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Chelated Ruthenium Complexes of Functionalized Pentaarylcyclopentadienes

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The Pd-catalyzed arylation of tetraphenylcyclopentadiene (**7**) and the classical "tetracyclone route" are tested as preparative entries to a variety of pentaarylcyclopentadienes **4** monofunctionalized in the *ortho*-position. The corresponding chelated ruthenium complexes **6** can be formed either thermally induced or by photochemical irradiation. These complexes contain stereogenic ruthenium centers. Enantiopure complexes **6f** and **6g**, with chiral oxazoline moieties, were tested for the asymmetric transfer hydrogenation of phenyl ketones **9**.

Introduction

Cyclopentadienyl ligands with a side chain bearing an additional donor ligand have attracted considerable attention for the formation of stabilized half-sandwich complexes,[1] some of which exhibit extraordinary catalytic activity, especially in the area of olefin polymerization.[2] To our knowledge no sterically demanding pentaarylcyclopentadiene congeners have been studied so far,[3] although their notoriously labile transition metal complexes[4] should profit from both chelate stabilization and steric shielding of the phenyl groups. In addition, the aryl substituents are predestined as anchor groups for donor ligands,[5] which might even carry chiral information. Of special interest are "stereogenic-at-metal complexes",[6,7] which recently gained importance in asymmetric synthesis.[8] Therefore we decided to

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(3) To our knowledge there is only one known kind of pentaarylated cyclopentadienyl ligand with one phenyl group functionalized with a donor atom (oxygen) in *ortho*-position. But no coordination is observed: (a) Colbran, S. B.; Craig, D. C.; Harrison, W. M.; Grimley, A. E. *J. Organomet. Chem.* **1991**, *408*, C33–C38. (b) Saadeh, C.; Colbran, S. B.; Craig, D. C.; Rae, A. D. *Organometallics* **1993**, *12*, 133–39. (c) Colbran, S. B.; Harrison, W. M.; Saadeh, C. *Organometallics* **1994**, *13*, 1061–1063. (d) Harrison, W. M.; Saadeh, C.; Colbran, S. B. *Organometallics* **1997**, *16*, 4254–4256. (e) Harrison, W. H.; Saadeh, C.; Colbran, S. P.; Craig, D. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3785–92. For examples of the utility of pentaphenylcyclopentadienyl ligands in asymmetric reactions, see: (f) Ruble, J. C.; Tweddell, J.; Fu, G. C. *J. Org. Chem.* **1998**, *63*, 2794–2795. (g) Tao, B.; Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123*, 353–354. (h) Martin-Matute, B.; Edin, M.; Bogár, K.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2004**, *43*, 6535, and ref [11]. (i) Ko, S.-B.; Baburaj, B.; Kim, M.-J.; Park, J. *J. Org. Chem.* **2007**, *72*, 6860–6864.

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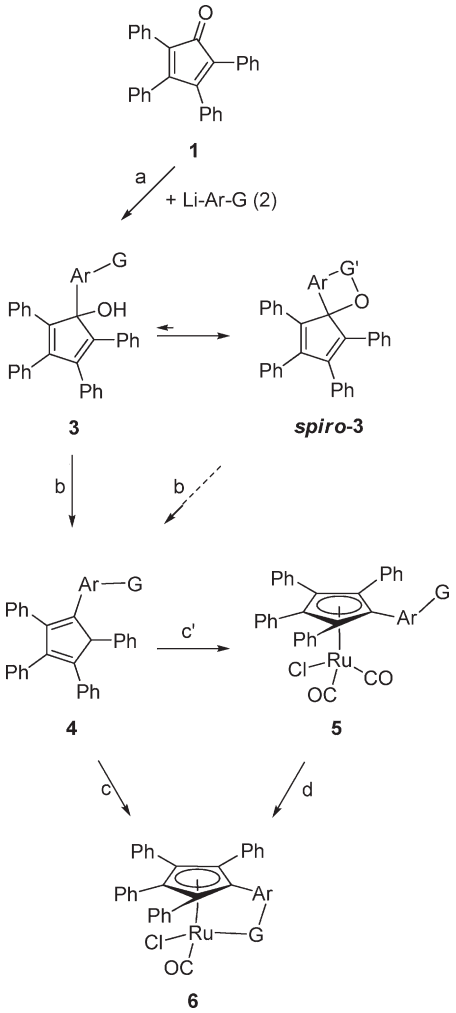
synthesize a couple of model compounds **4** as ligand precursors, preferring the classical tetracyclone route,[9] which can be easily scaled-up in contrast to our experiences with our palladium-catalyzed arylation of cyclopentadienes,[10] particularly of 1,2,3,4-tetraphenylcyclopenta-1,3-diene (**7**). These ligand precursors should eventually function as bidentate ligands in ruthenium complexes **6**, which are potential catalysts, for instance for transfer hydrogenations at phenyl ketones.

Results and Discussion

Tetracyclone (**1**) smoothly reacted at room temperature in THF or Et_2O with various functionalized lithioarenes **2**, generally to give the corresponding pentaarylcyclopentadienols **3** in moderate to good yields (Scheme 1, Table 2).

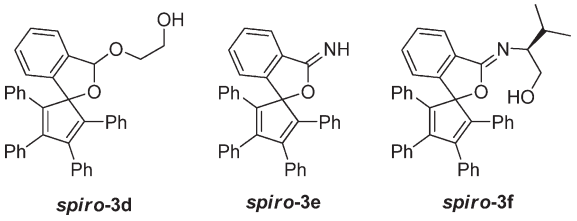
The ^1H NMR spectra of the cyclopentadienols **3a** and **3c** exhibit outstanding downfield shifts for the hydroxy protons: whereas the OH signal of the quinolinyl-substituted system **3c** appears at 10.91 ppm, the corresponding signal of the dimethylamino derivative **3a** was found even further downfield-shifted at 11.35 ppm. This effect is due to strong intramolecular hydrogen bonds (O−H−N), confirmed by X-ray structure analysis of suitable crystals (Figure 1). In addition, the IR spectrum of **3a** exhibits a broad absorption at 2500 cm^{-1}.

Scheme 1. Synthesis of Chelated Ru Complexes 6[a]



[a] Ar = aryl group, G, G′ = functional groups. (a) 1. functionalized aryl-Li reagent **2** in THF or Et_2O, 2. H^+/H_2O; (b) 1. strong base, 2. $LiAlH_4$; (c, c′) 1. $Ru_3(CO)_{12}$, toluene or xylene, decane, 160−175 °C, sealed tube, 2. $CHCl_3$ added, 160−175 °C, 3. silica gel; (d) *hv*.

However, in some cases—with an acetal, cyano, or oxazoline functionality in the *ortho*-position—a subsequent equilibrium favored the formation of spirocyclic isomers ***spiro*-3**, the acetal ***spiro*-3d**, and the imidic acid esters ***spiro*-3e** and ***spiro*-3f**.



Most interestingly, the subsequent desoxygenation succeeded through treatment with $LiAlH_4$ when starting both from tertiary alcohols **3** and from the spirocyclic isomers ***spiro*-3d** and ***spiro*-3e**, giving access to the functionalized pentaarylcyclopentadienes **4** in acceptable yields. In contrast, the usual reduction protocol[9c] with HBr/Zn failed. Commonly, a deprotonation of the alcohol with a strong base before the $LiAlH_4$ reduction was necessary. Therefore we decided to try the *in situ* reduction of the intermediary

(4) For examples of metal complexes stabilized by pendant donors, see: (a) Fryzuk, M. D.; Jafarpour, L.; Rettig, S. J. *Organometallics* **1999**, *18*, 4050–58. (b) Enders, M.; Fink, J.; Pritzkow, H. *Eur. J. Inorg. Chem.* **2000**, 1923–1925. (c) Buil, M. L.; Esteruelas, M. A.; Lopez, A. M.; Mateo, A. C. *Organometallics* **2006**, *25*, 4079–4089.

(5) For examples of bidentate cyclopentadienyl complexes with functionalized phenyl groups see refs 2g, 2h, 2j, and 2n−2p.

(6) For chiral cyclopentadienyl complexes with sidearm coordination—not cited in ref [1] or [2]—see for example: (a) Zeijden, A. A. H. v. d. *J. Organomet. Chem.* **1996**, *518*, 147–153. (b) Zeijden, A. A. H. v. d.; Jiminez, J.; Mattheis, C.; Wagner, C.; Merzweiler, K. *Eur. J. Inorg. Chem.* **1999**, 1919–1930. (c) Trost, B. M.; Vidal, B.; Thommen, M. *Chem.—Eur. J.* **1999**, *5*, 1055–1069. (d) Onitsuka, K.; Ajioka, Y.; Matsushima, Y.; Takahashi, S. *Organometallics* **2001**, *20*, 3274–3282. (e) Becker, E.; Mereiter, K.; Puchberger, M.; Schmid, R.; Kirchner, K.; Doppin, A. *Organometallics* **2003**, *22*, 3164–3170. (f) Doppiu, A.; Englert, U.; Salzer, A. *Chem. Commun.* **2004**, 2166–2167. (g) Brunner, H.; Köllnberger, A.; Mehmood, A.; Tsuno, T.; Zabel, M. *Organometallics* **2004**, *23*, 4006–4008. (h) Matsushima, A. Y.; Onitsuka, K.; Takahashi, S. *Organometallics* **2005**, *24*, 2747–2754. (i) Onitsuka, K.; Okuda, H.; Sasai, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 1454–1457.

(7) For general reviews on metal-centered stereochemistry see: (a) Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1194–1208. (b) Brunner, H. *Eur. J. Inorg. Chem.* **2001**, 905–912. (c) Ganter, C. *Chem. Soc. Rev.* **2003**, *32*, 130–138.

(8) (a) Muniz, K.; Bolm, C. *Chem.—Eur. J.* **2000**, *13*, 2309–2316. (b) Hamelin, O.; Rimbound, M.; Pécaut, J.; Fontecave, M. *Inorg. Chem.* **2007**, *46*, 5354–5360. (c) Gott, A. L.; Clarke, A. J.; Clarkson, G. J.; Scott, P. *Chem. Commun.* **2008**, 1422–1424. For an impressive example concerning the role of a stereogenic metal center of a non-cyclopentadienyl complex in metathesis reactions see: (d) Sattely, E.; Meek, S. J.; Malcomson, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 943–953. (e) Lee, Y.-J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 10652–10661.

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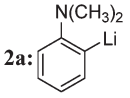
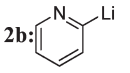
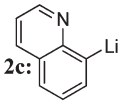
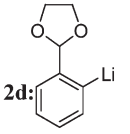
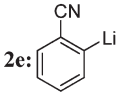
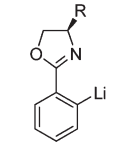
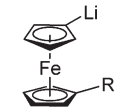
(10) (a) Miura, M.; Pivsa-Art, S.; Dyker, G.; Heiermann, J. *Chem. Commun.* **1998**, 1889–1890. (b) Dyker, G.; Heiermann, J.; Miura, M.; Inoh, J.-I.; Pivsa-Art, S.; Satoh, T.; Momura, M. *Chem.—Eur. J.* **2000**, *6*, 3426–3433. (c) Dyker, G.; Heiermann, J.; Miura, M. *Adv. Synth. Catal.* **2003**, *345*, 1127–1132.

Table 1. Crystallographic Data of 3a and 3c

	3a	**3c**
empirical formula	$C_{37}H_{31}NO$	$C_{38}H_{27}NO$
fw	505.63 g/mol	513.61 g/mol
cryst syst	monoclinic	monoclinic
space group	*P*2(1)	$P2_1/n$
a [Å]	10.112(19)	6.3367(13)
b [Å]	10.020(15)	20.450(4)
c [Å]	13.54(3)	21.361(4)
α [deg]	90	90
β [deg]	99.33(9)	92.10(3)
γ [deg]	90	90
V [Å^3]	1354(4)	2766.2(10)
T [K]	293(2)	293(2)
Z	2	4
no. of unique data	4290	4887
no. of refined params	309	366
R1 ($I > 2\sigma(I)$)	0.0622	0.0673
wR2 (all data)	0.1559	0.1768

Table 2. Synthesis of Compounds 3−6

	Yield[%]				
Li-Ar-G **2**	**3**	***spiro*-3**	**4**	**5**	**6**
 **2a:**	71	-	79	57	64
 **2b:**	84	-	90	45	-
 **2c:**	52	-	25[a]	-	51
 **2d:**	-	81	65[a]	-	-
 **2e:**	-	73	50	26[b]	
					
2f R= *i*-propyl		85	60[a]		49
2g R = *i*-butyl		n.i.	41[a]		55
2h R = benzyl		n.i.	46[a]		42
					
2i R = H	71		75	70	
2j R = PPh_2	55		77		

[a] Prepared by a one-pot procedure without isolation of **3** and **4**, respectively. [b] Yield based on converted **4e**; n.i.: not isolated.

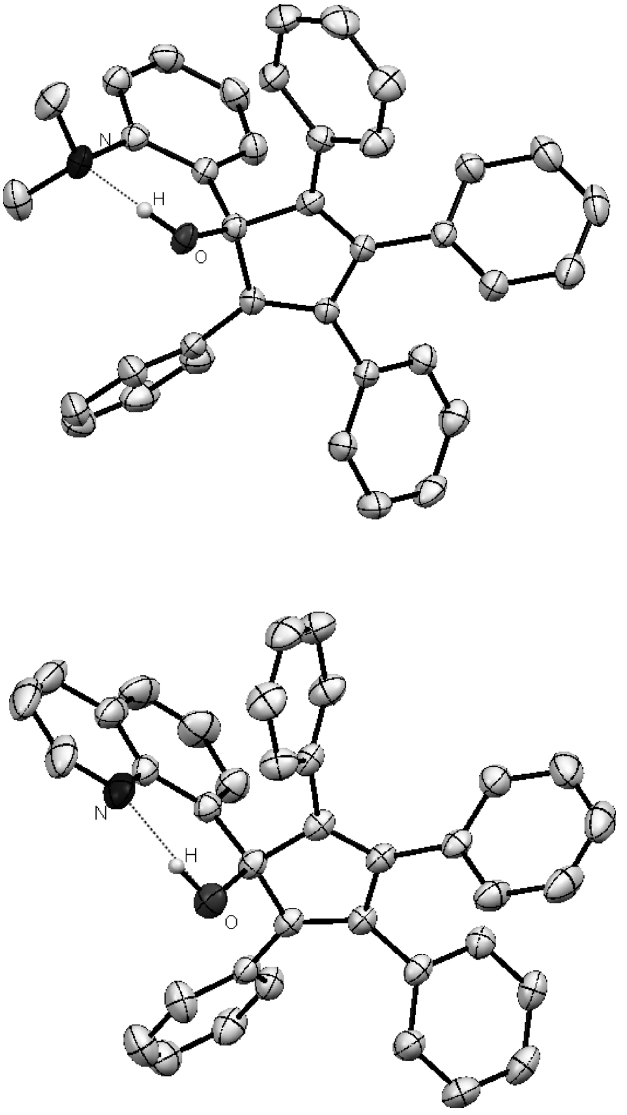


Figure 1. ORTEP representations of cyclopentadienols **3a** (top) and **3c** (bottom). Thermal ellipsoids are displayed at 50% probability. Hydrogens are omitted for clarity except the ones in the hydrogen bonds, shown with dashed lines.

