Cyclopenta[*l*]phenanthrenyl and Cyclopenta[*a*]acenaphthylenyl Half-Sandwich Complexes of Ruthenium as Racemization Catalysts for Secondary Alcohols

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Several half-sandwich complexes of ruthenium with cyclopenta[*l*]phenanthrenyl and cyclopenta[*a*]acenaphthylenyl ligands containing fused aromatic ring substituents on the cyclopentadienyl ring were prepared and characterized by NMR and X-ray crystallography. Activities of the complexes as racemization catalysts for secondary alcohols were preliminarily screened by using (*S*)-phenylethanol as the substrate. The catalytic activities of the fused-ring complexes depend strongly on the number of other substituents in the five-membered ring and are inferior to those reported earlier for chlorodicarbonyl(pentaphenylcyclopentadienyl)ruthenium, currently considered as the best catalyst candidate for dynamic kinetic resolution of secondary alcohols by combined enzyme/metal catalysis.

Introduction

Dynamic kinetic resolution (DKR) of secondary alcohols based on combined enzyme and metallocene catalysis was originally developed more than 10 years ago.[1] The use of efficient organometallic catalysts for racemization allows one to perform the resolutions under sufficiently mild conditions required for enzyme functioning. In recent years, this approach has been extensively investigated. Predominantly, pentasubstituted monocyclopentadienyl complexes of ruthenium have been utilized as racemization catalysts for alcohols.[2] Only a few examples based on indenyl[3] and aryl[4] ruthenium complexes have been described.

For further structural tuning as well as improvements in activities and stabilities of the racemization catalysts, the screening of new ligand modifications is desirable. Here, the indenyl ligand platform provides a number of opportunities for structural variation. Examples of transition metal complexes containing fused-ring, polycylic indenyl-type ligands, such as cyclopenta[*l*]phenanthrenyl[5] and cyclopenta[*a*]acenaphthylenyl,[6] are relatively scarce, but have been, in the context of catalytic α-olefin polymerization (mainly M = Zr),[5b,c] shown to result in enhanced catalyst properties. To our knowledge, ruthenium complexes containing cyclopenta[*l*]phenanthrenyl ligands have been reported in one case only: Hagiwara and co-workers recently utilized the 1,2,3-triphenyl cyclopenta[*l*]phenanthrenyl moiety as a ligand in their catalyst design for Suzuki−Miyara coupling.[7]

In the present paper we describe our initial results in the use of cyclopenta[*l*]phenanthrenyl and cyclopenta[*a*]acenaphthylenyl ligands as structural motifs for alcohol racemization catalysts with potential applications in DKR in combination with enzymes. The resulting monocyclopentadienyl ruthenium complexes combine the elements of the previously reported metallocene racemization catalysts containing polysubstituted Cp ligands with a flat polycyclic part. The specific purpose of the work was to investigate the relationships between the structures and catalytic activities of such half-sandwich metallocene complexes.

Results and Discussion

Synthesis and Characterization of the Catalysts and Ligand Pecursors. The substituted cyclopenta[*l*]phenanthrenyl ligand precursors **4a** and **4b** and the triphenyl-substituted cyclopenta[*a*]acenaphthylenyl ligand precursor **7** were prepared according to previously reported procedures.[5a,8] The *tert*-butyldimethylsiloxy-substituted ligand **4d** was synthesized by

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(1) (a) Larsson, A. L. E.; Persson, B. A.; Bäckvall, J.-E. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1211. For reviews, see: (b) Pàmies, O.; Bäckvall, J.-E. *Chem. Rev.* **2003**, *103*, 3247. (c) Martín-Matute, B.; Bäckvall, J.-E. *Curr. Opin. Chem. Biol.* **2007**, *11*, 226.

(2) (a) Leijondahl, K.; Borén, L.; Braun, R.; Bäckvall, J.-E. *Org. Lett.* **2008**, *10*, 2027. (b) Kim, M. J.; Choi, K. Y.; Kim, S.; Kim, D.; Han, K.; Ko, S.-B.; Park, J. *Org. Lett.* **2008**, *10*, 1295. (c) Eckert, M.; Brethon, A.; Li, Y.-X.; Sheldon, R. A.; Arends, I. W. C. E. *Adv. Synth. Catal.* **2007**, *349*, 2603. (d) Choi, J. H.; Choi, Y. K.; Kim, Y. H.; Park, E. S.; Kim, E. J.; Kim, M. J.; Park, J. *J. Org. Chem.* **2004**, *69*, 1972.

(3) (a) Koh, J. H.; Jung, H. M.; Kim, M. J.; Park, J. *Tetrahedron Lett.* **1999**, *40*, 6281. (b) Xi, Q.; Zhang, W.; Zhang, X. *Synlett* **2006**, 945.

(4) (a) Lee, D.; Huh, E. A.; Kim, J. M.; Jung, H. M.; Koh, J. H.; Park, J. *Org. Lett.* **2000**, *2*, 2377. (b) Dijksman, A.; Elzinga, J. M.; Li, Y.-X.; Arends, I. W. C. E.; Sheldon, R. A. *Tetrahedron: Asymmetry* **2002**, *13*, 879.

(5) (a) Schneider, N.; Prosenc, M.-H.; Brintzinger, H.-H. *J. Organomet. Chem.* **1997**, *545*−*546*, 291. (b) Schneider, N.; Huttenloch, M. E.; Stehling, U.; Kirsten, R.; Schaper, F.; Brintzinger, H. H. *Organometallics* **1997**, *16*, 3413. (c) Schneider, N.; Schaper, F.; Schmidt, K.; Kirsten, R.; Geyer, A.; Brintzinger, H. H. *Organometallics* **2000**, *19*, 3597. (d) Luttikhedde, H. J. G.; Leino, R.; Wilén, C.-E.; Näsman, J. H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39* (1), 229. (e) Rigby, S. S.; Decken, A.; Bain, A. D.; McGlinchey, M. J. *J. Organomet. Chem.* **2001**, *637*−*639*, 372. (f) Sun, J.; Berg, D. J.; Twamley, B. *Organometallics* **2008**, *27*, 683.

(6) (a) Repo, T.; Jany, G.; Hakala, K.; Klinga, M.; Polamo, M.; Leskelä, M.; Rieger, B. *J. Organomet. Chem.* **1997**, *549*, 177. (b) Aitola, E.; Hakala, K.; Byman-Fagerholm, H.; Leskelä, M.; Repo, T. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 373.

(7) Hoshi, T.; Nakazawa, T.; Saitoh, I.; Mori, A.; Suzuki, T.; Sakai, J.-i.; Hagiwara, H. *Org. Lett.* **2008**, *10*, 2063.

(8) (a) Eliasson, B.; Nouri-Sorkhabi, M. H.; Trogen, L.; Sethson, I.; Edlund, U.; Sygula, A.; Rabinovitz, M. *J. Org. Chem.* **1989**, *54*, 171. (b) Komatsu, K.; Fujiura, R.; Okamoto, K. *Chem. Lett.* **1988**, 265.

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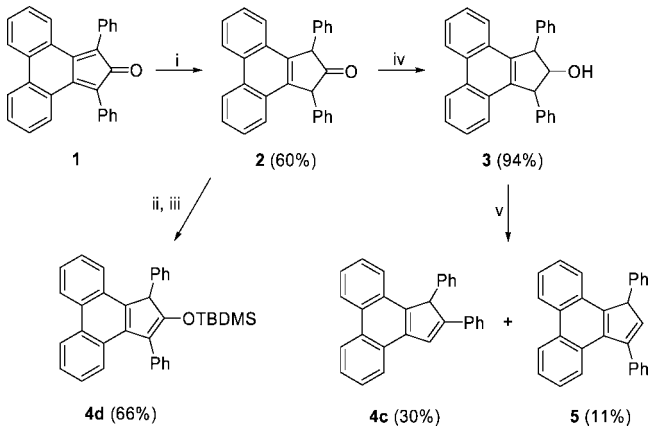
Scheme 1. Synthesis of the Ligand Precursors 4c and 4d[a]



[a] Conditions: (i) Zn/AcOH, reflux. (ii) NaH, THF, RT. (iii) TBDMSCl, THF, RT. (iv) $NaBH_4$, dioxane, reflux. (v) P_2O_5, benzene, reflux.

