*-**5**, (−)-*u*-**5**, and (±)-*u*-**5** (1.4 mM) in the presence of [*n*-$Bu_4$N][Δ-BINPHAT] (5.7 mM) in a mixture of $d_6$-acetone and $d_6$-benzene (1:4) with proposed absolute configurations of the major components. Right: CD spectra of (+)-*u*-**5** and (−)-*u*-**5** taken in $CH_2Cl_2$ at 293 K.

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(18) Lacour, J.; Londez, A.; Goujon-Ginglinger, C.; Buss, V.; Bernardinelli, G. *Org. Lett.* **2000**, *26*, 4185−4188.

(19) (a) Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908−915. (b) Flack, H. D.; Bernardinelli, G. *J. Appl. Crystallogr.* **2000**, *33*, 1143−1148. (c) Flack, H. D.; Bernardinelli, G. *Cryst. Eng.* **2003**, *6*, 213−223.

(20) Attar, S.; Nelson, J.; Fischer, J.; de Cian, A.; Sutter, J. P.; Pfeffer, M. *Organometallics* **1995**, *14*, 4559−4569.

doublet of the proton at the α position of the pyridyl group, which resonates at ca. δ 9.0 ppm. This allowed the assessment of the enantiomeric purity of each sample within the limits of accuracy of $^1$H NMR spectroscopy (ee 82% ± 2% for (+)-**5** and 89% ± 2% for (−)-**5**).

The slight deviation from absolute enantio-purity reported here for both enantio-enriched samples of **5** can be explained either by a contamination of *anti*-**17** by small amounts of *syn*-**17** and vice versa during the chromatographic resolution or—less likely in our opinion—by a partial racemization of either (+)-**5** or (−)-**5** by intramolecular trans-cyclometalation.[22]

Unfortunately, despite sustained efforts, the growth of enantiomorphic crystals of either (+)- or (−)-*u*-**5** did not succeed, which of course casts some doubt on the true nature of the absolute configurations at the Ru atom and at the chelate. Many attempts resulted in the crystallization of racemates or poorly enantio-enriched crystals unfit for absolute structure determination.[19c] Worthy to note, both complexes retained their CD spectra after 20 min in $CH_2Cl_2$ solutions at room temperature, suggesting that these enantiomers were persistent within this period of time. It would be tempting to suggest that upon the diastereoselective $Hg^{II}/Ru^{II}$ exchange reaction, the absolute planar configuration was retained in (+)- and (−)-**5**. Alas, there is not, at present, any other direct way of proving it than by X-ray diffraction analysis, provided that enantiomorphic crystals of configurationally stable species are analyzed and their chiroptical properties correlated with those of the starting enantio-enriched material. It is well known that configuration assessment by CD spectroscopy alone in the UV−visible domain is not a fully reliable method for planar-chiral (η⁶-arene)tricarbonylchromium complexes or half-sandwich ruthenium complexes.[13,23]

## Conclusion

The synthesis of highly enantioenriched metallo-arene complexes bearing planar chirality is attributed to one's ability to σ-bind a transition metal and minimize the risk of loss of the planar chirality as a result of the possible oxidation[24] of the π-coordinated metal, viz., the Cr center in this case. This is well exemplified by the overall sensitivity of complex **5** and its ability to readily lose the $Cr(CO)_3$ moiety. However, as suggested by the results presented here, chiral bischelates of Pd(II) can be used for the preparation of a pair of highly enantioenriched ortho-mercurated (η⁶-arene)tricarbonylchromium complexes via a reaction with $HgCl_2$, which takes place with retention of planar configuration. We are further investigating the synthesis of (*ent*)-**1** by alternative methods and the chemical applications of the chiral cycloruthenated complexes reported herein.