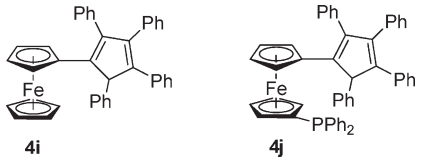
alkoxides from the reaction of lithioarenes **2** with tetracyclone (**1**), in analogy to earlier, alkyl-functionalized examples.[11] Thus, **4c−d** and **4f−h** were synthesized in a one-pot procedure, circumventing the isolation of the alcohols **3c**,**d** and spirocycles ***spiro*-3f−h**, respectively.

Remarkably, the oxazoline group as well as the nitrile remained intact despite the strongly reducing conditions. Nevertheless, the oxazoline-substituted cyclopentadienes **4f−h** contained minor impurities after column chromatography and were applied as crude products in the complexation step.

The ferrocenyl-substituted alcohol **3i** as well as its reduced derivative **4i** exhibit an aging phenomenon in chloroform solution, registered as an increasing broadening of the signals in the ^{1}H NMR spectrum, probably due to paramagnetic impurities being formed. Presumably, an acid-induced elimination of the hydroxyl group in **3i** and protonation of the double bond in **4i**, respectively, lead to the

(11) Martin-Matute, B.; Edin, M.; Bogár, K.; Kaynak, F. B.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2005**, *127*, 8817–8825.

formation of a cation, which is especially stabilized by the ferrocene moiety[12] and has paramagnetic character as proved by qualitative EPR measurements.



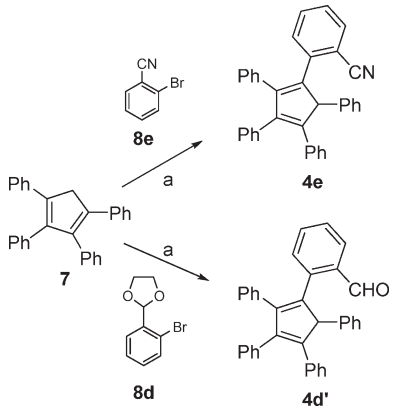
Thus, addition of trifluoro acetic acid to a $CDCl_3$ solution of the alcohol **3i** or cyclopentadiene **4i** leads to highly colored solutions and an extreme broadening of the ^1H NMR signals. In contrast, the NMR signals of the ferrocenyl alcohol **3j** are sharp. Presumably, the phosphinyl group intercepts the protonation of the alcohol functionality as the initial step of the carbocation formation.

This is confirmed by a test with the phosphinyl-substituted derivative **3j** in $CDCl_3$ solution in the NMR tube: upon treatment with a drop of trifluoroacetic acid, a significant change in color occurred and a change in chemical shifts, but no broadening of the NMR signals was observed. However, the addition of the stronger acid HBF_4 led to a tremendous darkening of the solution and a considerable broadening of the ^1H NMR signals.

Because of the lability of the ferrocenyl-substituted cyclopentadienols, they are especially easy to reduce by $LiAlH_4$ without prior deprotonation, giving the cyclopentadienes **4i** and **4j** in reasonable yields. Most interestingly, the reduction of the ferrocenyl alcohols **3i** and **3j** resulted virtually in single isomers of **4i** and **4j**; only small amounts of other double-bond isomers could be detected by NMR, and finally only one isomer was isolated. In both cases the isomer with the diene and the ferrocene moiety linearly conjugated should be thermodynamically favored. This was proved for the ferrocene **4j** through the HMBC spectrum: a ^3J-coupling of the cyclopentadienyl proton and the tertiary ferrocenyl carbon was clearly registered. In contrast, regularly a mixture of three double-bond isomers of cyclopentadienes **4** is expected: usually, the diagnostic signals of the double allylic protons at about 5 ppm allow the determination of the isomeric ratio. Thus, the cyclopentadiene **4b** exhibits three distinct singlets in the ^1H NMR at 5.18, 5.55, and 5.60 ppm in a ratio of 1:3.2:2.6 as well as three diagnostic ddd signals of the pyridine ring at 8.44, 8.47, and 8.54 ppm. In addition, with increasing steric demand of the *ortho*-substituents rotamers might become observable in the ^1H NMR spectrum.[10c] For example, the *ortho*-dimethylaminophenyl-substituted cyclopentadiene **4a** exhibits four different cyclopentadienyl protons and three singlets for the dimethylamino groups since two of them are isochronal. In contrast, only two isomers were observed after purification by washing with methanol in the ultrasonic bath for the dioxolane **4d** with one isomer remarkably predominating.

In the case of the nitrile-substituted derivative **4e** we could prove the feasibility of our alternative palladium-catalyzed approach[10] by applying the direct arylation to 1,2,3,4-tetraphenylcyclopenta-1,3-diene (**7**) and 2-bromobenzonitrile (**8e**) as coupling components (Scheme 2). **4e** was obtained in 78% yield, a superior result compared to the overall 34% yield of the two-step tetracyclone route. Equally, aldehyde **4d′** could also be synthesized by this method in 81% yield, starting from *ortho*-bromophenyl-1,3-dioxolane (**8d**) and 1,2,3,4-tetraphenylcyclopenta-1,3-diene (**7**), with the hydrolysis proceeding during workup. However, these are certainly special cases since nitrogen and phosphine *ortho*-substituents generally interfere with the Pd-catalyzed process. Thus, applying this method to the coupling reaction with 2-bromophenyloxazolines remained unsuccessful according to orientating results.

Scheme 2. Synthesis of Nitrile 4e and Aldehyde 4d′ by Pd-Catalyzed Arylation of Tetraphenylcyclopentadiene (7)[a]



[a] (a) 1. 5% $Pd(OAc)_2$, 10% PPh_3, Cs_2CO_3, DMF, 140 °C, 2 d; 2. *p*-TsOH.

The aldehyde **4d′**, the dioxolane **4d**, and the nitrile **4e** provide opportunities for further derivatization. For example, reductive amination of the aldehyde **4d′** would lead to a variety of amines with the tether extended by one methylene unit compared to cyclopentadiene **4a**. Orientating tests have already been successful and are currently the focus of ongoing studies.

We envisioned a ruthenation protocol reported by Bäckvall et al.[11] to be suitable for the synthesis of chelated ruthenium complexes with chiral metal centers. Indeed, the synthesis of the corresponding ruthenium chloride carbonyl complexes **5** generally succeeds by refluxing a toluene/decane mixture of pentaarylcyclopentadienes **4** and $Ru_3(CO)_{12}$ in a sealed tube, followed by treatment with chloroform. Usually the reaction mixture is directly submitted to column chromatography to give the corresponding complexes in moderate yields. Only in the case of the phosphinyl-substituted ferrocene **4j** did we fail to isolate a pure Ru complex. In contrast, the synthesis of the unsubstituted ferrocenyl complex **5i** worked very smoothly, which might imply an incompatibility of phosphinyl groups in this complexation reaction.

Similarly, the synthesis and the isolation of the nitrile complex **5e** succeeded in low yield. After chromatography the ^1H NMR spectrum appears to be quite pure. But the presence of the C−N absorption band at 2228 cm^{-1} (2223 cm^{-1} in the free ligand) suggests that the nitrile is not coordinated to the metal (N−Ru distance of 356 pm).

Within the resulting ruthenium complexes the interaction of the tethered ligand with the metal center strongly depends

(12) Similar observations were made in the ferrocene-tetracyclone adduct and its protonated form: (a) Gupta, H. K.; Stradiotto, M.; Hughes, D. W.; McGlinchey, M. J. *J. Org. Chem.* **2000**, *65*, 3652–3658. (b) Harrington, L. E.; Vargas-Baca, I.; Reginato, N.; McGlinchey, M. J. *Organometallics* **2003**, *22*, 663–669, and references therein for further examples of cations stabilized by ferrocene.

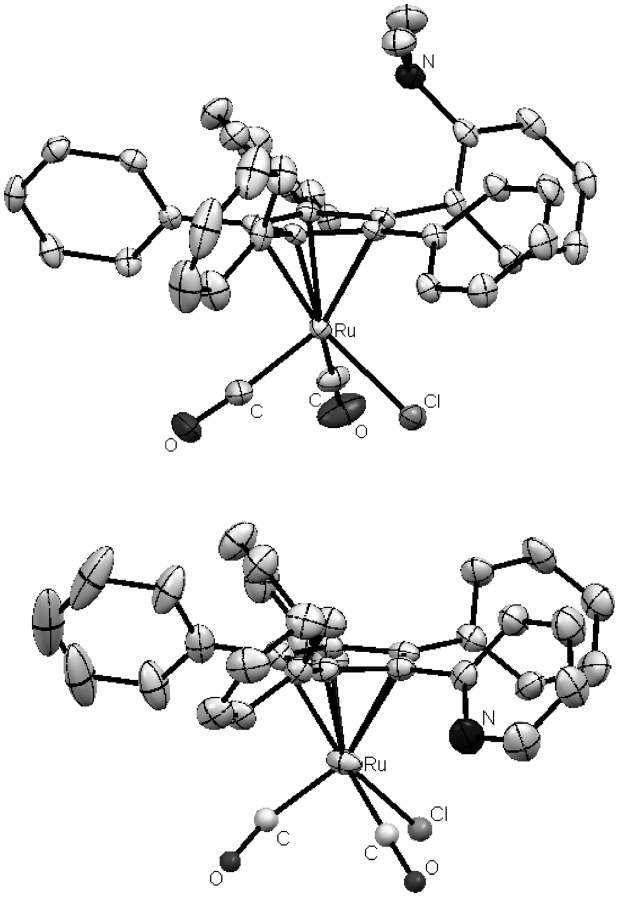


Figure 2. ORTEP representations of ruthenium complexes **5a** (top) and **5b** (bottom). Thermal ellipsoids are displayed at 50% (**5a**) and 30% (**5b**) probability. The carbonyl and chloride ligands in **5b** are systematically disordered and were not shown as ellipsoids. Hydrogens are omitted for clarity.

on the position of the donor atom: the X-ray crystal structure analyses of complexes **5a** and **5b** enable an informative comparison (Figure 2): whereas the nitrogen of the pyridine in **5b** is directed toward the ruthenium, we might postulate a weak electronic interaction between the nitrogen and the metal. In contrast, the dimethylamino group in the ruthenium dicarbonyl complex **5a** is orientated away from the metal, probably because of steric reasons.[13]

Nevertheless, an irradiation of a toluene solution of **5a** led to loss of a carbonyl group and to a subsequent intramolecular coordination of the nitrogen to the metal. This coordination is additionally indicated by a tremendous change in color from yellow to deep purple. Most interestingly, the coordination establishes the ruthenium as a stable stereogenic center, which makes the two methyl groups distinguishable in the ^{1}H NMR as they become diastereotopic. Remarkably, one methyl group experiences a chemical downfield shift of about 1 ppm (Figure 4). In addition, the structure has been proved by an X-ray analysis of suitable crystals (Figure 3).

In contrast, a corresponding photoinduced chelate formation could not be observed for the pyridine derivative **5b**,

(13) Similar observations were made with less sterically hindered cyclopentadienyl-aniline complexes: see refs [2g] and [2i] and for an indenyl complex: Baker, R. W.; Luck, I. J.; Turner, P. *Inorg. Chem. Commun.* **2005**, *8*, 817–820.

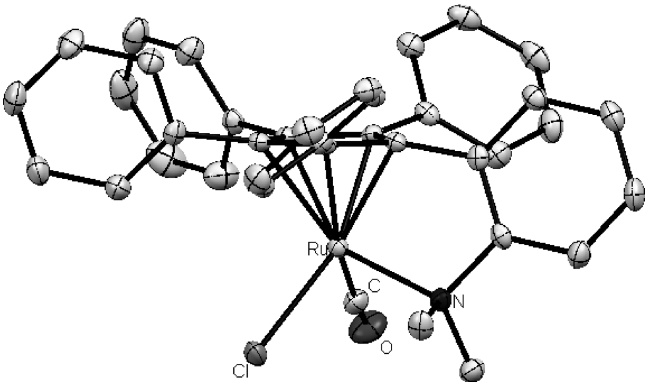


Figure 3. ORTEP representation of chelated ruthenium complex **6a**. Thermal ellipsoids are displayed with 50% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−CO 1.884(2), Ru−Cl 2.4377(5), Ru−N 2.225(2), range Ru−C_{Cp} 2.096(2)−2.270(2); Cl−Ru−CO 92.29(6), Cl−Ru−N 88.81(4), N−Ru−CO 95.17(8).

presumably due to the unfavorable distance of the donor nitrogen, which would afford a ring slippage before the pyridine nitrogen could coordinate to the ruthenium.[14] For similar reasons a chelation of the nitrile **5e** probably failed as well.

The reaction of **4c** with $Ru_3(CO)_{12}$ and $CHCl_3$ yielded a poorly soluble ruthenium complex. Although two CO absorption bands in the IR spectrum suggest the formation of a ruthenium dicarbonyl complex, the number of signals in the HMBC spectrum (the solubility for a good-quality ^{13}C NMR was too poor) implies the inequivalence of the phenyl groups and the cyclopentadienyl carbons, which is in accordance with the chelated complex **6c** with a stereogenic ruthenium atom.