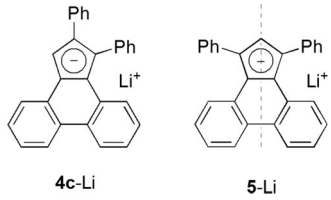


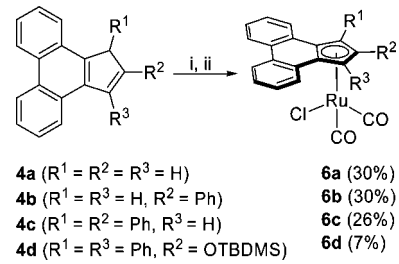
Figure 1. Lithium salts of the cyclopenta[*l*]phenanthrenyl ligand precursors **4c** and **5**.

silylation of the corresponding enolized ketone in a manner similar to that reported earlier for 1,3-dihydro-2-oxocyclopenta[*l*]phenanthrene,[5d] 2-indanone, and its analogues (Scheme 1).[9] The preparation of the diphenyl-substituted ligand precursor **4c** is likewise illustrated in Scheme 1. A similar transformation has been described earlier,[10] where the authors claimed the formation of the symmetrical 1,3-(diphenyl)cyclopenta[*l*]phenanthrene **5**. In our work, however, we observed a rearrangement taking place leading to a mixture of the 1,3- and 1,2-substituted products **5** and **4c** in 1:3 ratio. A similar rearrangement in the case of a trisubstituted analogue under acidic conditions has been described earlier.[11]

Structures of the compounds isolated here were also confirmed by NMR analysis of the corresponding anions. Upon deprotonation with *n*-BuLi in THF-d_8, compound **5** produced a highly symmetrical anion, while compound **4c** gave an unsymmetrical structure (Figure 1). The position of the double bond in **4c** was likewise confirmed by NMR spectroscopy. The two protons of the C_5 ring give rise to two doublets (^4J = 1.1 Hz) in the ^{1}H NMR spectrum at 5.42 and 7.81 ppm, respectively. In addition, a weak interaction (typical for allyl or *W*-coupling) between these protons was observed in the COSY spectrum, while a geminal coupling typical for a CH_2 group was absent.

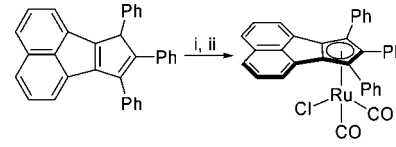
Next, the new ruthenium complexes **6a**−**d** and **8** containing cyclopenta[*l*]phenanthrenyl and cyclopenta[*a*]acenaphthylenyl ligands were prepared by reactions of dichlorotricarbonylruthenium dimer with the corresponding ligand precursors deprotonated with butyllithium (Schemes 1 and 2). The fairly low yields obtained represent the nonoptimized reaction conditions for metalation. In all cases siginificant amounts of starting ligand precursor were recovered during the reaction workup. Complex **6a** is unstable, decomposing rapidly in solutions and slowly in the solid state during storage at ambient temperature. All other polysubstituted complexes are stable when stored in air.

Scheme 2. Synthesis of the Ruthenium Complexes 6a−d[a]



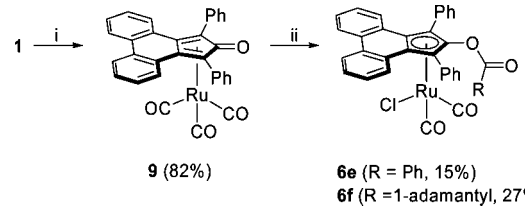
[a] Conditions: (i) *n*-BuLi/THF, −78 °C to RT. (ii) $[Ru(CO)_3Cl_2]_2$, RT.

Scheme 3. Synthesis of the Ruthenium Complex 8[a]



[a] Conditions: (i) *n*-BuLi/THF, −78 °C to RT. (ii) $[Ru(CO)_3Cl_2]_2$, RT.

Scheme 4. Synthesis of the Ruthenium Complexes 6e and 6f[a]



[a] Conditions: (i) $Ru_3(CO)_{12}$, mesitylene, 150 °C. (ii) RCOCl, toluene, 90 °C.

The synthesis of the trisubstituted cyclopenta[*l*]phenanthrenyl ruthenium complexes **6e** and **6f** containing an acyl substituent in position 2 of the C_5 ring commenced, in turn, from the phencyclone precursor **1** followed by oxidative acylation of the Ru(0) diene complex **9** with the corresponding acyl chlorides (Scheme 4).

In the ^{1}H NMR spectra of **6d** and **6f** two kinds of *o*- and *m*-protons and carbons were observed indicating restricted rotation of the phenyl rings. This rotation remained blocked in VT NMR experiments at 50 °C. The lithium salt of **4d** obtained by deprotonation with *n*-BuLi, however, showed in the ^{1}H NMR spectrum time-averaged symmetry with only one type of *o*- and *m*-protons and carbons (Figures 2 and 3). This observation may be due to rapid rotation of the phenyl rings in solution at ambient temperature, resulting in coinciding resonances. Another explanation, however, is the potential lability of the ionically bound lithium cation: a rapid exchange of Li^+ transitorily bound on

(9) See for example: (a) Leino, R.; Luttikhedde, H.; Wilén, C.-E.; Sillanpää, R.; Näsman, J. H. *Organometallics* **1996**, *15*, 2450. (b) Leino, R.; Luttikhedde, H. J. G.; Lehtonen, A.; Sillanpää, R.; Penninkangas, A.; Strandén, J.; Mattinen, J.; Näsman, J. H. *J. Organomet. Chem.* **1998**, *558*, 171. (c) Leino, R.; Luttikhedde, H. J. G.; Långstedt, L.; Penninkangas, A. *Tetrahedron Lett.* **2002**, *43*, 4149.

(10) Kreicberga, J.; Neilands, O.; Kampars, V. *Zh. Org. Khim.* **1975**, *11*, 1941.

(11) Dennis, G. D.; Edward-Davis, D.; Field, L. D.; Masters, A. F.; Maschmeyer, T.; Ward, A. J.; Buys, I. E.; Turner, P. *Aust. J. Chem.* **2006**, *59*, 135.

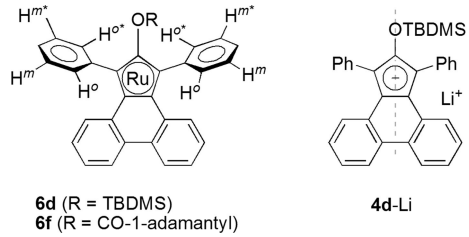


Figure 2. Top views of **6d**, **6f**, and **4d**-Li. Carbonyls and chlorine are omitted for clarity.

one side of the ligand and the other (even being located in the solvent independently from the anion) may also result in time-averaging of the NMR signals without rotation about the C−Ph bond.

X-ray Structures of Ruthenium Complexes. The molecular structures of the ruthenium complexes **6b**, **8**, and **9** were determined by X-ray crystallography and are elucidated, together with selected bond lengths and angles, in Figures 4−6. The ruthenium metal is η^5-coordinated in complexes **6b** and **8** (with similar Ru−C bond distances to all carbon atoms of the five-membered ring and η^4-coordinated in complex **9** with the longest Ru−C distance to the carbonyl carbon of the C_5 ring. The Ru−CO bond lengths are similar in all three complexes. In the η^5-coordinated complexes **6b** and **8** the cyclopenta[*l*]phenanthrenyl and cyclopenta[*a*]acenaphthylenyl moieties are nearly planar. A small distortion from planarity for the terminal C_6 ring of **6b** is observed, possibly due to repulsion of the partial negative charge on the ligand and the electronegative chlorine atom. In the η^4-diene complex **9** the ligand plane is significantly distorted, with one terminal C_6 ring tilted and the coordinated C_5 ring showing envelope geometry. The formal oxidation states +2 for **6b** and **8** and 0 for **9** are in good accordance with the elongated Ru−carbonyl and Ru−C_5 centroid distances in the latter complex. The Ru−C_5, Ru−carbonyl, and Ru−Cl distances are similar to those in analogous complexes containing (pentaphenyl)cyclopentadienyl[12] and (triphenyl)indenyl[2d] ligands.