## Experimental Section

All experiments were carried out under a dry atmosphere of argon with dry and degassed solvents. The cis-bischelated heteroleptic palladium(II) (*anti*/*syn*-**17**) complexes[6b] and [(η⁶-*p*-*i*PrC$_6$H$_4$Me)RuCl$_2$]$_2$[25] were synthesized following published procedures. Silica gel (Si 60, 40−63 μm) for column chromatography was purchased from Merck. NMR spectra were acquired on Bruker DRX 500 ($^{13}$C and $^1$H nuclei) and Bruker AV-300 ($^1$H) spectrometers at room temperature unless otherwise stated. Chemical shifts were reported in parts per million downfield of $Me_4Si$. IR spectra were measured on a Perkin-Elmer FT spectrometer. Elemental analyses (reported in percent mass) were performed at the analytical center of "Université Louis Pasteur" in Strasbourg. CD spectra (plot of $\Delta\epsilon$ (cm$^2$ mmol$^{-1}$) against $\lambda$ (nm)) were recorded in Geneva with a Jasco J715 spectropolarimeter and in Bonn at the Kekulé Institut für Organische Chemie with a Jasco J810 spectropolarimeter. For each compound, three acquisitions were performed ($c = 2 \times 10^{-4}$ M, 1 mm optical path quartz cell, 100 nm min$^{-1}$) and corrected against the blank spectrum of $CH_2Cl_2$ acquired in identical conditions.

**Experimental Procedure for the X-ray Diffraction Analysis of Compounds 5, 6, 6·HgCl$_2$, 9, and 10.** Acquisition and processing parameters are displayed in Table 1. Reflections were collected with a Nonius KappaCCD diffractometer using MoKα graphite-monochromated radiation ($\lambda$ = 0.71073 Å). The structures were solved using direct methods, they were refined against $|F|$, and for all pertaining computations, the Nonius OpenMoleN package was used.[26] Hydrogen atoms were introduced as fixed contributors. The absolute structure of (p*S*)-**1** ($x$ = 0.00(3)) was determined by refining the corresponding Flack's $x$ parameters.

**[*T*-4]-(*rel*)-*u*-Chloro(η⁶-*p*-cymene){2-[tricarbonyl(η⁶-phenyl-κ*C*²′)chromium(0)]pyridine-κ*N*}ruthenium(II), (±)-*u*-5.** A mixture of dimer [(η⁶-*p*-*i*PrC$_6$H$_4$Me)RuCl$_2$]$_2$ (290 mg, 0.47 mmol) and (±)-**1** (500 mg, 0.95 mmol) in 30 mL of dry acetone was stirred for 1 h at room temperature under argon. The resulting orange-red solution was filtered through Celite, and the solvent was removed under reduced pressure. The orange-red residue was purified by flash chromatography on silica gel at low temperature (0 °C). A yellow fraction containing unreacted (±)-**1** was eluted first with a mixture of 20% acetone in *n*-hexane, followed by an orange-red fraction corresponding to (±)-*u*-**5** (390 mg, 0.70 mmol, 73% yield), which was eluted with a mixture of 30−70% acetone in *n*-hexane. (±)-*u*-**5**: Anal. Calcd for $C_{24}H_{22}NO_3ClCrRu\cdot CH_2Cl_2$: C, 46.47; H, 3.72; N, 2.17. Found: C, 46.83; H, 3.98; N, 2.13. HRMS calcd for $C_{24}H_{22}NO_3Cl^{52}Cr^{102}Ru$ (FAB+): 560.9736. Found: 560.9734. MS (FAB+): *m*/*e* 561 [M]$^+$, 526 [M − Cl]$^+$, 477 [M − 3CO]$^+$, 425 [M − Cr(CO)$_3$]$^+$, 390 [M − Cl − Cr(CO)$_3$]$^+$. IR ($CH_2Cl_2$) ν(CO): 1872, 1949 cm$^{-1}$. $^1$H NMR ($CDCl_3$, 500 MHz): δ 9.25 (d, $^3J$ = 5.6 Hz, 1H, H$_{py}$), 7.77 (t, $^3J$ = 7.7 Hz, 1H, H$_{py}$), 7.49 (d, $^3J$ = 8.1 Hz, 1H, H$_{py}$), 7.22 (t, $^3J$ = 6.0 Hz, 1H, H$_{py}$), 6.50 (d, $^3J$ = 6.3 Hz, 1H, H$_{ArCr}$), 5.76 (d, $^3J$ = 6.3 Hz, 1H, H$_{p-cym}$), 5.70 (m, $^3J$ = 6.3 Hz, 3H, H$_{ArCr}$ + H$_{p-cym}$), 5.50 (t, $^3J$ = 6.3 Hz, 1H, H$_{ArCr}$), 5.36 (m, $^3J$ = 6.3 Hz, 2H, H$_{ArCr}$ + H$_{p-cym}$), 2.72 (m, $^3J$ = 6.9 Hz, 1H, (CH$_3$)C*H*$_{(p-cym)}$), 1.96 (s, 3H, CH$_{3(p-cym)}$), 1.25 (d, $^3J$ = 6.9 Hz, 3H, (C*H*$_3$)CH$_{(p-cym)}$), 1.14 (d, $^3J$ = 6.9 Hz, 3H, (C*H*$_3$)CH$_{(p-cym)}$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz): δ 236.1 (CO), 164.2, 155.1, 141.8, 137.5, 123.3, 120.1, 111.8, 106.7, 101.8, 93.4, 93.3, 92.9, 92.0, 91.8, 89.0, 87.5, 86.8, 30.7, 22.8, 21.6, 17.9.