This is in accordance with the observation that an irradiation did not lead to any conversion, although the position of the nitrogen donor is comparable to the dimethylamino derivative **5a**, which was easily decarbonylated to **6a** by irradiation (*vide supra*). These results suggest the presence of the chelated quinoline ruthenium complex **6c** rather than the dicarbonyl complex **5c**.[15]

The oxazoline-substituted cyclopentadienes **4f**−**h** directly led to chelated complexes **6f**−**h**, thermally induced at 175 °C without need of a photoinduced decarbonylation.

Because of their inherent chiral information, these oxazolinyl complexes are of special interest, allowing the formation of diastereomers with the second stereogenic center at the metal.[6,7] In all cases we were pleased to isolate only one diastereoisomer after chromatography of the reaction mixture with a diastereomeric ratio of at least 95:5 in the case of the isopropyl system **6f**. When the reaction was performed at the somewhat lower temperature of 160 °C, we observed impurities that could not be separated by chromatography. We assigned them to the nonchelated ruthenium dicarbonyl complex rather than to the other chelate diastereomer, as we

(14) Coordination of pyridine tethered to cyclopentadienyl ligands was observed when a methylene bridge was introduced: see refs [1w] and [2q]. (a) Paolucci, G.; Vignola, M.; Coletto, L.; Pitteri, B.; Benetollo, F. *J. Organomet. Chem.* **2003**, *687*, 161–170. (b) Krutko, D. P.; Kirsanov, R. S.; Belov, S. A.; Borzov, M. V.; Churakov, A. V. *J. Organomet. Chem.* **2007**, *692*, 1465–1471.

(15) Bidentate cyclopentadienyl quinoline complexes have been published mostly by Enders et al. See for example refs 1n, 1p, 1u, 2g, 2m, and [4b].

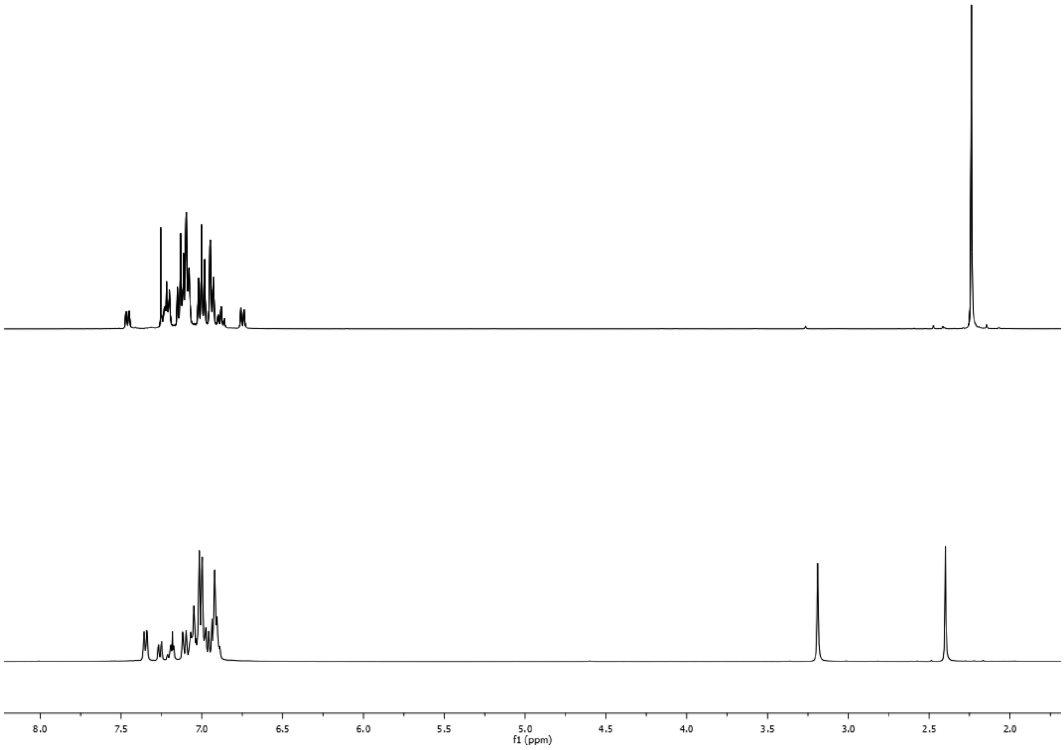


Figure 4. Comparison of the ^{1}H NMR spectra of **5a** (top) and its chelated derivative **6a** (bottom) with diastereotopic methyl groups.

Table 3. Crystallographic Data of 5a, 5b, and 6a

	5a	5b	6a
empirical formula	$C_{39}H_{30}NO_2ClRu$	$C_{24}H_{16}Cl_{0.67}N_{0.67}O_{1.33}Ru_{0.67}$	$C_{39.5}H_{36}NO_{2.5}ClRu$
fw	681.16 g/mol	426.05 g/mol	701.21 g/mol
cryst syst	monoclinic	orthorhombic	monoclinic
space group	*P*2(1)/*n*	*Pbca*	*C*2/*c*
a [Å]	8.7240(2)	20.623(4)	34.1453(9)
b [Å]	31.6975(8)	13.899(5)	10.6540(2)
c [Å]	12.0248(3)	20.763(5)	19.7747(6)
α [deg]	90	90	90
β [deg]	104.984(3)	90	115.737(3)
γ [deg]	90	90	90
V [Å^3]	3212.14(14)	5951(3)	6480.1(3)
T [K]	110(2)	223(2)	113(2)
Z	4	12	8
no. of unique data	7367	5209	6695
no. of refined params	399	365	418
R1 ($I > 2\sigma(I)$)	0.0288	0.0833	0.0239
wR2 (all data)	0.0571	0.2654	0.0561

detected $Ru(CO)_2$ fragments in the FAB mass spectra as well as two additional CO absorption bands in the IR spectrum.

Since we were able to get X-ray quality crystals of the chelated oxazolinyl complexes **6f**−**h** (Figures 5−7), we could determine the ruthenium center to have an *S*-configuration, which avoids steric interaction between the oxazoline moiety and the chloride. In addition, the substituents at the oxazoline—whether the isopropyl group of **6f**, the isobutyl group in **6g**, or the benzyl group in **6h**—are directed away from the crowded metal center. The pure diastereomers show a remarkable configurational stability.[7] Even after weeks at room temperature, solutions of the complexes in $CDCl_3$ did not show any evidence of an epimerization at the metal center.

Interestingly, the isobutyl-substituted oxazolinyl complex **6g** exhibits a double carbonyl absorption at 1952 and 1964 cm^{-1}. In contrast, complexes **6f** and **6h** both show only one distinct CO absorption in the IR spectrum.

We envisioned the enantiopure metal complexes **6f**−**6h** as potential catalysts for various enantioselective reactions. Thus, we applied these complexes in preliminary tests in the asymmetric transfer hydrogenation of prochiral phenyl ketones **9** with 2-propanol as hydrogen donor to give the

(16) Selected recent examples of asymmetric Ru(II)-catalyzed transfer hydrogenations of ketones with the 2-propanol/base system: (a) Hannedouche, J.; Clarkson, G. J.; Wills, M. *J. Am. Chem. Soc.* **2004**, *126*, 986–987. (b) Gomez, M.; Jansat, S.; Muller, G.; Aullon, G.; Maestro, M. A. *Eur. J. Inorg. Chem.* **2005**, 4341–4351. (c) Reetz, M. T.; Li, X. *J. Am. Chem. Soc.* **2006**, *128*, 1044–1045. (d) Fukuzawa, S.-I.; Suzuki, T. *Eur. J. Org. Chem.* **2006**, 1012–1016. (e) Enthaler, S.; Hagemann, B.; Bhor, S.; Anilkumar, G.; Tse, M. K.; Bitterlich, B.; Junge, K.; Erre, G.; Beller, M. *Adv. Synth. Catal.* **2007**, *439*, 853–860. (f) Baratta, W.; Chelucci, G.; Herdtweck, E.; Magnolia, S.; Siega, K.; Rigo, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7651–7654. (g) Ikariya, T.; Blacker, A. J. *Acc. Chem. Res.* **2007**, *40*, 1300–1308. (h) Chakka, S. K.; Andersson, P. G.; Maguire, G. E. M.; Kruger, H. G.; Govender, T. *Eur. J. Org. Chem.* **2010**, *5*, 972–980.

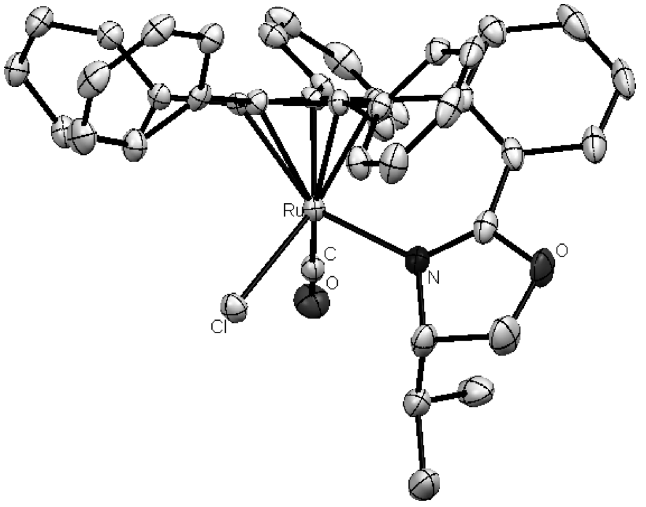


Figure 5. ORTEP representation of chiral chelated ruthenium complex **6f**. Thermal ellipsoids are displayed at 50% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−CO 1.875(2), Ru−Cl 2.4258(5), Ru−N 2.104(2), range Ru−C_{Cp} 2.117(2)−2.323(2); Cl−Ru−CO 89.43(7), Cl−Ru−N 90.88(5), N−Ru−CO 94.86(8).

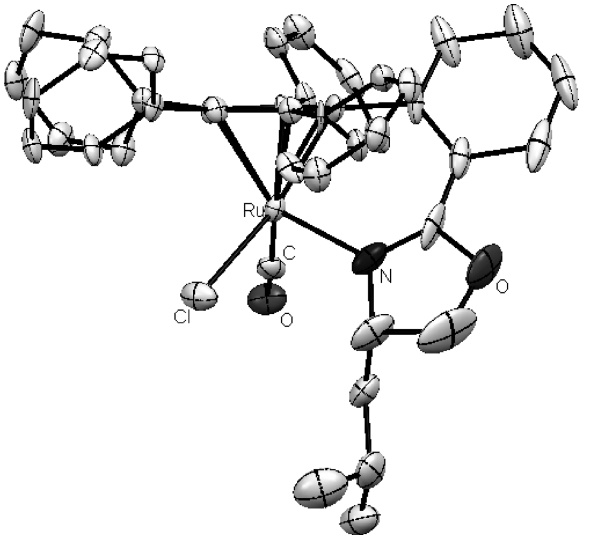


Figure 6. ORTEP representation of chiral chelated ruthenium complex **6g**. Thermal ellipsoids are displayed at 50% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru-CO 1.896(7), Ru−Cl 2.413(2), Ru−N 2.110(5), range Ru−CCp 2.132(7)-2.285(7); Cl−Ru−CO 89.6(2), Cl−Ru−N 90.0(2), N−Ru−CO 95.3(3).

benzylic alcohols **10**.[16] Acetophenone (**9a**) was chosen as the first model substrate and the isopropyl-substituted oxazoline complex **6f** as catalyst precursor in combination with different bases (Table 5), which are known for being crucial for yield and enantiomeric excess in transfer hydrogenations.[16]

As a result strong bases generally furnished phenylethanol (**10a**) in high yields after 3 h in refluxing 2-propanol with just 1 mol % of catalyst precursor **6f** (Table 5, entries 1−7). In contrast, the weaker carbonates afforded only minor amounts of **10a** (Table 5, entries 9−11). Furthermore, potassium-coordinated bases were more active than its sodium and lithium analogues.

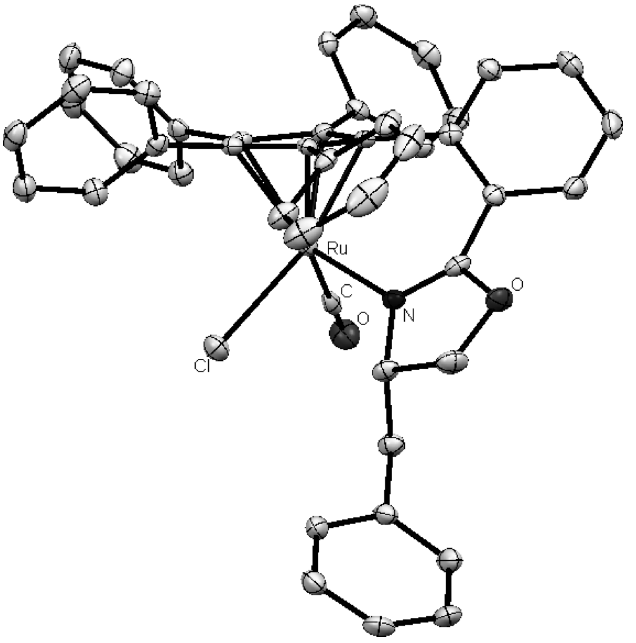


Figure 7. ORTEP representation of chiral chelated ruthenium complex **6h**. Thermal ellipsoids are displayed at 50% probability. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru−CO 1.890(2), Ru−Cl 2.422(6), Ru−N 2.118(2), range Ru−C_{Cp} 2.120(2)−2.311(2); Cl−Ru−CO 88.23(6), Cl−Ru−N 90.14(5), N−Ru−CO 95.26(8).