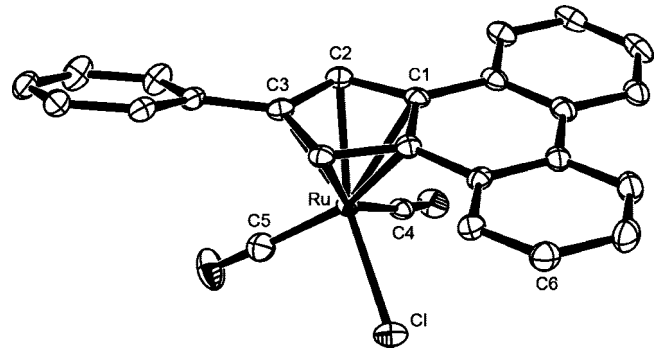


Figure 4. Molecular structure of **6b** (hydrogen atoms excluded for clarity, 50% probability ellipsoids). Selected distances (Å): Ru−C1 2.281(3), Ru−C2 2.196(3), Ru−C3 2.253(3), Ru−C4 1.898(3), Ru−C5 1.889(3), Ru−Cl 2.3988(7), Ru−Ct 1.899, C6−Pl1 0.078. Ct is the C_5 ring centroid. Pl1 is the plane calculated for the C_5 ring and two other C_6 rings.

Racemization of (*S*)-Phenylethanol. All ruthenium complexes prepared from **6a**−**f** and **8** were screened as catalysts for the racemization of (*S*)-α-phenylethanol **10**, a standard reference substrate utilized for initial investigation of catalytic activities in alcohol racemization and DKR (Scheme 5). The racemization reactions were carried out in toluene at ambient temperature by following the procedure described earlier by Bäckvall and co-workers.[12]

The unsubstituted cyclopenta[*l*]phenanthrenyl complex **6a** was found to be inefficient as a catalyst for the racemization reaction. With this complex, the racemization stops at 70% ee after 2 days. Somewhat better activities were obtained with the mono- and disubstituted complexes **6b** and **6c**. The racemization remained, however, fairly low, with 50% ee reached only after 4 and 2 days of reaction, respectively. Only in the case of the fully substituted complexes **6d** and **8** were acceptable activities obtained. The results are summarized in Figure 7.

The proposed mechanism for the racemization of secondary alcohols catalyzed by monoCp-ruthenium complexes has been

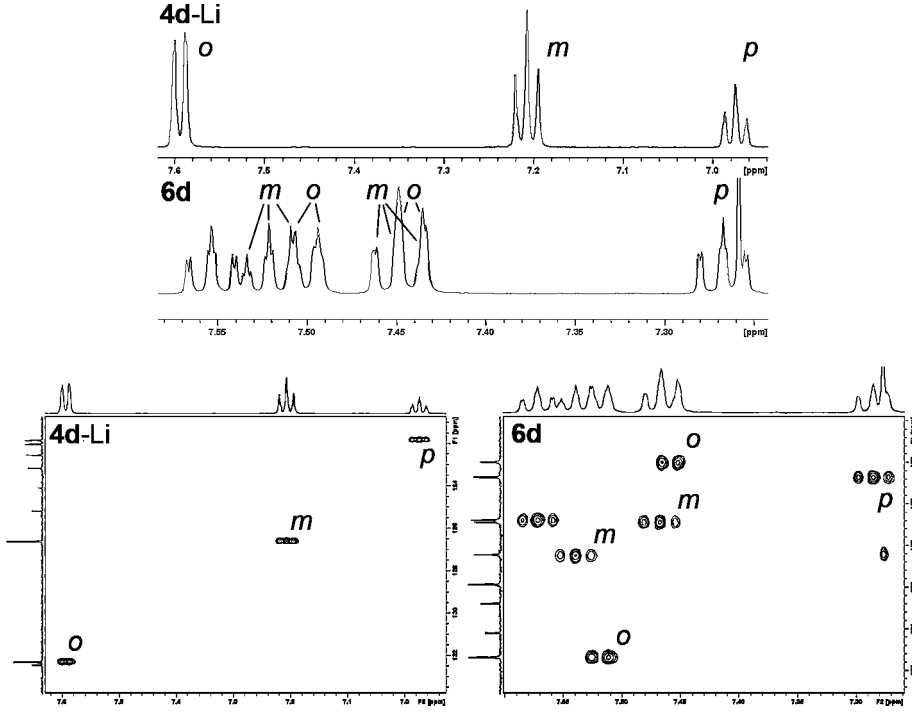


Figure 3. [1]H and HSQC-NMR of **6d** and **4d**-Li.

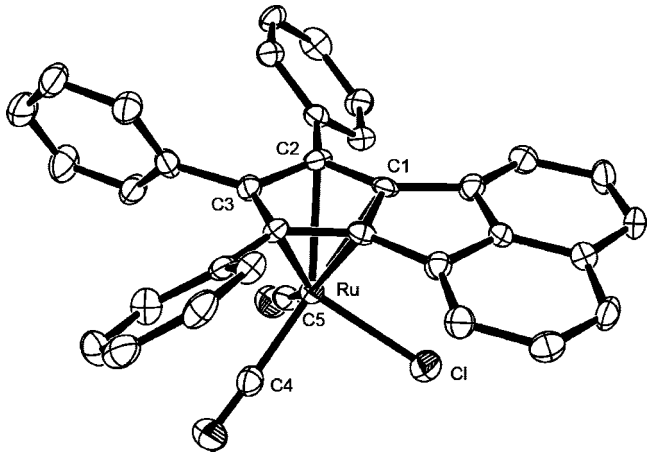


Figure 5. Molecular structure of **8** (hydrogen atoms excluded for clarity, 50% probability ellipsoids). Selected distances (Å): Ru−C1 2.293(4), Ru−C2 2.284(4), Ru−C3 2.204(3), Ru−C4 1.874(5), Ru−C5 1.902(5), Ru−Cl 2.4030(10), Ru−Ct 1.904. Ct is the closest C_5 ring centroid.

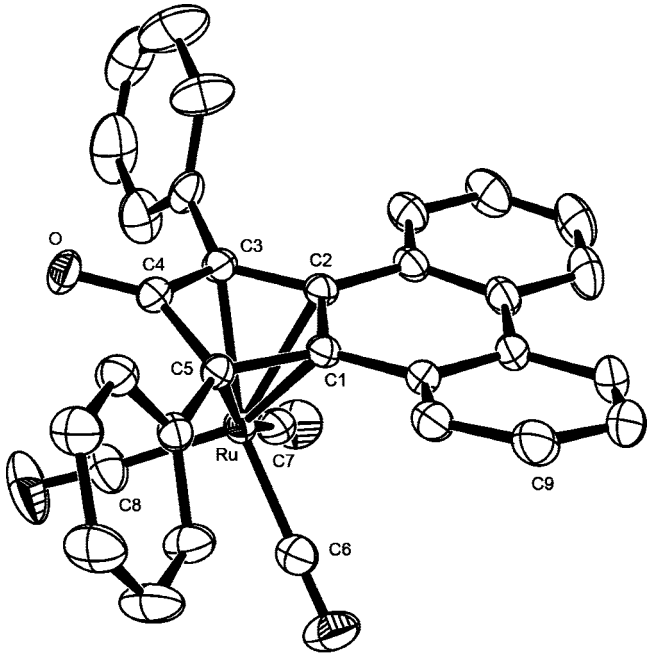
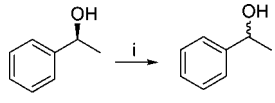


Figure 6. Molecular structure of **9** (hydrogen atoms excluded for clarity, 50% probability ellipsoids). Selected distances (Å): Ru−C1 2.2673(17), Ru−C2 2.2139, Ru−C3 2.2186, Ru−C4 2.4896(18), Ru−C5 2.220(7), Ru−C6 1.932(2), Ru−C7 1.936(2), Ru−C8 1.928(2), C4−O 1.227(2), Ru−Ct 1.919, C9−Pl1 0.493. Selected angles (deg): Pl2−Pl3 17.96. Ct is the C_5 ring centroid. Pl1 is the plane calculated for the two flat C_6 rings; Pl2 for C1, C2, C3, C4; Pl3 for C3, C4, C5, O.