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**(*rac*)-Chloro($\eta^6$-*p*-cymene)(2-phenylpyridine-$\kappa C,N$)ruthenium(II), (±)-6.** A mixture of $[(\eta^6\text{-}p\text{-}i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}_2]_2$ dimer (80 mg, 0.13 mmol), **7** (102 mg, 0.26 mmol), and [$Me_4$-NCl] (142 mg, 1.3 mmol) in 10 mL of dry acetone was stirred for 14 h at room temperature under argon. The resulting yellow-beige mixture was filtered through Celite. The yellow-orange filtrate was then stripped of solvents under reduced pressure to afford a yellow-beige solid **6** (90 mg, 0.21 mmol, 81% yield). HRMS calcd for $C_{21}H_{22}NCl^{102}Ru$, 422.0500; found, 422.0499. MS ($FAB^+$): *m/e* 425 $[M]^+$, 390 $[M - Cl]^+$. $^1H$ NMR ($CDCl_3$): $\delta$ 9.23 (d, $^3J = 5.6$ Hz, 1H, $H_{py}$), 8.15 (d, $^3J = 7.5$ Hz, 1H, $H_{py}$), 7.71 (d, $^3J = 7.9$ Hz, 1H, $H_{Ph}$), 7.66 (t, $^3J = 7.4$ Hz, 1H, HPh), 7.61 (d, $^3J = 7.7$ Hz, 1H, $H_{Ph}$), 7.17 (t, $^3J = 7.4$ Hz, 1H, $H_{py}$), 7.04 (m, $^3J = 7.7$ Hz, 2H, $H_{py} + H_{Ph}$), 5.57 (dd, $^3J = 6.0$ Hz, 2H, $H_{p-cym}$), 5.17 (d, $^3J = 6.0$ Hz, 1H, $H_{p-cym}$), 4.99 (d, $J^3 = 6.0$ Hz, 1H, $H_{p-cym}$), 2.42 (m, $^3J = 7.0$ Hz, 1H, $CH_3CH$), 2.04 (s, 3H, $CH_3$), 0.97 (d, $^3J = 7.0$ Hz, 3H, $CH_3CH$), 0.87 (d, $^3J = 7.0$ Hz, 3H, $CH_3CH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 181.2, 165.2, 154.5, 143.2, 139.5, 136.6, 129.4, 123.8, 122.4, 121.4, 118.7, 100.5, 100.4, 90.6, 89.5, 84.0, 82.2, 30.7, 22.5, 21.6, 18.7.