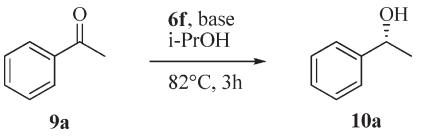
Table 4. Crystallographic Data of 6f−h

	6f	6g	6h
empirical formula	$C_{42}H_{34}NO_2ClRu$	$C_{44}H_{38}NO_2Cl_3Ru$	$C_{46}H_{34}NO_2ClRu$
fw	721.22 g/mol	820.17 g/mol	769.26 g/mol
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*P*2(1)2(1)2(1)	*C*2	*P*2(1)2(1)2(1)
a [Å]	12.4054(2)	35.5952(13)	10.7789(2)
b [Å]	16.6340(2)	12.2693(6)	11.2912(2)
c [Å]	16.6340(2)	17.6505(9)	28.9700(5)
α [deg]	90	90	90
β [deg]	90	100.756(4)	90
γ [deg]	90	90	90
V [Å^3]	3432.45(8)	7573.0(6)	3525.84(11)
T [K]	110(2)	110(2)	113(2)
Z	4	8	4
no. of unique data	7863	16172	6898
no. of refined params	426	895	460
R1 ($I > 2\sigma(I)$)	0.0245	0.0586	0.0201
wR2 (all data)	0.0517	0.1380	0.0417

Although the use of KO*t*Bu gave a quantitative yield of phenylethanol (**10a**), the ee values for KOH were significantly higher, still with excellent yield. Accordingly, we applied the catalytic system with 1 mol % of the catalyst precursor and 90 mol % of KOH for the asymmetric transfer hydrogenations of prochiral phenyl ketones **9** to elucidate the influence of both the substituent at the carbonyl carbon and the substituent on the oxazoline moiety (Table 6).

There was no distinct correlation between the steric demand of the phenyl ketone **9** and the obtained ee values for **10**, suggesting that steric reasons are not crucial for the chiral induction. On the other hand, the yield is unambiguously affected by the steric demand of the substituents at the carbonyl carbon. Nevertheless, yields above 90% were obtained for the ketones **9a−c** under individually optimized

Table 5. Transfer Hydrogenation of Acetophenone (9a) with 6f As Catalyst Precursor



9a **10a**

entry	S/C[a]	base	base (mol %)	yield[b]	ee[c]
1	100	KOH	90	95	38
2	100	KOH	35	68	30
3	67	KO*t*Bu	40	86	24
4	100	KO*t*Bu	100	99	20
5	100	NaOH	70	83	12
6	100	NaO*t*Bu	70	95	20
7	100	LiOtBu	70	79	2
8	67	LiOH	50	10	n.d.[d]
9	100	Na_2CO_3	70	≪1	n.d.[d]
10	100	K_2CO_3	70	< 1	n.d.[d]
11	100	Cs_2CO_3	70	5	n.d.[d]

[a] Substrate to catalyst ratio. Substrate concentration: 0.35−0.58 M. [b] Yield determined by GC with decane as internal standard. [c] ee determined by derivatization with Mosher's acid to its diastereomeric esters. The configuration was *R*, determined by comparison of the NMR of the ester with literature.[17] [d] n.d.: not determined.

conditions. The transfer hydrogenation of **9d** and **9e** still afforded the benzylic alcohols **10d** and **10e** in good yields of 84% and 70%, respectively. The ee values were generally moderate, with a maximum at 50% ee, achieved with desoxybenzoin (**9e**) as substrate.

π-Interactions of the benzyl group with the oxazoline moiety of the catalyst seem to be beneficial for the achieving highest ee values in our series. CH−π attractions were supposed to be responsible for the high enantioselectivities of Noyori's catalyst in the transfer hydrogenation,[18b] placing the threshold for these types of reactions clearly above 90% ee.[16a,c−h,18a]

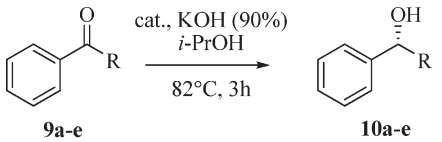
Conclusions

In conclusion, we have tested stoichiometric and catalytic preparative pathways for the synthesis of pentaphenylated cyclopentadienes monofunctionalized in one *ortho*-position. It was shown that the reaction with $Ru_3(CO)_{12}$ and chloroform yielded the corresponding cyclopentadienyl complexes. Chelation to the tethered functional group occurred either thermally induced or finally by photochemical irradiation. Thus, a stereogenic center might be induced at the ruthenium. When the tether is an enantiopure oxazoline, the complexes were isolated as single diastereomers. These novel enantiopure oxazoline ruthenium complexes showed high catalytic activity for the enantioselective transfer hydrogenation of phenyl ketones with 2-propanol as hydrogen donor. The corresponding benzylic alcohols were obtained in up to 99% yield and with ee values up to 50%. We intend to extend our tests to other Ru-catalyzed processes, focusing on the influence of π-interactions between substrate and catalyst.

(17) Ward, D. E.; Rhee, C. K. *Tetrahedron Lett*. **1991**, *32* (49), 7165–7166.

(18) (a) Fujii, A.; Hashiguchi, S.; Uematsu, N.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc*. **1996**, *118*, 2521–2522. (b) Yamakawa, M.; Yamada, I.; Noyori, R. *Angew. Chem., Int. Ed*. **2001**, *40*, 2818–2821.

Table 6. Catalytic Transfer Hydrogenations of Various Phenylketones 9 with 6f−h As Catalyst Precursors



9a-e **10a-e**

R = Me (**a**), *i*-Pr (**b**), *n*-Bu (**c**), Cy (**d**), Bnz (**e**)

entry		R	cat	S/C[a]	yield[b]	ee[c]
1	**a**	Me	**6f**	100	95	38
2	**a**	Me	**6g**	100	94	35
3	**a**	Me	**6h**	100	98	37
4	**b**	*i*-Pr	**6f**	100	44	22
5	**b**	*i*-Pr	**6g**	100	72	n.d.[f]
6	**b**	*i*-Pr	**6h**	100	58	n.d.[f]
7	**b**	*i*-Pr	**6f**	50	50	20
8	**b**	*i*-Pr	**6g**	50	94	32
9	**b**	*i*-Pr	**6h**	50	88	29
10	**c**	*n*-Bu	**6f**	100	47	n.d.[f]
11	**c**	*n*-Bu	**6f**	50	94	36
12	**c**	*n*-Bu	**6g**	50	99	43
13	**c**	*n*-Bu	**6h**	50	99	29
14	**d**	Cy	**6f**	100	30[e]	n.d.[f]
15	**d**	Cy	**6f**	50	76[e]	25
16	**d**	Cy	**6g**	50	84[e]	42
17	**d**	Cy	**6h**	50	67[e]	38
18	**e**	Bnz	**6f**	100	36	n.d.[f]
19	**e**	Bnz[d]	**6f**	50	69	43
20	**e**	Bnz	**6g**	50	70	50
21	**e**	Bnz[d]	**6h**	50	61	45

[a] Substrate to catalyst ratio. Substrate concentration: 0.30−0.65 M. [b] Yield determined by GC with internal standards: decane (**a**), tridecane (**b**), tetradecane (**c**), pentadecane (**e**). [c] ee determined by derivatization with Mosher's acid to its diastereomeric esters. The configuration was *R*, established by determination of the sign of rotation and comparison with literature. [d] 0.12 M. [e] Yield determined by ^{1}H NMR. [f] n.d.: not determined.

Experimental Section

General Procedures. All reactions were carried out under argon atmosphere in dried glassware. All workup procedures were carried out in air. Solvents were dried according to standard procedures. Chemicals were used as received from Acros, Aldrich, Strem, and Fluorochem, respectively. 8-Bromoquinoline,[19] 1-bromo-1′-diphenylphosphinoferrocene,[20] and 2-(2-bromophenyl)-1,3-dioxolane[21] (**8d**) and the enantiopure 2-bromophenyloxazolines[22] and phenyloxazolines,[22,23] respectively, were synthesized by literature procedures or slight modifications of these protocols. The data of all reproduced compounds were in accordance with literature except the ^{1}H NMR of 1-bromo-1′-diphenylphosphinoferrocene.[20] Melting points (uncorrected): Büchi; IR: Bruker Equinox 55; UV: Varian Cary 1; MS (EI, FAB, EI(HRMS)): Varian MATCH5; MS (MALDI-TOF): Bruker Autoflex, ABP matrix; MS (LIFDI): JMS-T100GCV; elemental analysis: Vario EL. NMR spectra (^{1}H and ^{13}C) were recorded on

(19) Wada, K.; Mizutani, T.; Kitagawa, S. *J. Org. Chem*. **2003**, *68*, 5123–5131.

(20) Butler, I. R.; Davies, R. L. *Synthesis* **1996**, *11*, 1350–1354. The literature contained a mistake in the reported ^{1}H NMR since one signal is missing. We found: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.99 (t, 2H, J=1.8 Hz), 4.15 (m, 2H), 4.32 (t, 2H, J=1.8 Hz), 4.42 (t, 2H, J=1.6 Hz), 7.28−7.42 ppm (m, 10H). The mp (97−101 °C) was in accordance with the one reported.

(21) Wytko, J. A.; Graf, E.; Weiss, J. *J. Org. Chem*. **1992**, *57*, 1015–1018.

(22) Zhou, Q.-L.; Pfaltz, A. *Tetrahedron* **1994**, *15*, 4467–4478.

(23) The ^{1}H NMR of (*S*)-4-isobutyl-2-phenyl-4,5-dihydrooxazole is published in: Fukuhara, T.; Hasegawa, C.; Hara, S. *Synthesis* **2007**, *10*, 1528–1534.

a Bruker DPX 200 and a Bruker DRX 400 and calibrated by the residual solvent peak or by TMS as an internal standard. All GC analyses were conducted on a Silicon OV-17 stationary phase (43 m, 0.28 mm).

1-(2-*N*,*N*-Dimethylaminophenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dienol (3a). TMEDA (1.0 mL, 6.4 mmol) and *N*,*N*-dimethylaniline (0.90 mL, 7.00 mmol) were added to a solution of *n*-BuLi (1.6 M in hexane, 4.0 mL, 6.4 mmol), and the mixture was heated at reflux temperature for 3 h. After cooling to room temperature tetracyclone (**1**) (1.70 g, 4.42 mmol) was added as a solid in small portions with additional THF (10 mL) within 30 min. The mixture was stirred for 16 h, hydrolyzed with brine (20 mL), and extracted with EtOAc (3 × 30 mL). The combined organic layers were dried ($MgSO_4$) and concentrated. The crude product was subjected to flash column chromatography (silica, PE/EtOAc, 5:1, R_f = 0.25, 0.28, 0.37, 0.48, 0.55 (tetracyclone (**1**)), 0.61), and the fractions containing R_f = 0.25 were recrystallized from EtOAc to give the tertiary alcohol **3a** as colorless crystals (1.59 g, 71%) with mp 186 °C. For a sufficient purity for the reduction step the crude product was suspended in EtOAc, and this mixture was treated in the ultrasonic bath. The cyclopentadienol **3a** thus obtained by filtration only contained minor tetracyclone impurity. IR (KBr): 3074 w, 3052 m, 3043 m, 3026 w, 2997 w, 2986 w, 2955 w, 2499 br m, 1595 m, 1573 m, 1483 s, 1439 m, 1328 w, 1280 w, 1176 m, 1163 m, 1137 w, 1096 m, 1072 w, 1046 w, 1027 m, 928 m, 865 w, 846 w, 811 w, 787 m, 771 m, 754 m, 743 m, 721 m, 700 s cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.28 (s, 6 H, CH_3), 6.94−6.97 (dd, J = 1.8, 7.6 Hz, 4 H), 7.02−7.12 (m, 16 H), 7.13−7.20 (m, 3 H), 7.53 (d, J = 7.6 Hz, 1 H), 11.35 ppm (s, 1 H, O*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 46.46 (*C*H$_3$), 94.91 (s, *C*OH), 124.01, 126.87, 126.96, 127.05, 127.52, 127.80, 127.87, 128.42, 130.14, 130.30 (all d), 133.62, 135.55, 136.05, 141.19, 150.66, 153.89 ppm (all s). UV−vis (MeCN): λ_{max} (log ε) 209 (4.52), 246 (4.35), 343 nm (3.70). MS (FAB): m/z (%) 528 (4) [M + Na]$^+$, 506 (100) [M + H]$^+$, 488 (8) [M − OH]$^+$. HRMS (EI): calcd for $C_{37}H_{31}NO$ 505.2406, found 505.2405.

1-(2-Pyridyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dienol (3b). To a solution of *t*-BuLi (1.48 M in pentane, 2.70 mL, 4.00 mmol) in Et_2O (4 mL) was added 2-bromopyridine (315 mg, 0.19 mL, 1.99 mmol) at −78 °C, and the mixture was stirred for 30 min. Tetracyclone (**1**) (620 mg,1.60 mmol) was added as a solid in small portions with additional Et_2O (25 mL) within 15 min, and the mixture was stirred and slowly warmed to room temperature over a period of 2 h. The mixture was hydrolyzed with aqueous NH_4Cl (1 N, 20 mL), and the precipitate was filtered and recrystallized from EtOAc to afford tertiary alcohol **3b** as colorless crystals (620 mg, 84%) with mp 207−210 °C. IR (KBr): 3242 br m, 3057 w, 3025 w, 1589 m, 1569 m, 1487 m, 1472 m, 1437 m, 1401 w, 1329 w, 1191 w, 1139 m, 1098 w, 1080 w, 1058 w, 1069 w, 1028 w, 1000 w, 977 w, 922 m, 851 w, 825 w, 792 m, 777 w, 755 w, 737 s, 708 s, 696 s cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.42 (s, 1 H, O*H*), 6.92−6.94 (d, J = 7.1 Hz, 4 H), 6.98−7.05 (m, 10 H, Ph*H*), 7.10−7.17 (m, 7 H, Ph*H*, Py-*H*5), 7.59 (d, J = 7.8 Hz, 1 H, Py-*H*6), 7.64−7.68 (t, J = 7.9 Hz, 1 H, Py-*H*4), 8.41 ppm (d, J = 4.8 Hz, 1 H, Py-*H*3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 89.82 (*C*OH), 119.72 (Py-*C*6), 122.86, 127.13, 127.35, 127.94, 128.17, 129.68, 130.23 (all d), 134.51, 135.47 (both s), 137.73 (Py-*C*4), 143.70 (s), 147.73 (all s), 148.01 (Py-*C*3), 157.91 ppm (Py-*C*1). UV−vis (CH_2Cl_2): λ_{max} (log ε) 215 (3.31), 246 (3.36), 346 nm (2.88). MS (EI, 70 eV): m/z (%) 463 (100) [M$^+$], 447 (5), 434 (70), 386 (15), 358 (75).. Anal. Calcd for $C_{34}H_{25}NO$: C 88.09, H 5.44, N 3.02. Found: C 87.76, H 5.73, N 2.77.