Scheme 5. Racemization of (*S*)-Phenylethanol[a]



[a] Conditions: (i) Catalyst **6a**−**f** or **8** 1 mol %, *t*-BuOK 3 mol %, toluene, RT.

elucidated earlier by Bäckvall and co-workers (Scheme 6). The reaction involves a shift of hydrogen from the alcohol to ruthenium accompanied by ring slippage of the Cp ring from

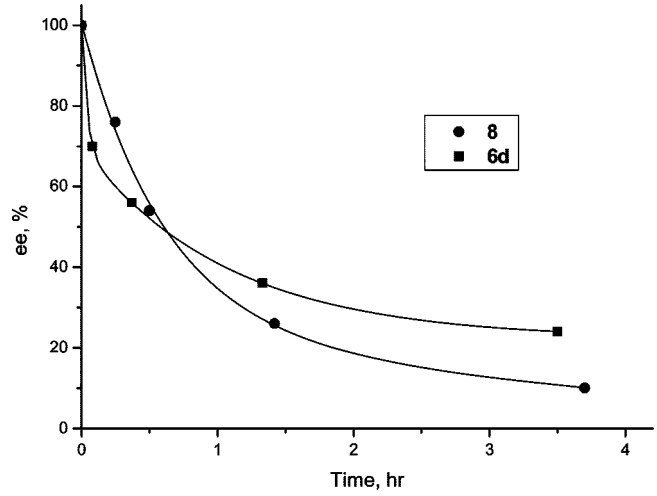
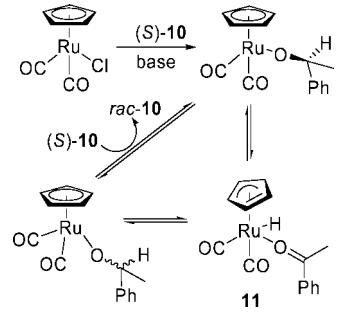


Figure 7. Racemization of (*S*)-phenylethanol catalyzed by **6d** and **8** (1 mol %).

Scheme 6. Racemization of (*S*)-Phenylethanol



η^5 to η^3. It is well known that the stabilities of Cp complexes generally increase with the increasing amount of substituents.[13] It is conceivable that in the case of the less substituted complexes **6a**−**c** the η^3-coordinated intermediate of type **10** (Scheme 6) might undergo further ring slippage and dissociation via η^1-coordination, leading to full decomposition of the catalyst. The low stability of **6a** in solution and the decomposition of **6b** and **6c** during the racemization reaction further support this hypothesis. The complexes prepared can be arranged in a series according to their phenylethanol racemization activities as **6a** < **6b** < **6c** ≪ **6d**, **8**, clearly demonstrating increasing activities with increasing number of C_5 ring substituents. Only the fully substituted complexes show acceptable activities. Accordingly, our attention next turned to the bulkier catalyst variants **6e** and **6f** of this type.

Both complexes **6e** and **6f** show activities similar to **6d** and **8** in the racemization of (*S*)-phenylethanol (Figure 8). The 2-benzoyl-substituted complex **6e** performs better when compared to its more congested adamantyl analogue **6f**, indicating that steric factors cannot be the only reason governing the catalytic activities. It might be speculated that the pendant phenyl functionality of the 2-benzoyl substituent may have a through-space stabilizing, coordinative intereaction with the ruthenium metal center. Similar intramolecular arene coordination is well known for Ti- and Zr-based mono(cyclopentadienyl) olefin polymerization catalysts.[14]

The racemization rates obtained with **6e** are, however, slower than those reported for the (pentaphenyl)cyclopentadienyl-based complex **12** (0.5 mol % of catalyst, 50% ee reached after ca. 5 min), currently considered as the lead catalyst structure, under similar reaction conditions.[12] On the other hand, complex **13**, structurally similar to **6e**, was by Park and co-workers reported

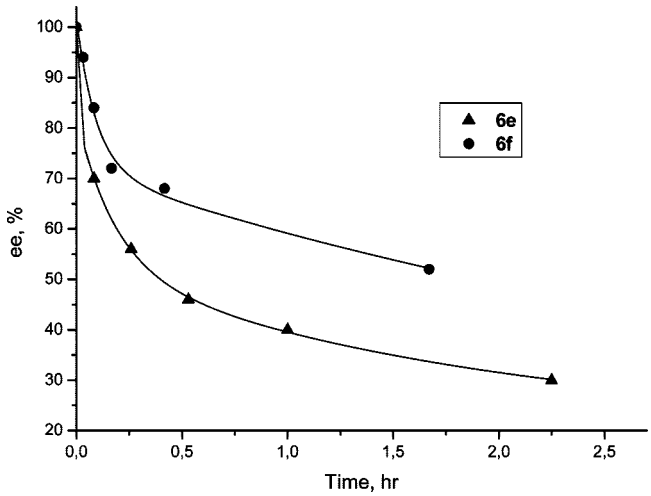


Figure 8. Racemization of (*S*)-phenylethanol catalyzed by **6e** and **6f** (1 mol %).

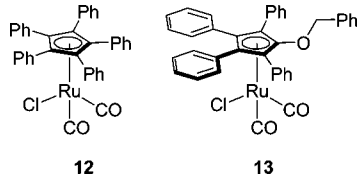


Figure 9. Structures of complexes **12** and **13** (structural analogues of **6e**).

to provide similar activities at 4 mol % concentration[15] to those observed here for **6e** at 1 mol % loading (for structures of **12** and **13**, see Figure 9).

The results obtained here may nevertheless be considered promising, clearly demonstrating variable racemization performance as a function of the ligand sterics, providing structure/reactivity trends to aid in future catalyst design.

Summary and Conclusions

To summarize, a series of half-sandwich ruthenium complexes with substituted cyclopenta[*l*]phenanthrenyl and cyclopenta[*a*]acenaphthylenyl ligands were prepared and characterized by NMR and in three cases by X-ray crystallography. The catalytic activities of the complexes in racemization of (*S*)-phenylethanol were investigated and were shown to depend strongly on the substitution pattern of the ligand framework. Acceptable racemization results were obtained with fully substituted complexes only. The racemization activities were, however, lower than those reported for chlorodicarbonyl(pentaphenyl)cyclopentadienylruthenium (**12**), currently considered as the best-performance catalyst for secondary alcohol racemization in DKR applications with enzymes. For this reason, neither extended investigations with other secondary alcohols nor attempts to pursue dymanic kinetic resolutions in combination with enzymes were carried out with these catalysts. In the present work, best performance was observed with a ligand structure containing a pendant aromatic moiety (benzoyloxy). Detailed NMR studies were carried out on a number of complexes and their cyclopenta[*l*]phenanthrenyl ligand anion lithium salts. Restricted rotation of phenyl substituents in the ligand five-membered rings was observed in some cases when moving from the lithium salts to transition metal coordination.

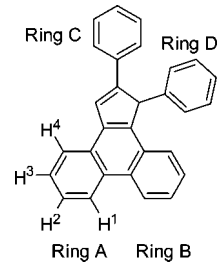


Figure 10. Labeling of substituted cyclopenta[*l*]phenanthrenyl fragments in the NMR spectral data.