**Complex (±)-6·$HgCl_2$.** A mixture of $[(\eta^6\text{-}p\text{-}i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}_2]_2$ (100 mg, 0.16 mmol) and **7** (127 mg, 0.33 mmol) in 10 mL of dry $CH_2Cl_2$ was stirred for 3 h at room temperature under argon. The resulting orange-red mixture was filtered over Celite. The filtered solution was then evaporated under reduced pressure to afford (±)-**6**·$HgCl_2$ (200 mg, 0.28 mmol, 87% yield). Anal. Calcd for $C_{21}H_{22}NCl_3RuHg$: C, 36.15; H, 3.15; N, 2.01; Hg, 28.78. Found: C, 36.48; H, 3.48; N, 1.78; Hg, 25.71. $^1H$ NMR ($CDCl_3$): $\delta$ 9.22 (d, $^3J = 5.8$ Hz, 1H, $H_{py}$), 8.34 (d, $^3J = 7.3$ Hz, 1H, $H_{py}$), 7.73 (t*, $^3J = 7.8$ Hz, 1H, $H_{Ph}$), 7.70 (m, 2H,$H_{Ph}$), 7.27 (t*, $^3J = 7.3$ Hz, 1H, $H_{py}$), 7.41 (t*, $^3J = 7.4$ Hz, 1H, $H_{Ph}$), 7.09 (dd, $^3J = 5.8$ Hz, 1H, $H_{py}$), 5.70 (d, $^3J = 5.9$ Hz, 1H, $H_{p-cym}$), 5.66 (d, $^3J = 5.8$ Hz, 1H, $H_{p-cym}$), 5.29 (d, $^3J = 6.1$ Hz, 1H, $H_{p-cym}$), 5.16 (d, $^3J = 5.9$ Hz, 1H, $H_{p-cym}$), 2.37 (m, $^3J = 6.8$ Hz, 1H, $CH_3CH$), 2.07 (s, 3H, $CH_3$), 0.94 (d, $^3J = 6.8$ Hz, 3H, $CH_3CH$), 0.85 (d, $^3J = 6.8$ Hz, 3H, $CH_3CH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 179.8, 165.9, 155.4, 145.7, 141.3, 138.1, 131.2, 126.0, 124.9, 122.9, 120.2, 102.7, 101.3, 92.2, 90.5, 85.9, 82.5, 31.6, 23.1, 22.7, 19.8. $^{199}Hg$ NMR ($CDCl_3$): $\delta$ −1262.

**[*T*4]-(*rel*)-*u*-Chloro($\eta^6$-*p*-cymene)[tricarbonyl($\eta^6$-*N*,*N*-dimethylbenzylamine-$\kappa C^{2'},N$)chromium(0)]ruthenium(II), (±)-*u*-9.** A mixture of dimer $[(\eta^6\text{-}p\text{-}i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}_2]_2$ (120 mg, 0.19 mmol) and (±)-**8** (200 mg, 0.39 mmol) in 20 mL of dry acetone was stirred for 6 h at room temperature under argon. The resulting orange-beige mixture was filtered through Celite, and the solvent was removed under reduced pressure. The orange-beige residue was purified by flash chromatography on silica gel at low temperature (0 °C). Unreacted (±)-**8** (pale yellow) was eluted first with a mixture of 20−40% acetone in *n*-hexane. Then, an orange-beige fraction of (±)-*u*-**9** (60 mg, 0.11 mmol, 28% yield) was eluted and evaporated to dryness. (±)-*u*-**9**: HRMS: calcd for $C_{22}H_{26}NO_3Cl^{52}Cr^{102}Ru$ 541.0050, found 541.0060. MS (FAB+): *m/e* 541 $[M]^+$, 506 $[M - Cl]^+$, 457 $[M - 3CO]^+$, 405 $[M - Cr(CO)_3]^+$, 398 $[M - Cl - Cr(CO)_2]^+$ 370 $[M - Cl - Cr(CO)_3]^+$. IR ($CH_2Cl_2$) $\nu$(CO): 1859, 1944 $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 6.25 (d, $J^3 = 6.0$ Hz, 1H, ArCr), 5.58 (d, $^3J = 5.5$ Hz, 1H, $H_{p-cym}$), 5.54 (d, $^3J = 5.5$ Hz, 1H, $H_{p-cym}$), 5.43 (m, 2H, $H_{ArCr+p-cym}$), 5.15 (m, $^3J = 6.5$ Hz, 2 H, $H_{ArCr}$), 4.97 (d, $^3J = 5.5$ Hz, 1 H, $H_{p-cym}$), 4.07 (d, $^2J = 14.0$ Hz, 1H, $CH_2$), 3.13 (d, $^4J = 4.6$ Hz, 6H, $N(CH_3)_2$), 2.88 (m, $^3J = 6.8$ Hz, 1 H, $CH_3CH$), 2.61 (d, $^2J = 14.0$ Hz, 1 H, $CH_2$), 2.27 (s, 3H, $CH_3$), 1.25 (m, $^3J = 6.8$ Hz, 6 H, $CH_3CH$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): $\delta$ 236.2 (CO), 139.3, 117.2, 103.2, 102.6, 102.5, 94.7, 90.8, 90.6, 88.5, 88.2, 85.3, 68.7, 56.8, 55.4, 30.7, 24.2, 21.7, 19.3.