1-(8-Quinolinyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dienol (3c). To a solution of 8-bromoquinoline (435 mg, 2.10 mmol) in dry THF (5 mL) was added *n*-BuLi (1.6 M in hexane, 1.50 mL, 2.40 mmol) at −100 °C within 20 min, and the mixture was stirred for 30 min. Tetracyclone (**1**) (411 mg, 1.07 mmol) was added in several portions with additional THF (25 mL). The mixture was stirred at room temperature for 16 h and hydrolyzed with aqueous NH_4Cl (2 N, 5 mL), and the separated organic layer was dried with $MgSO_4$. After evaporation of the solvents, EtOAc was added to the residue and the mixture was treated in the ultrasonic bath. The precipitate was isolated by filtration to yield tertiary alcohol **3c** as a pale yellow solid (370 mg, 52%) with mp 239−241 °C. IR (KBr): 3423 br w, 3052 w, 3027 w, 1594 w, 1496 m, 1494 m, 1438 w, 1369 w, 1245 w, 1125 w, 1051 w, 1027 w, 776 m, 763 m, 694 s cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.87−6.94 (m, 6 H, Ph*H*), 6.99−7.03 (m, 8 H, Ph*H*), 7.06−7.11 (m, 6 H, Ph*H*), 7.22 (dd, J = 4.3, 8.4 Hz, 1 H, Qui-*H*3), 7.48 (t, J = 7.7 Hz, 1 H, Qui-*H*6), 7.66 (dd, J = 1.2, 8.1 Hz, 1 H, Qui-*H*5), 7.99 (dd, J = 1.3, 7.4 Hz, 1 H, Qui-*H*7), 8.07 (dd, J = 1.7, 8.4 Hz, Qui-*H*4, 1 H), 8.43 (dd, J = 1.8, 4.2 Hz, 1 H, Qui-*H*2), 10.91 ppm (s, 1 H, O*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 94.57 (*C*OH), 120.21 (Qui-*C*3), 126.36, 126.60 (both d), 126.72 (Qui-*C*7), 126.94 (d), 127.20 (Qui-*C*6), 127.26 (d), 127.64 (Qui-*C*5), 128.75 (Qui-*C*4a), 129.86, 129.95 (both d), 135.05 (s), 135.34 (Qui-*C*8), 135.43 (s), 137.20 (Qui-*C*4), 141.31 (s), 146.45 (Qui-*C*2), 148.69 (Qui-*C*8a), 149.50 ppm (s). UV−vis (MeCN): λ_{max} (log ε) 215 sh (4.55), 231 (4.59), 244 sh (4.50), 340 nm (3.86). MS (FAB): m/z (%) 536 (5) [M + Na]$^+$, 514 (100) [M + H]$^+$; 496 (22) [M − OH]$^+$. HRMS (EI): calcd for $C_{38}H_{27}NO$ 513.2093, found 513.2090.

1-(2,3,4,5-Tetraphenylcyclopenta-2,4-dienol-1-yl)ferrocene (3i). To a solution of ferrocene (564 mg, 2.97 mmol) in dry THF (5 mL) was added *t*-BuLi (1.48 M in pentane, 1.70 mL, 2.56 mmol) at 0 °C, and the mixture was stirred for 15 min. After warming to room temperature tetracyclone (**1**) (412 mg, 1.07 mmol) was added as a solid in small portions with additional THF (15 mL). The mixture was stirred for 30 min, hydrolyzed with water (5 mL), and extracted with MTBE (2 × 15 mL). The combined organic extracts were dried with Na_2SO_4 and concentrated, and the crude product was subjected to flash column chromatography (silica, PE/EtOAc, 10:1; R_f = 0.19, 0.41, 0.56, 0.78; PE/EtOAc 25:1 → 5:1). The fraction with R_f = 0.78 afforded ferrocene (300 mg, 54% recovery), the fraction with R_f = 0.56 gave **1** (55 mg, 13% recovery), and the fraction with R_f = 0.49 yielded ferrocenyl alcohol **3i** (375 mg, 0.66 mmol, 71% based on converted tetracyclone (**1**)) as a yellow-orange powder, which decomposes at 215 °C. IR (KBr): 3464 m, 3079 w, 3051 w, 3027 w, 1954 w, 1898 w, 1595 w, 1572 w, 1487 m, 1439 w, 1409 w, 1380 w, 1347 w, 1313 w, 1274 w, 1237 w, 1216 w, 1180 w, 1155 w, 1119 m, 1105 m, 1073 m, 1063 m, 1047 m, 1027 s, 999 m, 914 w, 811 m, 779 w, 771 w, 754 s, 747 m, 725 m, 697 vs, 616 w, 579 m, 547 m cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.74 (br s, 1 H, O*H*), 3.68 (br s, 5 H, Fc*H*$_5$), 3.90 (br s, 2 H, Fc*H*$_2$H$_2$), 4.03 (br s, 2 H, FcH$_2$*H*$_2$), 6.92 (br d, 4 H, J = 5.0 Hz, Ph*H*), 6.03 (br d, J = 5.31 Hz, 6 H, Ph*H*), 7.22−7.30 (br m, 6 H, Ph*H*), 7.40 ppm (br d, J = 7.01 Hz, 4 H, Ph*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 66.68, 67.26 (both Fc*Cp*H$_4$), 68.42 (Fc*Cp*H$_5$), 86.86, 94.33 (both s), 126.52, 127.03, 127.26, 127.60, 129.91, 130.73 (all d), 135.04, 136.05, 142.06, 146.58 ppm (all s). UV−vis (MeCN): λ_{max} (log ε) 211 (4.77), 245 (4.58), 358 nm (3.58). MS (FAB): m/z (%) 593 (6) [M + Na]$^+$, 570 (100) [M]$^+$, 553 (15) [M − OH]$^+$. Anal. Calcd for $C_{39}H_{30}FeO$: C 82.11, H 5.30. Found: C 81.80, H 5.24.

1-(2,3,4,5-Tetraphenylcyclopenta-2,4-dienol-1-yl)-1′-diphenylphosphinoferrocene (3j). To a solution of 1-bromo-1′-diphenylphosphinoferrocene (1.10 g, 2.45 mmol) in dry THF (10 mL) was added *n*-BuLi (1.6 M in hexane, 1.50 mL, 2.40 mmol) at −78 °C, and the mixture was stirred for 15 min. During slow warming to room temperature tetracyclone (**1**) (845 mg, 2.20 mmol) was added in several portions with additional THF (35 mL). The mixture was stirred for 30 min at room temperature, hydrolyzed with water (15 mL), and extracted with MTBE (2 × 15 mL). The combined organic extracts were dried with Na_2SO_4 and concentrated, and the crude product was subjected to flash column chromatography (PE/EtOAc, 15:1 → 2:1; silica, PE/EtOAc, 15:1; R_f = 0, 0.17, 0.29, 0.47 (**1**), 0.54 (Fe(C_5H_5)($C_5H_4PPh_2$)). The fraction with R_f = 0.17 afforded ferrocenyl

alcohol **3j** (620 mg, 51%) as a yellow-orange solid with mp 197−200 °C. IR (KBr): 3480 m, 3050 w, 3051 w, 3027 w, 1952 w, 1884 w, 1813 w, 1762 w, 1596, 1571 w, 1560 w, 1488 m, 1478 m, 1434 m, 1362 m, 1307 w, 1180 w, 1159 m, 1120 m, 1069 m, 1027 m, 940 w, 865 m, 830 m, 779 w, 742 s, 697 s, 579 w, 547 w cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.58 (d, $J = 0.7$ Hz, 1 H, O*H*), 3.58 (d, $J = 1.0$ Hz, 4 H, $(PPh_2)FcH_4$), 3.75 (t, $J = 1.8$ Hz, 2 H, $(C_5Ph_4OH)FcH$), 3.85 (t, $J = 1.8$ Hz, 2 H, $(C_5Ph_4OH)FcH$), 6.78 (dd, $J = 2.0$, 7.5 Hz, 4 H, Ph*H*), 6.88−6.92 (m, 6 H, Ph*H*), 7.12−7.26 ppm (m, 20 H, Ph*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 67.61 ppm, 68.76 (both $(C_5Ph_4OH)FcCH$), 71.54 (d, J_{C-P} = 3.8 Hz, Fc*C*-PPh_2), 73.38 (d, J_{C-P} = 14.5 Hz, H*C*Fc(PPh_2)), 76.08 (d, J_{C-P} = 5.6 Hz, H*C*Fc(PPh_2)), 87.09, 94.70 (both s), 126.65, 127.16, 127.39, 127.74 (all d), 128.30 (d, $J_{C-P} = 6.9$ Hz), 128.71, 130.03, 130.83 (all d), 135.58 (d, $J_{C-P} = 19.4$ Hz), 135.16, 136.05, 138.83 (d, $J_{C-P} = 9.3$ Hz, P(*C*C_5H_5)), 142.10, 146.67 ppm (all s). UV−vis (MeCN): λ_{max} (log ε) 224 (4.35), 243 (4.35), 359 nm (3.27). MS (FAB): *m*/*z* (%) 793 (10) $[M + O + Na]^+$, 770 (100) $[M + O]^+$, 754 (53) $[M]^+$. Anal. Calcd for $C_{51}H_{39}FeOP$: C 81.17, H 5.21. Found: C 81.02, H 5.09.

2-(2,3,4,5-Tetraphenyl-3′*H*-spiro[cyclopenta[2,4]diene-1,1′-isobenzofuran]-3′-yloxy)ethanol (*spiro*-3d). To a solution of 2-(2-bromophenyl)-1,3-dioxolane (700 mg, 3.05 mmol) in THF (15 mL) was added *n*-BuLi (1.6 M in hexane, 2.20 mL, 3.52 mmol) at −65 °C, and the mixture was stirred for 30 min. Tetracyclone (**1**) (1.76 g, 3.35 mmol) was added as a solid in several portions with additional THF (30 mL) within 30 min, and the mixture was stirred at room temperature for 12 h. The mixture was hydrolyzed with aqueous NH_4Cl (1 N, 20 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were dried with $MgSO_4$ and concentrated, and the crude product was subjected to flash column chromatography (silica, PE/EtOAc, 5:1; R_f = 0.10, 0.24, 0.38, 0.48). The fraction with R_f = 0.24 afforded ***spiro*-3d** (740 mg, 81%) as a slightly yellow foam, which was suspended in MeOH and treated in the ultrasonic bath to give an off-white solid with mp 156−158 °C. IR (KBr): 3450 w, 3078 w, 3050 w, 3027 w, 2926 w, 2870 w, 1597 m, 1573 w, 1489 m, 1460 w, 1441 m, 1383 w, 1344 w, 1266 w, 1226 w, 1190 w, 1117 br m, 1094 m, 1071 m, 1049 m, 1030 m, 967 s, 937 w, 913 w, 812 w, 785 w, 752 m, 742 m, 697 vs cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.98 ppm (br s, 1 H, O*H*), 3.32−3.37 (m, 1 H, OCH_2CH_2OH), 3.40−3.45 (m, 1 H, OCH_2CH_2OH), 3.71 (t, J = 8.8 Hz, 2 H, OCH_2CH_2OH), 6.18 (s, 1 H, OC*H*O), 6.79 (d, $J = 6.8$ Hz, 2 H), 6.91−6.93 (m, 6 H); 6.70−7.12 (m, 12 H), 7.27−7.33 (m, 3 H), 7.37−7.41 ppm (dt, $J = 2.1$, 6.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 61.14 (OCH_2CH_2OH), 71.71 (OCH_2CH_2OH), 102.25 (*C*O), 108.62 (O*C*O), 120.72, 123.64, 126.91, 126.94, 127.04, 127.49, 127.61, 127.69, 128.38, 129.47, 129.71, 129.95, 129.98, 130.10 (all d, two d signals are missing due to overlapping), 134.38, 134.57, 134.61, 134.68, 139.18, 139.98, 142.22, 142.63, 145.66, 146.07 ppm (all s). UV−vis (MeCN): λ_{max} (log ε) 248 (4.31), 361 nm (3.61). MS (FAB): *m*/*z* (%) 557 (10) $[M + Na]^+$, 534 (100) $[M]^+$, 517 (51) $[M - OH]^+$, 473 (61) $[M - HOC_2H_4O]^+$. HRMS (EI): calcd for $C_{38}H_{30}O_3$ 534.2195, found 534.2191.

2,3,4,5-Tetraphenyl-3′*H*-spiro[cyclopenta[2,4]diene-1,1′-isobenzofuran]-3′-imine (*spiro*-3e). To a solution of 2-bromobenzonitrile (780 mg, 4.30 mmol) in dry THF (5 mL) was added *n*-BuLi (1.6 M in hexane, 2.70 mL, 4.32 mmol) at −78 °C, and the mixture was stirred for 30 min. Tetracyclone (**1**) (990 g, 2.60 mmol) was added as a solid in several portions with additional THF (50 mL) within 30 min, and the mixture was stirred at room temperature for 12 h. The mixture was hydrolyzed with water (30 mL) and extracted with MTBE (2 × 15 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. The crude product was subjected to flash column chromatography (silica, PE/EtOAc, 2:1; R_f = 0.25, 0.44, 0.63, 0.81). The fraction with R_f = 0.25 yielded *spiro*-compound ***spiro*-3e** (930 mg, 73%) as a colorless solid with mp 225 °C. IR (KBr): 3287 m, 3081 w, 3052 w, 3023 w, 1768 w, 1685 s, 1600 w, 1574 w, 1489 m, 1466 m, 1442 m, 1334 m, 1229 s, 1255 m, 1217 w, 1163 w, 1145 m cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.79−6.81 (dd, $J = 1.5$, 7.8 Hz, 4 H), 6.94−7.04 (m, 10 H), 7.09−7.18 (m, 6 H), 7.36−7.40 (t, J = 7.3 Hz, 1 H), 7.42 (d, $J = 7.8$ Hz, 1 H), 7.51 (t, $J = 7.6$ Hz, 1 H), 7.78 ppm (d, $J = 7.6$ Hz, 1 H). The NH proton was not detected. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 99.92 (*C*-O), 120.85, 124.55, 127.42, 127.51, 127.96, 128.09, 129.10, 129.15, 130.06 (all d), 130.97 (s), 132.67 (d), 133.39, 134.32, 142.72, 144.10, 145.73 (all s), 167.67 ppm (*C*=N). UV−vis (MeCN): λ_{max} (log ε) 243 (4.54), 347 nm (3.80). MS (EI, 70 eV): *m*/*z* (%) 487 (100) $[M]^+$, 459 (5), 410 (5), 382 (15). Anal. Calcd for $C_{36}H_{25}NO$: C 88.68, H 5.17, N 2.87. Found: C 88.88, H 5.18, N 2.65.