Experimental Section

General Remarks. All manipulations with air- and moisture-sensitive compounds were performed under an inert atmosphere of argon using standard Schlenk techniques. Solvents were purchased from standard vendors and dried by standard procedures (THF, benzene, toluene were redistilled from Na/benzophenone ketyl, DCM was redistilled from calcium hydride, and pentane, hexane, heptane were redistilled from sodium). NMR spectra were recorded on a Bruker Avance 600 MHz spectrometer. Assignment of NMR signals is based on 1DTOCSY, NOE-diff, COSY, and HSQC experiments. Chiral GC analyses were performed on a HP 5890 series II gas chromatograph equipped with a Varian capillary column CP7502. Phencyclone (**1**) was prepared according to a litterature procedure.[11,16] Solutions of anions of **4c**,**d** and **5** in THF-d_8 were prepared directly in NMR tubes from the corresponding cyclopentadienes and *n*-BuLi using syringe-septum techniques. (*S*)-α-Phenylethanol was obtained by enzymatic kinetic resolution of the racemate and purified by column chromatography. Commercially available (*S*)-α-phenylethanol (Aldrich, 97%) yielded unreproducible results. Potassium *tert*-butoxide, required for activation of the racemization catalyst, should be freshly sublimated in order to obtain reproducible results.

The following labeling of the cyclopenta[*l*]phenanthrene derivatives was applied in the assignment of NMR signals (Figure 10):

General Procedures for Preparation of the Complexes 6a−d and 8. A solution of ligand precursor **1a−d** or **3** (0.5 mmol) in 3 mL of THF was cooled to −78 °C followed by addition of 0.31 mL (0.5 mmol) of a 1.6 M solution of *n*-BuLi in hexane via syringe. The reaction mixture was stirred for 15 min at −78 °C and allowed to warm to RT. Next, a solution of tricarbonyldichlororuthenium(II) dimer (128 mg, 0.25 mmol) in 2 mL of THF was added via syringe. The mixture was stirred for 2 h at RT, then evaporated with silica and purified by column chromatography using DCM−hexane as eluent. All products were obtained as yellow (**6a−d**) or brown (**8**) microcrystalline powders. Yields: **6a** 30%, **6b** 30%, **6c** 26%, **6d** 7%, **8** 27%.

Chlorodicarbonyl(η^5-cyclopenta[*l*]phenanthryl)ruthenium(II) (6a). ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 5.82 (t, ^3J = 2.7 Hz 1H, Cp-*H*), 5.95 (d, ^3J = 2,7 Hz, 2H, Cp-*H*), 7.66 (dd, ^3J = 7.2, 7.9 Hz, 2H, 3-*H*), 7,72 (ddd, 2H, ^3J = 8.4, 7.2, ^4J = 1.4, 2-*H*), 7.98 (dd, 2H, ^3J

(12) Martín-Matute, B.; Edin, M.; Bogár, K.; Kaynak, B.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2005**, *127*, 8817.

(13) (a) Heeg, M. J.; Janiak, C.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4529. (b) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. (c) Miller, E. J.; Landon, S. J.; Brill, T. B. *Organometallics* **1985**, *4*, 533. (d) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H.; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839.

(14) (a) Sassmannshausen, J.; Powell, A. K.; Anson, C. E.; Wocadlo, S.; Bochmann, M. *J. Organomet. Chem.* **1999**, *592*, 84. (b) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Angew. Chem.* **2001**, *40*, 2516. (c) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Organometallics* **2002**, *21*, 5122.

(15) Kim, N.; Ko, S.-B.; Kwon, M. S.; Kim, M.-J.; Park, J. *Org. Lett.* **2005**, *7*, 4523.

(16) Wooi, G. Y.; White, J. M. *Org. Biomol. Chem.* **2005**, *3*, 972.

= 7.9, ^4J = 1.4 Hz, 4-*H*), 8.54 (d, ^3J = 8.4 Hz, 1-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 72.34 (Cp), 89.59 (Cp), 107.30, 124.28, 125.02, 125.42, 128.26, 129.35, 131.15, 195.76 (*C*═O). MS: exact mass calcd. for $C_{19}H_{11}{}^{102}Ru^{35}ClO_2$ 407.9491, found 407.9490; 380 (M^+ − CO), 352 (M^+ − 2CO).

Chlorodicarbonyl(η^5-2-phenylcyclopenta[*l*]phenanthryl)ruthenium(II) (6b). ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 6.34 (s, 2H, Cp-*H*), 7.46 (dd, ^3J = 8.0, 6.6 Hz, 2H, *m*-Ph), 7.47 (t, ^3J = 6.6 Hz, 1H, *p*-Ph), 7.66 (d, ^3J = 8.0 Hz, 2H, *o*-Ph), 7.68 (dd, ^3J = 7.8, 7.7 Hz, 2H, 3-*H*), 7.72 (ddd, ^3J = 8.0, 7.7 Hz, ^4J = 1,1 Hz, 2H, 2-*H*) 8.06 (dd, ^3J = 7.8, ^4J = 1.1 Hz, 2H, 4-*H*), 8.54 (d, ^3J = 8.0 Hz, 2H, 1-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 69.46 (Cp-*C*), 106.01, 113.69, 124.31 (1-*C*), 125.19, 125.34 (4-*C*), 126.82 (*o*-*C*), 128.25 (2-*C*), 129.18 (*p*-*C*), 129.25 (3-*C*), 130.05, 130.28 (*m*-*C*), 131.10, 195.60 (*C*═O). MS: exact mass calcd for $C_{25}H_{15}{}^{102}Ru^{35}ClO_2$ 483.9804, found 483.9600; 455.97 (M^+-CO), 427.97 (M^+ − 2CO).

Chlorodicarbonyl(η^5-1,2-diphenylcyclopenta[*l*]phenanthryl)ruthenium(II) (6c). ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 7.22 (ur, 1H, Ph), 7.23 (d, ^3J = 7.0 Hz, 1H, *o*-Ph(c)), 7.26−7.30 (m, 3H, Ph), 7.27 (d, ^3J = 7.0 Hz, 1H, *o*-Ph (c)), 7.35 (d, ^3J = 8.0 Hz, 1H, *o*-Ph (d)), 7.40 (ur, 1H, Ph), 7.43 (d, ^3J = 8.0 Hz, 1H, *o*-Ph (d)), 7.52 (dd, ^3J = 7.6, 7.6 Hz, 1H, 2b- or 3b-*H*), 7.60 (ur, 1H, Ph), 7.61 (dd, ^3J = 7.6, 7.6 Hz, 1H, 2b- or 3b-*H*), 7.70 (dd, ^3J = 7.8, 7.8 Hz, 1H, 2a- or 3a-*H*), 7.73 (dd, ^3J = 7.8, 7.8 Hz, 1H, 2a- or 3a-*H*), 7.97 (d, ^3J = 7.6 Hz, 1H, 4b-*H*), 8.12 (d, ^3J = 7.8 Hz, 1H, 4a-*H*), 8.54 (d, ^3J = 7.6 Hz, 1H, 1b-H), 8.55 (d, ^3J = 7.8, 1H, 1a-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 70.94 (Cp), 95.68 (Cp), 103.32, 105.72, 116.06, 124.16 (1a-*C*), 124.18 (1b-*C*), 125.05, 125.36 (4a-*C*), 125.89, 126.52 (*o*-Ph), 127.64 (Ph), 128.23 (2a- or 3a-*C*), 128.35 (2 carbons, *o*-Ph), 128.80 (Ph), 128.99 (Ph), 129.12 (2b- or 3b-*C*), 129.22 (2a- or 3a-*C*), 129.25 (*o*-Ph), 129.45 (Ph), 129.76 (2b- or 3b-*C*), 129.98, 131.11, 131.25 (o-Ph), 131.72, 132.18, 134.71 (4b-*C*), 196.04 (*C*═O), 196.29 (*C*═O). MS: exact mass calcd for $C_{31}H_{19}{}^{102}Ru^{35}ClO_2$(+Na) 583.0015, found 583.0010; exact mass calcd for $C_{31}H_{19}{}^{102}Ru^{35}ClO_2$(+K) 598.9754, found 598.9727.