**Typical Procedure for the Synthesis of *u*- and *l*-Bis{2[tricarbonyl($\eta^6$-phenylene-$\kappa C^{1'}$)chromium(0)]pyridine-$\kappa N$}palladium(II), 13 and (*ent*)-14.** Complexes **3** and (±)-**1** were dissolved in dry acetone under argon atmosphere, and the resulting red-orange solution was stirred for about 12 h. The mixture was then filtered through Celite, silica gel was added to the filtrate, and the suspension was evaporated to dryness. The coated silica was placed on the top of a $SiO_2$ column packed in *n*-pentane at 0 °C. Various impurities consisting of decomposition products and unreacted material were removed in a first yellow to pale orange band eluted with a mixture of 20% acetone in *n*-pentane. A large orange band consisting of a mixture of **14** and **13** was eluted with a mixture of 40−50% acetone in *n*-pentane. Silica gel was added to this latter fraction, and the resulting suspension was stripped of solvent. The resulting coated silica gel was submitted to a second chromatographic separation on a $SiO_2$ column packed in a mixture of 90% $CHCl_3$ and *n*-pentane at 0 °C.

**Complex (+)-14.** This compound was prepared from (*pR*,*7S*)-**3** (600 mg, 1.10 mmol) and (±)-**1** (700 mg, 1.32 mmol) in dry acetone (40 mL), 24 h. Flash column chromatography in $SiO_2$ with 30% acetone in *n*-pentane afforded first two small fractions (one yellow and other orange-brown), which were discarded. Then, with pure acetone, the last orange-red fraction consisting of a mixture of (+)-**14** and **13** (600 mg, 0.87 mmol, 79% conversion) was obtained. The two diasteroisomers were separated by low-temperature (0 °C) chromatography in $SiO_2$ with a 5% *n*-pentane/$CHCl_3$ mixture. Two orange fractions were obtained. The first fraction was identified as corresponding to (+)-**14** (110 mg, 0,16 mmol, 15% yield) followed by one second orange-red fraction, which was always obtained as a mixture of (+)-**14** and **13** (160 mg, 21% yield). Spectroscopic and analytical data for this complex were in agreement with those obtained for racemate (±)-**14**.[6b] $[\alpha]_D$ ($CH_2Cl_2$, 25 °C): +1300 (*c* 0.04 g/100 mL). CD ($CH_2Cl_2$, *c* 0.2 mM): $\lambda(\Delta\epsilon)$ 225 (−3.5, shoulder), 249 (−11.2), 275 (+13.9), 321 (−9.1), 407 (+4.5, shoulder), 447 (+7.1).