(*S*)-3-Methyl-2-(2,3,4,5-tetraphenyl-3′*H*-*spiro*[cyclopenta-[2,4]diene-1,1′-isobenzofuran]-3′-ylideneamino)butan-1-ol (*spiro*-3f). To a solution of (*S*)-2-(2-bromophenyl)-4-isopropyl-4,5-dihydrooxazole (950 mg, 3.54 mmol) in dry THF (7 mL) was added *n*-BuLi (1.6 M in hexane, 2.2 mL, 3.52 mmol) at −78 °C, and the mixture was stirred for 1 h. Tetracyclone (**1**) (670 mg, 1.75 mmol) was added as a solid in several portions with additional THF (25 mL) within 30 min, and the mixture was stirred at room temperature for 12 h. The mixture was hydrolyzed with aqueous NH_4Cl (1 N, 20 mL) and extracted with EtOAc (3 × 30 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated. The crude product was subjected to flash column chromatography (silica, PE/EtOAc, 2:1; R_f = 0.17, 0.48, 0.60, 0.72, 0.83). The fraction with R_f = 0.17 afforded ***spiro*-3f** (850 mg, 85%) as a slightly yellow foam. Crystallization from DCM/PE yielded colorless crystals with mp 126−128 °C. IR (KBr): 3079 w, 3052 w, 3028 w, 2956 w, 2869 w, 1700 s, 1598 w, 1490 w, 1467 w, 1441 w, 1288 w, 1246 w, 1132 w, 1100 w, 1073 m, 1058 m, 1029 w, 964 m, 935 w, 774 m, 741 m cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.62 (d, $J = 6.7$ Hz, 3 H, C*H*$_3$), 0.83 (d, $J = 6.7$ Hz, 3 H, C*H*$_3$), 1.49 (br t, $J = 6.4$ Hz, 1 H, O*H*) 1.68−1.80 (sep, $J = 6.8$ Hz, 1 H, $CH(CH_3)_2$), 3.54−3.66 (m, 2 H, CH_2OH), 3.82 (td, J = 3.5, 7.5 Hz, 1 H, $NCHCH_2$), 6.73−6.75 (m, 2 H, Ph*H*), 6.83−6.85 (m, 2 H, Ph*H*), 6.93−7.03 (m, 10 H, Ph*H*), 7.09−7.17 (m, 6 H, Ph*H*), 7.36 (td, $J = 1.1$, 7.6 Hz, 1 H, *m*-*H* Ph−C=N), 7.43 (d, $J = 7.7$ Hz, 1 H, *m*-*H* Ph−C=N), 7.48 (td, $J = 1.1$, 7.4 Hz, 1 H, *p*-*H* Ph−C=N), 7.74 (d, $J = 7.6$ Hz, 1 H, *o*-*H* Ph−C=N); δ 19.26, 19.61 (*C*H$_3$), 30.39 (*C*H$(CH_3)_2$), 64.45 (N*C*HCH_2OH), 65.23 (NCH*C*H$_2$OH), 100.06 (*C*-O), 120.75 (*m*-*C*H Ph−C=N), 124.12 (*o*-*C*H Ph−C=N), 127.32, 127.48, 127.51, 127.94, 127.98, 128.13, 128.96, 129.18, 129.30, 130.11, 130.17 (all d), 132.02 (*p*-*C*H Ph−C=N), 132.26 (d), 133.62, 133.72, 134.33, 143.22, 143.35, 143.64, 143.75, 144.68 (all s), 159.77 ppm (*C*=N), 4 signals are missing due to overlapping. UV−vis (MeCN): λ_{max} (log ε) 240 (4.48), 344 nm (3.80). MS (FAB): *m*/*z* (%) 573 (100) $[M]^+$, 542 (65) $[M - CH_2OH]^+$, 530 $[M - C_4H_9]^+$ (10), 487 (15) $[M - CH_2OH - C_4H_9 + H]^+$, 472 (10) $[M - NC_5H_{10}OH]^+$. Anal. Calcd for $C_{41}H_{35}NO_2$: C 85.83, H 6.15, N 2.44. Found: C 85.91, H 6.43, N 2.26.

1-(2-*N*,*N*-Dimethylaminophenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-diene (and isomers) (4a). To a solution of alcohol **3a** (1.09 g, 2.16 mmol) in dry THF (40 mL) was added *n*-BuLi (1.6 M in hexane, 2.0 mL, 3.2 mmol) at room temperature, and the mixture was stirred for 30 min. $LiAlH_4$ (230 mg, 6.08 mmol) was added in several portions, and the mixture was stirred for 2 h, hydrolyzed with aqueous NH_4Cl (2 N, 40 mL), and filtrated. The layers were separated, and the aqueous layer was extracted with EtOAc (25 mL). The organic extracts were dried (Na_2SO_4) and concentrated. The crude product was suspended in MeOH (8 mL) and treated in the ultrasonic bath for 1 h. The precipitate was isolated by filtration to afford cyclopentadiene **4a** (mixture of isomers) (1.86 g, 79%) as a pale yellow powder with mp 144−147 °C. IR (KBr): 3077 w, 3058 w, 3022 w, 2975 w, 2935 w, 2909 w, 2853 w, 2820 w, 2776 w, 1597 m, 1574 w, 1488 s, 1452 m, 1441 m, 1429 w, 1316 w br, 1193 w, 1157 w, 1098 w, 1071 w, 1051 w, 952 w, 930 w, 909 w, 836 w, 801 w, 787 w, 772 m, 757 m, 721 m, 693 s cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.27, 2.44, 2.73

(s, 6 H, N(CH_3)$_2$), 5.05, 5.16, 5.65, 6.09 (s, 1 H, 6.2:4.6:1.7:1, CpC-*H*), 6.48 (t, J = 7.1 Hz, one isomer), 6.52−6.54 (dd, J = 1.8, 7.6 Hz, one isomer), 6.63 (d, J = 8.08 Hz, one isomer), 6.75 (d, J = 8.1 Hz, one isomer), 6.80−6.82 (dd, J = 1.0, 7.3 Hz, one isomer), 6.83−6.93 (m, 3 H), 6.93−7.07 (m, 11 H), 7.07−7.14 (m, 3 H), 7.14−7.19 (m, 3 H), 7.19−7.26 (m, 2 H), 7.27−7.31 (m, 1 H), 7.32−7.36 ppm (dd, J = 1.6, 7.5, one isomer). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 42.34, 43.06, 43.40, 45.97 (all CH_3), 57.09, 60.61, 62.01, 62.79 (all Cp-*C*H), 117.32, 118.14, 118.60, 120.78, 120.91, 121.83 (all d), 124.84 (assignment not possible), 126.09, 126.16, 126.17, 126.26, 126.30, 126.36, 126.40, 126.48, 126.53, 126.63, 126.85, 127.12, 127.22, 127.54, 127.70, 127.71, 127.82, 127.85, 127.87, 127.92, 127.98, 128.13, 128.36, 128.39, 128.41, 128.68, 128.72, 128.83, 128.98, 129.04, 129.12, 129.48, 129.59, 129.68, 129.97, 130.31, 130.33, 130.35, 132.10, 132.86, 132.98 (all d), 135.29, 135.77, 136.15, 136.36, 136.76, 136.79, 136.87, 137.03, 137.10, 139.00, 139.42, 141.85, 143.74, 144.19, 144.36, 144.56, 145.06, 145.44, 145.60, 145.77, 147.01, 148.29, 149.23, 151.76, 152.23, 152.36, 153.77 ppm (all s). UV−vis (MeCN): λ_{max} (log ε) 210 (4.49), 242 (4.36), 361 nm (3.76). MS (EI, 70 eV): m/z (%) 489 (100) $[M]^+$, 398 (75). HRMS (EI): calcd for $C_{37}H_{31}N$ 489.2456, found 489.2455.

1-(2-Pyridyl)-2,3,4,5-tetraphenylcyclopenta-2,4-diene (and isomers) (4b). To a mixture of alcohol **3b** (900 mg, 1.94 mmol) in dry THF (20 mL) was added *n*-BuLi (1.6 M in hexane, 1.25 mL, 1.94 mmol) at −78 °C, and the mixture was stirred for 10 min. $LiAlH_4$ (230 mg, 5.97 mmol) was added in small portions, and the mixture was stirred for 30 min and hydrolyzed with water (2 mL), aqueous KOH (2 mL, 15%), and water (15 mL). EtOAc (20 mL) was added, the mixture was transferred into a separation funnel, and the aqueous layer was separated with its solid contents. The solid in the organic layer was isolated by filtration and washed with EtOAc (5 mL), acetone (5 mL), and CH_2Cl_2 (5 mL) to give cyclopentadiene **4b** (mixture of isomers) (780 mg, 90%) as a poorly soluble off-white solid with mp 265 °C. Also after extended drying *in vacuo* THF keeps being enclatherated. IR (KBr): 3076 w, 3053 w, 3025 w, 2996 w, 2924 w, 2967 w, 1597 w, 1683 m, 1560 w, 1487 m, 1458 m, 1442 m, 1430 m, 1384 w, 1334 w, 1312 w, 1279 w, 1172 w, 1150 w, 1124 w, 1091 w, 1072 w, 1028 w, 1012 w, 994 w, 936 w, 918 w, 908 w, 838 w, 790 m, 774 m, 761 m, 741 m, 719 m, 694 s, 618 w, 567 w, 557 m, 542 m cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.79−1.90 (m, THF), 3.68−3.80 (m, THF), 5.18, 5.55, 5.60 (all s, 1 H, 1:3.2:2.6, CpC-*H*), 6.78 (dt, J = 0.9, 7.8 Hz, "0.4 H"), 6.85−6.89 (ddd, J = 1.1, 4.9, 7.4 Hz, "0.4 H"), 6.95−7.25 (m, 20 H), 7.29 (dd, J = 1.1, 8.1 Hz, "0.8 H"), 7.41−7.46 (m, "0.8 H"), 8.43−8.45, 8.47−8.49, 8.53−8.55 ppm (all ddd, J = 0.8, 1.7, 4.9 Hz, J = 0.9, 1.7, 4.8 Hz, J = 0.9, 1.7, 4.9 Hz, 1 H, all Py-*H*3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 61.70, 62.80, 64.79 (all Cp*C*H), 121.01, 121.56, 121.87, 123.99, 126.41, 126.60, 126.66, 126.70, 126.86, 127.08, 127.25, 127.92, 127.97, 128.03, 128.11, 128.21, 128.41, 128.73, 128.79, 129.06, 129.16, 129.28, 130.08, 130.17, 130.22, 130.24 (all d), 135.23, 135.36, 135.94, 136.22 (all s), 136.46, 136.49 (no assignment possible), 136.76, 138.52, 144.43, 145.27, 145.53 (all s), 149.27, 149.32, 149.50 (all Py-*C*3), 149.50, 154.49, 159.32 ppm (all Py-*C*1), several signals are missing due to overlapping and noise. UV−vis (MeCN): λ_{max} (log ε) 212 (4.26), 247 (4.11), 341 nm (3.84). MS (EI, 70 eV): m/z (%) 447 (100) $[M]^+$, 369 (8) $[M - C_5H_4N]^+$. HRMS (EI): calcd for $C_{34}H_{25}N$, 447.1987, found 447.1979.

1-(2-(1,3-Dioxolan-2-yl)phenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-diene (and isomer) (4d). To a solution of 2-(2-bromophenyl)-1,3-dioxolane (706 mg, 3.08 mmol) in dry THF (10 mL) was added *n*-BuLi (1.6 M in hexane, 2.20 mL, 3.52 mmol) at −78 °C, and the mixture was stirred for 30 min. Tetracyclone (**1**) (855 mg, 2.23 mmol) was added in several portions with additional THF (60 mL), and the mixture was stirred at room temperature for 2 h. $LiAlH_4$ (250 mg, 6.59 mmol) was added, and the mixture was stirred for 1 h. After hydrolyzation with water (30 mL), the organic layer was filtered through a plug of silica. Evaporation afforded a yellow foam, which was suspended in MeOH and treated in the ultrasonic bath. The precipitate was isolated by filtration to afford acetal **70** (mixture of two isomers) (750 mg, 65%) as a colorless solid with mp 155−157 °C. IR (KBr): 3055 w, 3022 w, 2949 w, 2888 w, 2854 w, 1598 w, 1490 m, 1442 w, 1395 w, 1109 w, 1073 m, 1028 w, 992 w, 965 w, 948 w, 772 m, 757 m, 730 w, 698 s cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.70−3.78, 3.83−3.94, 3.94−4.01, 4.05−4.19 (all m, 4 H, CH_2CH_2), 5.12, 5.18 (5:1, both s, 1 H, CpC*H*), 5.60, 5.91 (1:5, both s, 1 H, OC*H*O), 6.90 (d, J = 8.5 Hz, major isomer), 6.94−7.11 (m, 16 H, Ph*H*), 7.11−7.20 (m, 3 H, Ph*H*), 7.20−7.28 (m, 2 H, Ph*H*), 7.29−7.33 (dd, J = 1.1, 8.7 Hz, major isomer, Ph*H*), 7.41−7.46 (m, minor isomer, Ph*H*, *o*-PhC*H*-COO), 7.56−7.62 ppm (dd, J = 7.8, 0.9 Hz, major isomer, *o*-PhC*H*-COO). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 61.88, 62.33 (both Cp*C*H), 64.89, 65.02, 65.20, 65.26 (all CH_2CH_2), 101.63, 101.78 (both O*C*O), 125.86 (*o*-Ph*C*H−COO), 126.32, 126.37, 126.40, 126.46, 126.51, 126.67, 126.73, 127.47, 127.67, 127.71, 127.75, 127.78, 127.84, 128.15, 128.35, 128.37, 128.55, 128.58, 128.74, 128.81, 129.01, 129.17, 129.72, 129.94, 130.03, 130.15, 131.26 (all d), 135.41, 135.69, 135.72, 135.74, 135.77, 135.90, 135.92, 136.15, 136.21, 136.47, 138.50, 138.61, 142.52, 142.62, 144.28, 144.53, 145.70, 146.22, 146.79 ppm (all s). UV−vis (MeCN): λ_{max} (log ε) 361 (3.73), 244 (4.26), 217 nm (4.29). MS (EI, 70 eV): m/z (%): 518 (100) $[M]^+$, 490 (82) $[M - C_2H_4]^+$, 474 (45) $[M - C_2H_4 - O]^+$. Anal. Calcd for $C_{38}H_{30}O_2$: C 88.00, H 5.83. Found: C 87.68, H 5.42.