Chlorodicarbonyl(η^5-2-(*tert*-butyldimethylsiloxy)-1,3-diphenylcyclopenta[*l*]phenanthryl)ruthenium(II) (6d). ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ −0.55 (s, 6H, Si−C*H*$_3$), 0.46 (s, 9H, *t*-Bu), 7.27 (t, ^3J = 7.7 Hz, 2H, *p*-Ph), 7.44 (d, ^3J = 8.5 Hz, 2H, *o*-Ph), 7.45 (dd, ^3J = 7.7, 8.5 Hz, 2H, *m*-Ph), 7.50 (d, ^3J = 8.5, 2H, *o*-Ph), 7.51 (dd, ^3J = 7.7, 8.5 Hz, 2H, *m*-Ph), 7.55 (dd, ^3J = 8.1, 7.6 Hz, 2H, 2-*H*), 7.62 (dd, ^3J = 7.6, 7.6 Hz, 2H, 3-*H*), 8.01 (d, ^3J = 7.6 Hz, 2H, 4-*H*), 8.49 (d, ^3J = 8.1 Hz, 2H, 1-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ −4.65 (Si-*C*H$_3$), 18.01 (*C*(CH$_3$)$_3$), 24.87 (C(*C*H$_3$)$_3$), 86.00, 123.86 (1-*C*), 125.62, 126.99 (*o*-Ph), 127.35 (*p*-C), 128.39 (2-*C*), 128.44 (*m*-Ph), 129.22 (*m*-Ph), 129.93 (3-*C*), 130.39, 131.10, 131.68 (*o*-Ph), 135.42 (4-*C*), 196.49 (*C*═O). MS: exact mass calcd for $C_{37}H_{33}{}^{102}Ru^{35}ClO_3$(+Na) 713.0829, found 713.0802; exact mass calcd for $C_{37}H_{33}{}^{102}Ru^{35}ClO_3$(+Na − CO) 685.0880, found 685.0860.

Chlorodicarbonyl(η^5-1,2,3-triphenylcyclopenta[*a*]acenaphthylenyl)ruthenium(II) (8). ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 7,17 (ur, 2H, Ph), 7.24−7.27 (m, 1H, Ph), 7.35−7.39 (m, 6H, Ph), 7.54 (dd, ^3J = 7.1, 8.1 Hz, 2H, 2-*H*) 7.55−7.57 (m, 4H), 7.79 (d, ^3J = 7.1 Hz, 2H, 3-*H*), 7.89 (d, ^3J = 8.1 Hz, 2H, 1-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 100.38 (Cp), 106.77 (Cp), 108.06, 123.19 (3-*C*), 128.00 (1-*C*), 128.15 (Ph), 128.20 (2-*C*), 128.48 (Ph), 128.65 (Ph), 129.11 (Ph), 129.66, 129.90, 130.26, 130.68 (Ph), 130.77, 132.21 (Ph), 138.53, 197.03 (*C*═O). MS: exact mass calcd for $C_{35}H_{21}{}^{102}Ru^{35}ClO_2$(+Na) 633.0171, found 633.0167; exact mass calcd for $C_{35}H_{21}{}^{102}Ru^{35}ClO_2$(+K) 648.9911, found 648.9892.

Tricarbonyl(η^4-1,3-diphenylcylopenta[*l*]phenanthren-2-one)ruthenium(0) (9). A mixture of 0.76 g (2 mmol) of phencyclone (**5**), 0.32 g (0.5 mmol) of triruthenium dodecacarbonyl, and 5 mL of mesitylene was heated to 150 °C with stirring for 24 h. The reaction mixture was cooled to RT, and argon was bubbled through the mixture to remove the carbon monoxide released followed by heating at the same temperature for an additional 4 h. After cooling to RT, the mixture was diluted with 5 mL of hexane. The precipitate was separated by filtration, redissolved in 10 mL of toluene, and separated from a small amount of insoluble byproduct **2** by filtration. Finally, 0.7 g (82%) of **9** was obtained as a greenish microcrystalline solid. ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 7.26 (dd, ^3J = 8.2, 7.6 Hz, 2H, 3-*H*), 7.45 (d, ^3J = 8.2 Hz, 2H, 4-*H*), 7.48 (dd, ^3J = 8.2, 8.0 Hz, 2H, *m*-Ph), 7.49 (dd, ^3J = 8.2, 7.5 Hz, 2H, *m*-Ph), 7.54 (d, ^3J = 8.0 Hz, 2H, *o*-Ph), 7.55 (d, ^3J = 7.5 Hz, 2H, *o*-Ph), 7.57 (dd, ^3J = 8.2, 7.6 Hz, 2H, 2-*H*), 7.58 (t, ^3J = 8.2 Hz, 2H, *p*-Ph), 8.52 (d, ^3J = 8.2 Hz, 2H, 1-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 82.14 (cyclopentadienone), 97.54 (cyclopentadienone), 124.06 (1-*C*), 126.00, 126.50 (4-*H*), 127.87 (3-*H*), 128.34 (*m*-Ph), 128.86 (*m*-Ph), 128.92 (1-*H*), 129.42 (*p*-Ph), 130.94, 131.33 (*o*-Ph), 132.83, 134.75 (*o*-Ph), 177.58 (═C−*C*O−C═), 193.64 (C═O). MS: exact mass calcd for $C_{32}H_{19}{}^{102}RuO_4$(+H) 569.0327, found 569.0330; exact mass calcd for $C_{32}H_{19}{}^{102}RuO_4$(+H − CO) 541.0378, found 541.0394; exact mass calcd for $C_{32}H_{19}{}^{102}RuO_4$(+H − 2CO) 513.0429, found 513.0410.

General Procedures for Preparation of the Complexes 6e and 6f. A mixture of 57 mg (0.1 mmol) of **9**, 0.1 mmol of the corresponding acyl chloride, and 2 mL of toluene was heated at 90 °C for 12 h. The solvent was evaporated and the residue purified by column chromatography using DCM−hexane as eluent. The products were obtained as yellow microcrystalline solids. Yields: **6e** 15%, **6f** 27%.

Chlorodicarbonyl(η^5-2-benzoyloxy-1,3-diphenylcyclopenta[*l*]-phenanthryl)ruthenium(II) (6e). ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 7.30 (dd, ^3J = 8.1, 7.5 Hz, 2H, *m*-Bz), 7.33 (dd, ^3J = 7.5, 7.8 Hz, 2H, 3-*H*), 7.37 (dd, ^3J = 8.2, 8.0 Hz, 2H, *m*-Ph), 7.41 (dd, ^3J = 8.2, 7.6 Hz, 2H, *m*-Ph), 7.49 (t, ^3J = 8.0 Hz, 2H, *p*-Ph), 7.49 (t, ^3J = 7.5 Hz, 2H, *p*-Bz), 7.59 (d, ^3J = 8.2 Hz, 2H, *o*-Ph), 7.59 (d, ^3J = 7.5 Hz, 2H, *o*-Ph) 7.62 (dd, ^3J = 8.2, 7.8 Hz, 2H, 2-*H*), 7.70 (d, ^3J = 7.9 Hz, 2H, *o*-Bz), 7.92 (d, ^3J = 7.5 Hz, 2H, 4-*H*), 8.54 (d, ^3J = 8.2 Hz, 2H, 1-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 89.31 (Cp), 99.06 (Cp), 124.09 (1-*C*), 125.06, 126.91 (*o*-Ph), 127.69 (3-*C*), 128.51 (*m*-Bz), 128.63 (*m*-Ph), 128.78, 129.01(2-*C*), 129.29 (*m*-Ph), 129.38 (*p*-Ph), 129.97 (*o*-Bz), 131.40 (*o*-Ph), 131.58, 133.35, 133.57 (4-*C*), 134.16 (*p*-Bz), 163.24 (Ph-*C*═O), 195.61 (*C*═O). MS: exact mass calcd for $C_{38}H_{23}{}^{102}Ru^{35}ClO_4$(+Na) 703.0226, found 703.0227.