**Complex (−)-14.** The procedure was similar to that described above for the other enantiomer. The conditions were slightly modified as follows: (*pS*,*7R*)-**3** (650 mg, 1.19 mmol) and (±)-**1** (753 mg, 1.43 mmol), dry acetone (40 mL), 24 h at room temperature. Flash chromatography over silica gel with 30% and then 100% of acetone in *n*-pentane afforded one last orange fraction corresponding to a mixture of **14** and **13**. A second column carried out in order to purify the latter mixture at low temperature (0 °C) with 5% *n*-pentane in $CHCl_3$ afforded a first orange-red fraction of pure (−)-**14** (50 mg, 0,073 mmol, 6% yield) followed by an admixture of (−)-**14** and **13**. Spectroscopic and analytical data for this complex were in agreement with those obtained for racemate (±)-**13**. $[\alpha]_D$ ($CH_2Cl_2$, 25 °C): −1025 (*c* 0.04 g/100 mL). CD ($CH_2Cl_2$, *c* 0.2 mM): $\lambda(\Delta\epsilon)$ 225 (+3.7, shoulder), 249 (+11.4), 275 (−14.1), 321 (+9.0), 407 (−4.5, shoulder), 447 (−7.3).

**(−)-2-[Tricarbonyl($\eta^6$-2′-chloromercuriophenyl-$\kappa C^{2'}$)-chromium(0)]pyridine-$\kappa N$, (−)-1 (mainly (p*S*)-1).** A mixture of (p*S*,p*S*,*7R*)-*anti*-**17** (170 mg, 0.250 mmol) and $HgCl_2$ (136 mg, 0.500 mmol) in dry $CH_2Cl_2$ (30 mL) was stirred at room temperature under argon for 3 h. An excess of pyridine was added dropwise, and the orange-brown resulting mixture was stirred for an additional 5 min and then filtered through Celite. The orange filtrate was stripped of solvents. The product was purified by low-temperature (0 °C) flash chromatography over silica gel. Yellow pale **16** (10 mg, 0.019 mmol) was eluted with a mixture of 20% acetone in *n*-hexane, followed by yellow (−)-**1** (66 mg, 0.125 mmol), which was eluted with a mixture of 30−40% acetone in *n*-hexane. A last orange-red fraction corresponding to a mixture of (−)-**4** (21 mg, 0.041 mmol) and **18** (17 mg, 0.034 mmol) in a ratio of 1.2:1 was eluted with mixtures of 50−70% acetone in *n*-hexane. The spectroscopic and analytical data for (−)-**1** were in agreement with those published for the racemate (±)-**1**[3] (87.6% conversion). (−)-**1** (mainly (p*S*)-**1**): $[\alpha]_D$ ($CH_2Cl_2$, 25 °C): − 67.5 (*c* 0.04 g/100 mL). CD ($CH_2Cl_2$, *c* 0.2 mM): $\lambda(\Delta\epsilon)$ 223 (10.9), 241 (2.9), 263 (−1.4), 305 (7.5), 357 (−0.6), 423 (−1.3).

**(+)-1 (mainly (p*R*)-1).** The procedure for this reaction was similar to that described previously. The conditions were slightly changed as follows: (p*R*,p*S*,*7R*)-*syn*-**17** (160 mg, 0.235

mmol) and $HgCl_2$ (128 mg, 0.470 mmol) in dry $CH_2Cl_2$ (30 mL) for 3 h at room temperature. Low-temperature (0 °C) flash chromatography over silica gel was used. Yellow pale **16** (15 mg, 0.029 mmol) was eluted with a mixture of 20% acetone in *n*-hexane, followed by (+)-**1** (35 mg, 0.066 mmol), which was eluted with a mixture of 30−40% acetone in *n*-hexane. A last orange-red fraction corresponding to a mixture of (+)-**4** (31 mg, 0.060 mmol) and **18** (25 mg, 0.050 mmol) in a ratio of 1.2:1 was eluted with mixtures of 50−70% acetone in *n*-hexane. The spectroscopic and analytical data for (+)-**1** were in agreement with those published for the racemate (±)-**1** (87.4% conversion). (+)-**1** (mainly (p*R*)-**1**): $[\alpha]_D$ ($CH_2Cl_2$, 25 °C): +46.0 (*c* 0.04 g/100 mL). CD ($CH_2Cl_2$, *c* 0.2 mM): $\lambda(\Delta\epsilon)$ 223 (−13.2), 241 (−3.0), 263 (2.9), 305 (−7.5), 357 (1.6), 423 (1.7).