General Procedure for the Palladium-Catalyzed Arylation of Tetraphenylcyclopentadiene (7) with *ortho*-Functionalized Bromobenzenes. A mixture of the *ortho*-functionalized bromobenzene (1.25 mmol), tetraphenylcyclopentadiene (**7**) (1 mmol), Cs_2CO_3 (652 mg, 2.0 mmol), $Pd(OAc)_2$ (14 mg, 5 mol %), and PPh_3 (34 mg, 10 mol %) in DMF (10 mL) in a screw-capped flask was heated to 140 °C for 2 days. After cooling to rt CH_2Cl_2 (50 mL) and *p*-TsOH (1.5 g) were added, and the mixture was stirred for 10 min. The mixture was filtrated over a short plug of silica and eluted with CH_2Cl_2 (50 mL). After evaporation and drying *in vacuo* (1mbar, 75 °C) the sticky crude product was subjected to flash column chromatography (silica, PE/EtOAc).

1-(2-Formylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-diene (and isomers) (4d′). According to the general procedure, the reaction of 2-(2-bromophenyl)-1,3-dioxolane (**8d**) (286 mg, 1.25 mmol) yielded after chromatography (PE/EtOAc, 20:1; R_f = 0, 0.12, 0.18−0.27 (**4d′**), 0.42, 0.48, 0.54) cyclopentadiene **4d′** (mixture of isomers) (382 mg, 81%) as a yellow foam with mp 149−151 °C. IR (KBr): 3056 m, 3024 m, 1694 s, 1596 m, 1572 w, 1491 m, 1441 m, 1385 w, 1266 w, 1192 w, 1072 w, 1027 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.09, 5.16, 5.25, 5.25 (all s, 1:11:7.1:2, 1 H, all CpC-*H*), 6.77 (dd, J = 1.6, 8.2 Hz, minor isomer), 6.85−6.90 (m, 1 H), 6.90−6.95 (m, 2 H), 6.95−7.04 (m, 9 H), 7.04−7.13 (m, 5 H), 7.13−7.28 (m, 4 H), 7.31 (t, J = 7.5 Hz, 1 H), 7.34−7.41 (m, 1 H), 7.45−7.52 (td, J = 1.3, 7.5 Hz, one isomer), 7.61 (t, J = 8.2 Hz, minor isomer), 7.73, 7.79 (both dd, J = 0.8, 7.4 Hz; J = 1.1, 7.7 Hz, major isomers), 9.72, 9.97, 10.20, 10.26 ppm (all s, 1 H, C*H*O). ^{13}C NMR ($CDCl_3$, 100 MHz): 62.35, 63.14, 64.89 (all Cp*C*-H), 126.64, 126.75, 126.78, 126.83, 127.03, 127.07, 127.23, 127.42, 127.50, 127.75, 127.78, 127.80, 127.84, 127.87, 127.92, 128.00, 128.05, 128.08, 128.13, 128.25, 128.30, 128.57, 128.67, 128.69, 128.79, 128.83, 128.88, 128.94, 128.99, 129.94, 130.06, 130.11, 131.21, 131.39, 132.13 (all d), 132.98 (s), 133.54, 133.88, 133.99 (all d), 134.61, 134.72, 134.76, 135.14, 135.32, 135.34, 135.55, 136.74, 137.54, 137.73, 140.21, 140.38, 140.40, 140.52, 143.31, 143.95, 144.23, 146.52, 146.71, 146.86, 148.72, 149.08 (all s), 191.15, 191.23, 191.36 ppm (all *C*HO). UV−vis (MeCN): λ_{max} (log ε) 216 (4.43), 247 (4.40), 331 nm (3.97). MS (EI, 70 eV): m/z (%) 474 (100) $[M]^+$, 383 (15). HRMS (EI): calcd for $C_{36}H_{26}O$ 474.1984, found 474.1972.

1-(2-Cyanophenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-diene (and isomers) (4e). According to the general procedure, the reaction of 2-bromobenzonitrile (460 mg, 1.24 mmol) yielded

after chromatography (PE/EtOAc, 10:1; R_f = 0.05, 0.22−0.28 (**4e**), 0.48, 0.53, 0.63) cyclopentadiene **4e** (mixture of isomers) (450 mg, 77%) as a yellow foam with mp 91 °C. IR (KBr): 3078 w, 3056 m, 3024 w, 2223 w, 1597 m, 1574 w, 1488 m, 1441 m, 1384 w, 1332 w, 1281 w, 1266 w, 1178 w, 1157 w, 1127 w, 1072 m, 1028 m, 912 w, 803 w, 757 m, 696 s, 563 w, 549 w, 517 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.12, 5.24, 5.27, 5.33, 5.69 (all s, 1 H, 6.8:1:4.4:3.4:3.5, CpC-*H*), 6.85 (d, J = 7.7 Hz, minor isomer), 6.90−7.24 (m, 21 H), 7.23−7.54 ppm (3 H, several d). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 59.65, 62.65, 62.71, 63.32, 63.49 (all Cp*C*H), 109.70, 112.92, 113.39, 114.15, 114.23, 117.97, 118.55, 118.71, 119.02 (all s, *C*≡N and *CC*≡N), 126.57, 126.70, 126.73, 126.78, 126.81, 126.91, 126.97, 127.57, 127.62, 127.71, 127.88, 127.94, 128.03, 128.05, 128.10, 128.13, 128.17, 128.51, 128.61, 128.75, 128.78, 128.82, 128.85, 128.91, 129.05, 129.07, 129.13, 130.06, 130.09, 130.17, 130.20, 130.29 (all d), 130.85 (s), 131.68, 131.85, 132.11, 132.58 (no unambiguous assignment possible), 132.76, 132.97, 133.20, 134.73, 134.93, 135.00, 135.11, 135.39, 135.51, 135.53, 135.71, 135.76, 135.95, 136.78, 137.18, 137.72, 140.52, 140.87, 140.98, 141.02, 141.60, 142.98, 143.41, 143.92, 145.28, 146.68, 146.89, 146.94, 147.22, 147.42, 149.36, 150.18 ppm (all s). UV−vis (MeCN): λ_{max} (log ε) 213 (4.44), 308 (3.86), 331 nm (3.90). HRMS (EI): calcd for $C_{36}H_{25}N$ 471.1987, found 474.1984.

Alternatively, **4e** was synthesized by reduction of ***spiro*-3e** according to the general procedure for the reduction of the ferrocenyl alcohols **3i−j** (*vide infra*). ***spiro*-3e** (608 mg, 1.25 mmol) and $LiAlH_4$ (75 mg, 1.98 mmol) gave after chromatography (PE/EtOAc, 10:1; R_f = 0, 0.1, 0.22−0.28 (**4e**)) nitrile **4e** (295 mg, 50%), whose spectroscopic data are in accordance with the product from the palladium-catalyzed reaction.

General Procedure for the Reduction of the Ferrocenyl Alcohols 3i−j to Cyclopentadienes 4i−j. The ferrocenyl alcohol was dissolved in THF (5 mL), lithium aluminum hydride (in excess) was added, and the mixture was stirred for 16 h. The mixture was hydrolyzed with water (15 mL) and extracted with MTBE (3 × 15 mL). The combined organic extracts were filtered through a short plug of silica, and the filtrate was evaporated. The resulting foam was suspended in MeOH and treated in the ultrasonic bath. The product was isolated by filtration. Column chromatography of the mother liquor afforded additional product.

1-(2,3,4,5-Tetraphenylcyclopenta-1,3-dienyl)ferrocene (4i). According to the general procedure the reaction of ferrocenyl alcohol **3i** (475 mg, 083 mmol) and $LiAlH_4$ (150 mg, 3.96 mmol) yielded cyclopentadiene **4i** (345 mg, 75%) as a red-orange powder with mp 97−102 °C. TLC, silica: PE/EtOAc, 50:1; R_f = 0.03, 0.07, 0.20 (**4i**). IR (KBr): 3078 w, 3054 m, 3022 m, 2923 w, 2853 w, 1944 w, 1871, 1598 m, 1574 w, 1491 m, 1441 m, 1410 w, 1384 w, 1331 w, 1259 w, 1177 w, 1156 w, 1105 m 1070 m, 1028 w, 1001 m, 942 w, 911 w, 867 w, 817 m, 766 m, 696 s, 565 m, 537 w, 504 cm^{-1} m. The best quality ^{1}H NMR spectrum was obtained directly after isolation of the product at 200 MHz. Later signal broadening became more obvious. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.83 (s, 1 H, FcC*H*, (C_5Ph_4)FcC*H*), 3.91 (s, 6 H, FcC*H*, (C_5Ph_4)FcC*H*), 3.99 (s, 2 H, Fc*H*, (C_5Ph_4)FcC*H*), 4.97 (s, 1 H, CpC*H*, (C_5Ph_4)FcC*H*), 6.88−6.94 (m, 6 H), 7.01−7.31 ppm (m, 14 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 61.97 (Cp*C*H), 66.60, 68.21, 68.27, 68.45 (all (C_5Ph_4)Fc*C*H), 69.18 (Fc*C*H), 80.64 (s, Fc*C*-C_5Ph_4), 126.00, 126.54, 126.90, 127.63, 127.78, 128.02, 128.49, 128.96, 129.90, 129.99 (all d), 135.41, 135.98, 137.61, 139.55, 142.81, 143.85, 144.70, 145.59 ppm (all s), two signal are missing due to overlapping. UV−vis (MeCN): λ_{max} (log ε) 207 (4.59), 240 (4.30), 368 (3.86), 456 nm (3.09). MS (EI, 70 eV): m/z (%) 554 (100) $[M]^+$, 489 (18) $[M-C_5H_5]$. HRMS (EI): calcd for $C_{39}H_{30}Fe$ 554.1697, found 554.1695.

1-Diphenylphosphino-1′-(2,3,4,5-tetraphenylcyclopenta-1,3-dienyl)ferrocene (4j). According to the general procedure the reaction of ferrocenyl alcohol **3j** (280 mg, 0.37 mmol) and $LiAlH_4$ (38 mg, 1 mmol) yielded cyclopentadiene **4j** (210 mg, 77%) as a red powder or foam with mp 106−109 °C. TLC, silica: PE/toluene, 3:2; R_f = 0, 0.18 (**4j**). IR (KBr): 3050 w, 3022 w, 2922 w, 2852 w, 1945 w, 1874 w, 1804 w, 1743 w, 1598 m, 1572 w, 1491 m, 1478 m, 1450 w, 1433 m, 1382 w, 1325 w, 1306 w, 1179 w, 1158 w, 1120 w, 1080 w, 1069 w, 1026 m, 999 w, 942 w, 910 w, 887 w, 867 w, 842 m, 767 m, 742 m, 727 w, 695 s, 631 w, 565 w cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.68 (td, J = 1.4, 2.9 Hz, 1 H, (PPh_2)FcC*H*), 3.81 (dt, J = 1.3, 2.6 Hz, 1 H, (C_5Ph_4)FcC*H*), 3.84 (dt, J = 1.3, 2.5 Hz, 1 H, (C_5Ph_4)FcC*H*), 3.88−3.90 (m, 2 H, (C_5Ph_4)FcC*H*), 3.98 (td, J = 1.2, 2.4, 1 H, (PPh_2)FcC*H*), 4.04 (ddd, J = 1.2, 2.4, 3.4 Hz, 1 H, (PPh_2)FcC*H*), 4.15 (dd, J = 2.3, 3.0 Hz, 1 H, (PPh_2)FcC*H*), 5.07 (s, 1 H, CpC*H*), 6.95−7.02 (m, 7 H), 7.07−7.10 (m, 4 H), 7.15 (br s, 2 H), 7.21 (t, 3 H), 7.26−7.34 ppm (m, 14 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 61.98 (Ph_4Cp*C*H), 68.05, 69.09, 69.89, 70.0 (all (PPh_2)Fc*C*H), 72.56−72.66 (two overlapping d signals, (PPh_2)Fc*C*H), 73.41 (d, $J_{C,P}$ = 4.5 Hz), 74.89 (d, $J_{C,P}$ = 18.5 Hz) (all (C_5Ph_4)Fc*C*H), 76.44 (d, $J_{C,P}$ = 6.6 Hz, Fc*C*-PPh_2), 81.63 (Fc*C*-C_5Ph_4), 126.19, 126.65, 126.70, 127.08, 127.77, 127.93, 128.21, 128.25, 128.27, 128.43, 128.59, 128.63, 128.66, 129.17, 130.15, 130.14 (all d, no assignment possible to C,P coupling), 133.30 (d, $J_{C,P}$ = 19.0 Hz), 133.76 (d, $J_{C,P}$ = 19.4 Hz) (both d), 135.51, 136.03, 137.51 (all s), 138.83 (d, $J_{C,P}$ = 10.2 Hz), 139.52 (d, $J_{C,P}$ = 10.5 Hz) (both s), 139.59, 143.60, 143.73, 144.22, 146.31 ppm (all s). UV−vis (MeCN): λ_{max} (log ε) 215 (4.70), 246 (4.57), 368 (3.54), 458 nm (3.27). MS (EI, 70 eV): m/z (%) 738 (100) $[M]^+$, 553 (7) $[M - PPh_2]^+$, 489 (16) $[M - C_5H_4PPh_2]^+$. Anal. Calcd for $C_{51}H_{39}FeP$: C 82.93, H 5.32. Found: C 82.76, H 5.39.