Chlorodicarbonyl(η^5-2-adamantanoyloxy-1,3-diphenylcyclopenta[*l*]phenanthryl)ruthenium(II) (6f). ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 1.28 (d, ^3J = 2.5 Hz, 6H, α-adamantyl-*H*). 1.46 (d, ^2J = 12.5 Hz, 3H, equatorial δ-adamantyl-*H*), 1.57 (d, ^2J = 12.5 Hz, 3H, axial δ-adamantyl-*H*), 1.80 (t, ^3J = 2.5 Hz, 3H, β-adamantyl-*H*), 7.32 (dd, ^3J = 8.2, 7.5 Hz, 2H, 2-*H*), 7.42 (t, ^3J = 7.2 Hz, *p*-Ph), 7.50 (dd, ^3J = 8.1, 7.2 Hz, 2H, *m*-Ph), 7.51 (d, J = 8.1, 2H, *o*-Ph), 7.56 (dd, ^3J = 8.1, 7.2, 2H, *m*-Ph), 7.60 (d, ^3J = 8.1 Hz, 2H, *o*-Ph), 7.61 (dd, ^3J = 7.5, 7.5 Hz, 2H, 3-*H*), 7.84 (d, ^3J = 7.5 Hz, 2H, 4-*H*), 8.54 (d, ^3J = 8.2 Hz, 2H, 1-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 27.39 (β-adamantyl-*C*), 35.98 (δ-adamantyl-*C*, a,e), 37.85 (α-adamantyl-C), 40.52 (γ-adamantyl-C), 88.97 (Cp), 99.68 (Cp), 124.06 (1-*C*), 125.07, 126.93 (*o*-Ph), 127.65 (1-*C*), 128.51 (*p*-Ph), 128.89, 128.95 (4-*C*), 129.22 (2 carbons, *m*-Ph), 131.66 (*o*-Ph), 131.58, 133.22, 133.78 (3-*C*), 174.12 (Ad-*C*═O), 195.55 (*C*═O). MS: exact mass calcd for $C_{42}H_{33}{}^{102}Ru^{35}ClO_4$(+Na) 761.1009, found 761.0999, exact mass calcd for $C_{42}H_{33}{}^{102}Ru^{35}ClO_4$(+K) 777.0748, found 777.0728.

1,3-Dihydro-1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthren-2-one (2,5-dihydrophencyclone) (2). A suspension of 1.91 g (5 mmol) of phencyclone **1** and 0.98 g (15 mmol) of zinc powder in 50 mL of glacial acetic acid was refluxed until the green color of **5** dissappeared (ca. 2 h). The mixture was evaporated, and the residue boiled with 200 mL of xylene and filtered hot from zinc powder. Xylene was evaporated, the residue was suspended in a small amount of DCM, and the precipitate was separated by filtration giving fraction A, enriched in the *cis*-isomer. The filtrate was

evaporated, the residue was suspended in a small amount of acetone, and the precipitate formed was separated by filtration, giving fraction B, enriched in the *trans*-isomer. Configurational assignment of the NMR spectra has been reported earlier.[17] *trans*-**2** was obtained as a mixture with *cis*-**2** with some NMR signals overlapping. Total yield: 1.14 g (60%). *cis*-**2** ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 5.20 (s, 2H, Ph-C*H*), 7.17−7.27 (m, 8H, Ph), 7.49 (dd, ^3J = 8.1, 7.0, 2H phenanthrene-*H*), 7.58 (d, ^3J = 8.1 Hz, 2H, phenanthrene-*H*), 7.68 (dd, ^3J = 8.4, 7.0, 2H, phenanthrene-*H*), 8.82 (d, ^3J = 8.4 Hz, 2H, phenanthrene-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 58.93, 123.38, 126.52, 126.95, 127.12, 127.27, 128.17, 128.56, 128.76, 131.21, 135.53, 137.37, 210.55. *trans*-**2** ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 5.26 (s, 2H, Ph-C*H*), 7.14−7.29 (m, 8H, Ph-*H*), 7.49 (ur, 2H), 7.58 (d, ^3J = 8.0 Hz, 2H), 7.69 (ur, 2H), 8.79 (d, ^3J = 8.4 Hz, 2H).

2-(*tert*-Butyldimethylsiloxy)-(1,3-diphenyl)cyclopenta[*l*]phenanthrene (4d) and 2-(*tert*-Butyldimethylsiloxy)(1,3-diphenyl)cyclopenta[*l*]phenanthrenyllithium (4d-Li). A suspension of 100 mg (0.26 mmol) of **2** (mixture of isomers) and 40 mg (1 mmol) of 60% sodium hydride in mineral oil in 3 mL of THF was stirred overnight. Then 75 mg (0.5 mmol) of TBDMSCl was added, and the obtained clear solution was stirred for 24 h. The reaction mixture was distributed between chloroform and water, the organic phase was separated, dried over sodium sulfate, and evaporated, and the residue was purified by column chromatography (eluent DCM−hexane). **4d** (85 mg, 66%) was obtained as an oil, solidifying upon storage. ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ −0.34 (s, 3H, Si-CH_3), −0.11 (s, 3H, Si-CH_3), 0.66 (s, 9H, tBu), 4.80 (s, 1H, Cp-H), 7.19−7.22 (m, 1H), 7.26−7.28 (m, 5H), 7.37 (ur, 1H), 7.40−7.55 (m, 8H), 7.72 (d, ^3J = 8.3 Hz, 2H, 4-*H*), 8.64 (d, ^3J = 8.2 Hz, 1H, 1-*H*), 8.72 (d, ^3J = 8.2 Hz, 1H, 1-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ −4.62 (Si-*C*H_3), −4.23 (Si-*C*H_3), 18.08 (Si-*C*$(CH_3)_3$), 25.40 (Si-C$(CH_3)_3$), 56.01 (Cp, C−O−Si), 122.42, 123.20, 123.24, 123.38, 124.32, 125.44, 125.49, 125.59, 126.58, 126.98, 127.33, 127.84, 128.56, 128.76, 128.90, 131.06, 134.34, 136.31, 138.41, 138.71, 162.72.

4d-Li. ^{1}H NMR (THF-d_8, 600.13 MHz, aromatic part): δ 6.83δ6.86 (m, 4H, 2- and 3-*H*), 6.97 (t, ^3J = 7.3 Hz, 2H, *p*-Ph), 7.21 (dd, ^3J = 7.9, 7.3 Hz, 4H, *m*-Ph), 7.59 (d, ^3J = 7.9 Hz, 4H, *o*-Ph), 8.20−8.22 (m, 2H, 4-*H*), 8.33−8.35 (m, 2H, 1-*H*). ^{13}C NMR (THF-d_8, 150.9 MHz, aromatic part): δ 105.50, 113.58, 116.91(2- or 3-*C*), 121.84 (*p*-Ph), 122.02 (1-*C*), 122.52 (2- or 3-*C*), 123.15 (4-*C*), 124.07, 125.17, 126.61 (*m*-Ph), 132.29 (*o*-Ph), 132.43, 143.67.

2,3-Dihydro-1,3-diphenyl-1*H*-cyclopenta[*l*]phenanthren-2-ol (3). Sodium borohydride (0.4 g, 10 mmol) was added to a boiling suspension of 0.5 g (1.3 mmol) of **2** (mixture of isomers) in dioxane. The mixture was refluxed for 1 h, cooled to RT, quenched with 5% HCl, and evaporated. The residue was treated with DCM, and the insoluble portion was filtered off. The filtrate was evaporated. **3** (0.47 g, 94%; mixture of stereoisomers) was obtained as a white powder. ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 4.77−4.82 (m, 1H), 5.20−5.22 (m, 1.5H), 5.35−5.39 (m, 0.5 H), 7.14−7.21 (m, 7H), 7.29−7.33 (m, 2H), 7.38−7.42 (m, 2H), 7.46−7.55 (m, 2H), 7.61−7.66 (m, 3H), 8.76 (d, ^3J = 8.3 Hz, 1H), 8.80 (d, ^3J = 8.3 Hz, 1H).