**[*SP*-4−4]-(p*S*,1*R*)-Chloro,{*N*,*N*-dimethyl-1-[tricarbonyl-(η⁶-phenylene-κ*C*²′)chromium(0)]ethylamine-κ*N*}(pyridine)palladium(II), (p*S*,1*R*)-18.** This complex could not be obtained exempt of impurities due to its air sensitivity. $^1$H NMR spectroscopic data for this product were deduced by difference. $^1$H NMR ($C_3D_6O$): $\delta$ 8.96 (d, $^3J$ = 5.0 Hz, 2H, $H_{py}$), 5.09 (t*, $^3J$ = 7.6 Hz, 1H, $H_{py}$), 7.65 (dd, $^3J$ = 7.6 Hz, 2H, $H_{py}$), 5.56 (d, $^3J$ = 6.4 Hz, 1H, $H_{ArCr}$), 5.37 (t*, $^3J$ = 6.4 Hz, 1H, $H_{ArCr}$), 5.22 (t*, $^3J$ = 6.4 Hz, 1H, $H_{ArCr}$), 4.26 (d, $^3J$ = 6.4 Hz, 1H, $H_{ArCr}$), 4.16 (m, 1H, C*H*Me), 3.21 (s, 3H, N(C$H_3$)$_2$), 2.77 (s, 3H, N(C$H_3$)$_2$), 1.49 (m, 3H, CHC$H_3$).

**(+)-*u*-5.** A mixture of $[(\eta^6\text{-}p\text{-}i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}_2]_2$ (20 mg, 0.066 mmol) and (+)-**1** (35 mg, 0.066 mmol) in 10 mL of dry acetone was stirred for 1.5 h at room temperature under argon. The resulting orange-red solution was stripped of solvents. Unreacted (+)-**1** was removed by low-temperature (0 °C) flash chromatography over silica gel with a mixture ranging from 20 to 40% of acetone in *n*-hexane. An orange-red fraction corresponding to (+)-*u*-**5** (23 mg, 0.041 mmol, 62% yield) was eluted with a mixture of 50−70% acetone in *n*-hexane. Spectroscopic and analytical data of this complex were in agreement with those obtained for the racemate (±)-*u*-**5**. (+)-*u*-**5**: $[\alpha]_D$ ($CH_2Cl_2$, 25 °C): +493 (*c* 0.04 g/100 mL). ee = 82%. CD ($CH_2Cl_2$, *c* 0.2 mM): $\lambda(\Delta\epsilon)$ 200 (+21.0), 239 (−13.7), 277 (+10.1), 317 (−3.4), 374 (−5.2), 430 (4.4).

**(−)-*u*-5.** The procedure was similar to that described above: $[(\eta^6\text{-}p\text{-}i\text{PrC}_6\text{H}_4\text{Me})\text{RuCl}_2]_2$ (20 mg, 0.066 mmol) and (−)-**1** (35 mg, 0.066 mmol) in 10 mL of dry acetone for 1.5 h at room temperature. Low-temperature (0 °C) flash chromatography over silica gel afforded (−)-*u*-**5** (13 mg, 35% yield). Spectroscopic and analytical data for this complex were in agreement with those for racemate (±)-*u*-**5**. (−)-*u*-**5**: $[\alpha]_D$ ($CH_2Cl_2$, 25 °C): −545 (*c* 0.04 g/100 mL). ee = 89%. CD ($CH_2Cl_2$, *c* 0.2 mM): $\lambda(\Delta\epsilon)$ 200 (−27.0), 239 (17.3), 277 (−11.3), 317 (5.1), 374 (6.9), 430 (−6.1).

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**Supporting Information Available:** Crystallographic data compiled in CIF format for complexes **5**, **6**, **6**·$HgCl_2$, **9**, **10**, and (p*S*)-**1** and $^1$H NMR spectra of (+)- and (−)-**4** and -**5** in the presence of TRISPHAT and BINPHAT anions. This material is available free of charge via the Internet at http://pubs.acs.org.

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