1,2-Diphenylcyclopenta[*l*]phenanthrene (4c), 1,2-diphenylcyclopenta[*l*]phenanthrenyllithium (4c-Li), 1,3-diphenylcyclopenta[*l*]-phenanthrene (5), and 1,3-diphenylcyclopenta[*l*]phenanthrenyllithium (5-Li). Phosphorus pentoxide (0.3 g, 2 mmol) was added to a boiling solution of 0.3 g (0.78 mmol) of **3** in 30 mL of benzene. The mixture was refluxed for 5 min, cooled to RT, washed with water, and evaporated. The residue was purified by column chromatography (eluent DCM−hexane). Two fractions were isolated: 30 mg (11%) of **5** (first band, dark blue in UV) and 85 mg (30%) of **4c** (second band, bright blue in UV) as white solids. **4c** ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 5.37 (d, ^4J = 1.1 Hz, Cp-*H*), 7.07 (t, ^3J = 7.3 Hz, 1H, *p*-Ph), 7.14 (dd, ^3J = 7.9, 7.3 Hz, 2H, *m*-Ph), 7.18 (t, ^3J = 7.3 Hz, 1H, *p*-Ph), 7.20 (d, ^3J = 7.9 Hz, 2H, *o*-Ph), 7.29 (dd, ^3J = 8.4, 7.3 Hz, 2H, *m*-Ph), 7.38 (dd, ^3J = 8.0, 7.5 Hz, 1H, 3b-*H*), 7.46 (dd, ^3J = 8.3, 7.5 Hz, 1H, 2b-*H*), 7.61 (d, ^3J = 8.4 Hz, 1H, *o*-Ph), 7.66 (dd, ^3J = 7.8, 8.0 Hz, 1H, 2a-*H*), 7.69 (dd, ^3J = 7.8, 8.3 Hz, 1H, 3a-*H*), 7.76 (d, ^4J = 1.1 Hz, 1H, Cp-*H*), 7.83 (d, ^3J = 8.0 Hz, 1H, 4b-*H*), 8.28 (d, ^3J = 8.0 Hz, 1H, 4a-*H*), 8.64 (d, ^3J = 8.3 Hz, 1H, 1b-*H*), 8.71 (d, ^3J = 8.3 Hz, 1H, 1a-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 57.42 (Cp-C*H*), 123.38 (1a-*C*), 123.44 (1b-*C*), 123.86 (4b-*C*), 124.63 (4a-*C*), 124.69 (Cp-*C*H), 125.25 (2b-*C*), 126.20 (2a-*C*), 126.59 (*o*-Ph), 126.63 (3a-*C*), 126.70 (*p*-Ph), 126.73 (3b-*C*), 127.35 (*p*-Ph), 128.50 (*m*-Ph), 128.52 (*o*-Ph), 128.84 (*m*-Ph), 128.86, 129.44, 130.76, 135.15, 138.96, 139.48, 143.13, 153.20. Due to complexity of the spectrum, one signal corresponding to a quaternary carbon atom is not visible.

Compound **4c**-Li: ^{1}H NMR (THF-d_8, 600.13 MHz): δ 6.71 (t, ^3J = 7.3 Hz, 1H, *p*-Ph), 6.79 (dd, ^3J = 8.1, 7.4 Hz, 1H, 3b-*H*), 6.83 (dd, ^3J = 8.1, 7.4 Hz, 1H, 2b-*H*), 6.85 (s, 1H, Cp-*H*), 6.91 (dd, ^3J = 8.1, 7.4 Hz, 1H, 2a-*H*), 6.91 (dd, ^3J = 8.2, 7.3 Hz, 2H, *m*-Ph), 7.10 (t, ^3J = 7.3 Hz, 1H, *p*-Ph), 7.15 (dd, ^3J = 8.1, 7.4 Hz, 1H, 3a-*H*), 7.18 (d, ^3J = 8.2 Hz, 2H, *o*-Ph), 7.20 (dd, ^3J = 8.0, 7.3 Hz, 2H, *m*-Ph), 7.37 (d, ^3J = 8.0 Hz, 2H, *o*-Ph), 7.78 (d, ^3J = 8.1 Hz, 1H, 4b-*H*), 8.07 (d, ^3J = 8.1 Hz, 1H, 4a-*H*), 8.26 (d, ^3J = 8.1 Hz, 1H, 1a-*H*), 8.27 (d, ^3J = 8.1 Hz, 1H, 1b-*H*). ^{13}C NMR (THF-d_8, 150.9 MHz): δ 98.74 (Cp-*C*H), 115.24, 117.62 (2b-*C*), 117.93 (2a-*C*), 120.64 (*p*-Ph), 121.33, 121.37 (4a-*C*), 122.17 (1b-*C*), 122.23 (1a-*C*), 122.79 (4b-*C*), 123.00 (*p*-Ph), 123.37 (3b-*C*), 124.06, 124.18 (3a-*C*), 124.96, 125.94, 126.59 (*m*-Ph), 127.11 (*m*-Ph), 127.63, 127.75 (*o*-Ph), 132.39 (*o*-Ph), 133.01, 133.74.

Compound **5**: ^{1}H NMR ($CDCl_3$, 600.13 MHz): δ 5.09 (d, ^3J = 1.8 Hz, 1H, Cp-*H*), 6.58 (d, ^3J = 1.8 Hz, 1H, Cp-*H*), 7.16 (ur, 2H), 7.20 (ur, 1H), 7.26 (ur, 2H), 7.34 (ur, 1H), 7.40−7.48 (m, 4H), 7.58 (ur, 1H), 7.75 (d, ^3J = 8.2 Hz, 1H, 4-*H*), 7.86 (d, ^3J = 8.2 Hz, 1H, 4-*H*), 8.71 (d, ^3J = 8.2 Hz, 1H, 1-*H*), 8.76 (d, ^3J = 8.2 Hz, 1H, 1-*H*). ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 55.70 (Cp-*C*H), 123.25, 123.34, 124.86, 125.33, 125.55, 125.75, 125.88, 126.67, 126.79, 127.55, 128.03, 128.12, 128.32, 128.84, 128.97, 129.66, 131.21, 138.27, 138.73, 139.14, 140.73, 143.25, 145.15. Due to complexity of the spectrum, one signal corresponding to a quaternary carbon atom is not visible.

Compound **5**-Li: ^{1}H NMR (THF-d_8, 600.13 MHz): δ 6.39 (s, 1H, Cp-*H*), 6.90 (ur, 2H, 2-*H*), 6.91 (t, ^3J = 7.0 Hz, 2H, *p*-Ph), 6.92 (ur, 2H, 3-*H*), 7.16 (dd, ^3J = 7.0, 7.4 Hz, 4H, *m*-Ph), 7.58 (d, ^3J = 7.4 Hz, 4H, *o*-Ph), 8.32 (d, ^3J = 7.7 Hz, 2H, 4-*H*), 8.33 (d, ^3J = 7.7 Hz, 2H, 1-*H*). ^{13}C NMR (THF-d_8, 150.9 MHz): δ 117.86, 117.87, 117.89 (2-*C*), 121.29 (*p*-Ph), 122.23 (1-*C* + Cp-*C*H), 123.09 (3-*C*), 123.20 (4-*C*), 126.02, 126.87 (*m*-Ph), 128.57 (*o*-Ph), 133.25, 145.72.

General Procedure for the Racemization Reactions. Potassium *tert*-butoxide (0.7 mg, 6 μmol) and 2 μmol of complex (**6a**−**f** or **8**) were mixed in 1 mL of toluene. The mixture was stirred for 5 min at RT. Then a solution of 24 mg (200 μmol) of (*S*)-α-phenylethanol **10** in 1 mL of toluene was added. Derivatization of samples (propionic anhydride in the presence of pyridine and DMAP) was performed in order to achieve a better resolution and to stop the racemization process. The ratio of the enantiomers formed was determined by chiral GC (oven temperature 100 °C, retention times 10.13 min (*S*) and 11.30 min (*R*)).

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Supporting Information Available: X-ray diffraction data for complexes **4b**, **8**, and **9** in CIF format and copies of NMR spectra of the complexes prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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