Chlorodicarbonyl-η^5-[1-(2-*N*,*N*-dimethylaminophenyl)-2,3,4,5-tetraphenylcyclopentadienyl]ruthenium(II) (5a). A mixture of $Ru_3(CO)_{12}$ (115 mg, 0.18 mmol) and cyclopentadiene **4a** (285 mg, 0.54 mmol) in a mixture of toluene (2 mL) and decane (4 mL) in a screw-capped flask was placed in a preheated oil bath at 160 °C and was stirred for 2 days. After cooling to room temperature, chloroform (0.5 mL) was added and the mixture was stirred for 1.5 h at 160 °C. At room temperature the reaction mixture was directly subjected to flash column chromatography (silica, toluene). The second yellow fraction yielded ruthenium complex **5a** (210 mg, 57%) as an orange-yellow foam. Crystallization by slow diffusion of methanol into a solution of **5a** in dichloromethane afforded orange crystals that decompose at 187−190 °C. IR (KBr): 3061 w, 2669 w, 2934 w, 2858 w, 2826 w, 2775 w, 2036 vs, 1988 vs, 1596 w, 1578 w, 1566 w, 1499 m, 1477 w, 1446 m, 1429 w, 1406 w, 1329 w, 1262 w, 1198 w, 1180 w, 1158w, 1134 w, 1097 w, 1076 w, 1055 w, 1030 w, 953 w, 938 w, 914 w, 845 w, 800 w, 763 m, 754 m, 736 m, 725 w, 697 m, 570 m cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.24 (s, 6 H, CH_3), 6.74 (d, J = 8.1 Hz, 1 H), 6.88 (t, J = 7.3 Hz, 1 H), 6.93 (d, J = 7.3 Hz, 4 H), 7.00 (t, J = 7.3 Hz, 4 H), 7.08−7.15 (m, 10 H), 7.20−7.25 (m, 3 H), 7.46 ppm (dd, J = 7.6, 1.4 Hz, 1 H, (NMe_2)Ph*H*3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 41.86 (CH_3), 103.51, 105.31, 109.01 (all Cp*C*), 119.38, 121.93 (both d), 123.20 (s), 127.20, 128.00, 128.08, 129.29, 129.87 (all d), 130.18, 130.22 (both s), 130.88, 132.42 (all d), 135.75 ((NMe_2)Ph-*C*3), 151.69 (s), 197.00 ppm (Ru-*C*O). UV−vis (MeCN): λ_{max} (log ε) 222 (4.50), 360 nm (3.17). MS (FAB): m/z (%) 704 (7) $[M + Na]^+$, 681 (18) $[M]^+$, 646 (45) $[M - Cl]^+$, 625 (100) $[M - 2CO]^+$, 588 (45) $[M - 2CO - Cl]^+$.

Chlorodicarbonyl-η^5-[1-(2-pyridyl)-2,3,4,5-tetraphenylcyclopentadienyl]ruthenium(II) (5b). A mixture of $Ru_3(CO)_{12}$ (210 mg, 0.33 mmol) and cyclopentadiene **4b** (447 mg, 0.97 mmol) in a mixture of toluene (2 mL) and decane (4 mL) in a screw-capped flask was placed in a preheated oil bath at 160 °C and was stirred for 3 days. After cooling to room temperature, chloroform (1 mL) was added and the mixture was stirred for 1.5 h at 160 °C. The solvents were evaporated, and the crude product was purified by flash column chromatography (TLC silica: PE/CH_2Cl_2, 1:1 → 1:4). The orange-yellow fraction yielded ruthenium complex **5b** (285 mg, 46%) as a yellow solid. Crystallization by slow diffusion of methanol into a solution of **5b** in dichloromethane afforded yellow-orange crystals that decompose at 182−185 °C. IR (KBr): 3086 w, 3057 w, 3025 w, 2048 vs, 1988 vs,

1585 m, 1566 w, 1541 w, 1502 w, 1481 w, 1445 w, 1420 w, 1384 w, 1285 w, 1181 w, 1155 w, 1073 w, 1029 w, 993 w, 914 w, 843 w, 810 w, 788 w, 746 m, 697 s, 572 w cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.99 (dd, J = 3.3, 5.2 Hz, 4 H), 7.03−7.11 (m, 11 H), 7.11−7.23 (m, 6 H), 7.35 (dt, J = 1.0, 7.8 Hz, 1 H, Py-*H*6), 7.50 (td, J = 1.8, 7.7 Hz, 1 H, Py-*H*5), 8.42 ppm (ddd, 1 H, J = 0.9, 1.7, 4.8 Hz, Py-*H*3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 104.19, 106.15, 109.12 (all Cp*C*), 123.02 (Py-*C*4), 127.61, 127.87, 128.08, 128.54, 128.55 (all d), 129.53, 129.82 (both s), 131.95, 132.37, 136.24 (Py-*C*5), 149.43 (Py-*C*3), 150.78 (Py-*C*1), 196.77 ppm (Ru-*C*O). UV−vis (MeCN): λ_{max} (log ε) 219 (4.45), 265 (sh, 4.20), 361 nm (3.04). MS (FAB): m/z (%): 662 (2) $[M + Na]^+$, 640 (10) $[M + H]^+$, 604 (8) $[M - Cl]^+$, 583 (30) $[M - 2CO]^+$, 548 (40) $[M - 2CO - Cl]^+$, 486 (10), 464 (100).

Chlorodicarbonyl[η^5-1-(2-cyanophenyl)-2,3,4,5-tetraphenylcyclopentadienyl]ruthenium(II) (5e). A mixture of $Ru_3(CO)_{12}$ (129 mg, 0.20 mmol) and cyclopentadiene **4e** (283 mg, 0.61 mmol) in a mixture of toluene (1.5 mL) and decane (3 mL) in a screw-capped flask was placed in a preheated oil bath at 160 °C and was stirred for 2 days. After cooling to room temperature, chloroform (0.5 mL) was added and the mixture was stirred for 1.5 h at 160 °C. The solvents were evaporated, and the residue was subjected to chromatography (TLC: silica, PE/CH_2Cl_2 1:1; R_f = 0, 0.25, 0.34−0.42 (**4e**, 140 mg recovered), 0.50, 0.56, 0.72, 0.84). The yellow fraction with R_f = 0.25 yielded slightly impure ruthenium complex **5e** as a yellow solid (50 mg, 26%, based on converted **4e**) that could be further purified by crystallization from CH_2Cl_2/MeOH to give a yellow solid that decomposes at 190 °C, but still contained minor impurities and CH_2Cl_2. IR (KBr): 3109 w, 3059 w, 3031 w, 2991 w, 2959 w, 2922 w, 2852 w, 2228 w, 2049 vs, 2004 vs, 1972 m (impurity), 1635w, 1597 w, 1578 w, 1500 w, 1442 m, 1420 w, 1387 w, 1314 w, 1277 w, 1187 w, 1158 w, 1097 w, 1075 w, 1028 w, 1003 w, 920 w, 908 w, 853 w, 847 w, 780 m, 761 m, 732 m, 705 s, 695 s, 625 w, 605 w, 580 m, 568 m, 552 cm^{-1} s. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.98 (dd, J = 1.1, 8.3 Hz, 4 H), 7.03−7.18 (m, 14 H), 7.23 (ddd, J = 1.5, 6.6, 2.9 Hz, 2 H), 7.39 (td, J = 1.1, 7.7 Hz, 1 H), 7.51−7.56 (m, 2 H), 7.93 ppm (d, J = 7.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 104.18, 113.55, 115.46, 115.69 (all s, 3 × Cp*C*), 127.85, 128.33, 128.49, 128.78, 128.97, 129.15 (all d), 129.49 (s), 131.99, 132.42, 132.77 (all d), 133.54 (s), 136.57 (d), 196.49 ppm (*C*O), one carbon is missing due to overlapping and noise. UV−vis (MeCN): λ_{max} (log ε) 216 (4.52), 249 (sh, 4.33), 359 nm (3.40). MS (MALDI-TOF): m/z (%) 1216 (26) $[2M - 2CO]^+$, 1181 (100) $[2M - 2CO - Cl]^+$, 572 (68) $[M - 2CO - Cl]^+$.

Chlorodicarbonyl-η^5-[1-ferrocenyl-2,3,4,5-tetraphenylcyclopentadienyl]ruthenium(II) (5i). A mixture of $Ru_3(CO)_{12}$ (48 mg, 0.075 mmol) and ferrocene **4i** (120 mg, 0.21 mmol) in a mixture of toluene (0.5 mL) and decane (1 mL) in a screw-capped flask was placed in a preheated oil bath at 160 °C and was stirred for 2 days. After cooling to room temperature, chloroform (0.5 mL) was added and the mixture was stirred for 1.5 h at 160 °C. After cooling to room temperature the reaction mixture was directly subjected to flash column chromatography (silica, toluene). The deep red band yielded ruthenium complex **5i** (110 mg, 70%) as a red-purple solid. Crystallization by slow diffusion of methanol into a solution of **5i** in dichloromethane afforded red-purple crystals that decompose at 250 °C. IR (KBr): 3083 w, 3056 w, 3020 w, 2030 vs, 1980 vs, 1638 br w, 1601 w, 1578 w, 1501 w, 1479 m, 1444 m, 1390 w, 1356 w, 1345 w, 1315 w, 1180 w, 1159 w, 1106 w, 1074 w, 1045 w, 1030 w, 1002 w, 909 w, 873 w, 860 w, 820 w, 781 w, 769 m, 724 w, 699 m, 583 m, 570 m, 541 w, 500 w cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.47 (s, 2 H, (C_5Ph_4)Fc-C*H*), 3.99 (s, 5 H, Fc-C*H*), 4.10 (s, 2 H, (C_5Ph_4)Fc-C*H*), 7.01 (t, J = 7.3 Hz, 4 H), 7.08 (d, J = 7.3 Hz, 6 H), 7.42 (s, 6 H), 7.64 ppm (s, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 69.84, 69.88, 69.91 (all Fc*C*H), 74.97 (Fc*C*-C_5Ph_4), 99.68, 110.30, 115.75 (all Cp*C*), 127.66, 128.30, 128.54, 128.89 (all d), 129.76, 131.86 (both s), 132.10, 133.69 (both d), 196.74 ppm (Ru-*C*O). UV−vis (MeCN): λ_{max} (log ε) 214 (4.60), 382 (3.24), 478 nm (3.17). MS (FAB): m/z (%) 745 (36) $[M - 1]^+$, 711 (37) $[M - Cl]^+$, 690 (100) $[M - 2CO]^+$, 655 (100) $[M - 2CO - Cl]^+$.

Chlorocarbonyl-η^5-[1-(2-*N*,*N*-dimethylaminophenyl)-2,3,4,5-tetraphenylcyclopentadienyl]ruthenium(II) (6a). A solution of complex **5a** (98 mg, 0.14 mmol) in toluene (200 mL) was irradiated for 12 h with a high-pressure mercury lamp (125 W). The solvent was evaporated, and the residue was subjected to column chromatography (silica, toluene). The obtained purple fraction was recrystallized from CH_2Cl_2/MeOH to give the decarbonylated ruthenium complex **6a** as a deep purple solid (57 mg, 64%) that decomposes at 251 °C. IR (KBr): 3109 w, 3082 w, 3055 w, 3026 w, 2971 w, 2924 w, 2905 w, 2863 w, 2833 w, 2785 w, 1942 vs, 1600 w, 1578 w, 1502 m, 1464 w, 1444 m, 1413 w, 1385 w, 1312 w, 1262 w 1178 w, 1155 w, 1132 w, 1094 w, 1073 w, 1028 w, 999 w, 912 w, 802 w, 755 m, 735 m, 697 s, 621 w, 600 w, 582 m, 556 m cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.40 (s, 3 H, CH_3), 3.19 (s, 3 H, CH_3), 6.89−7.07 (m, 18 H), 7.11 (d, J = 9.1 Hz, 2 H), 7.17−7.20 (m, 1 H), 7.26 (d, J = 7.6 Hz, 1 H), 7.35 ppm (dd, J = 1.4, 7.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.69, 59.47 (both *C*H_3), 91.25, 92.09, 92.27, 102.51, 108.97 (all Cp*C*), 120.77, 127.20, 127.53, 127.62, 127.68, 127.76, 127.82, 127.85, 127.97 (no unambiguous assignment possible), 129.67 (d), 130.81 (s), 131.16, 131.34, 131.43, 131.58, 131.65, 131.78, 132.18, 132.27 (no unambiguous assignment possible), 132.52 (d), 165.38 (s), 204.35 ppm (Ru-*C*O). UV−vis (MeCN): λ_{max} (log ε) 245 (4.16), 383 (3.01), 503 nm (2.70). MS (FAB): m/z (%) 652 (5) $[M - 1]^+$, 625(100) $[M - CO]^+$, 618 (50) $[M - Cl]^+$, 590 (20) $[M - CO - Cl]^+$, 588 (30), 572 (35), 560 (20).

Chlorocarbonyl-η^5-[1-(8-quinolinyl)-2,3,4,5-tetraphenylcyclopentadienyl]ruthenium(II) (6c). To a solution of 8-bromoquinoline (455 mg, 2.10 mmol) in THF (5 mL) was added *n*-BuLi (1.6 M in hexane, 1.35 mL, 2.16 mmol) at −100 °C within 20 min, and the mixture was stirred for 30 min. Tetracyclone (**1**) (576 mg, 1.50 mmol) was added in several portions with additional THF (30 mL), and the mixture was stirred for 2 h at room temperature. $LiAlH_4$ (150 mg, 4.00 mmol) was added in small portions, and the mixture was stirred for 1 h, hydrolyzed with water (30 mL), and extracted with EtOAc (2 × 30 mL). The combined organic extracts were filtrated over a plug of silica (EtOAc), the filtrate was evaporated, MeOH was added to the residue, and the mixture was sonicated in the ultrasonic bath. The crude cyclopentadiene **4c** (188 mg, 25%) was isolated by filtration as a yellowish, poorly soluble powder, dried *in vacuo*, and subjected to the complexation step without further purification. HRMS (EI): calcd for $C_{38}H_{27}N$ 497.2143, found 497.2155. A mixture of $Ru_3(CO)_{12}$ (48 mg, 0.07 mmol) and quinoline **4c** (111 mg, 0.22 mmol) in a mixture of xylene (1 mL) and decane (2 mL) in a screw-capped flask was placed in a preheated oil bath at 160 °C and was stirred for 3 days. After cooling to room temperature, chloroform (0.5 mL) was added and the mixture was stirred for 1.5 h at 160 °C. The resulting red precipitate was isolated by filtration, dissolved in CH_2Cl_2, and filtrated over a short plug of silica. Evaporating of dichloromethane yielded ruthenium complex **6c** (75 mg, 52%, based on the assumption of pure **4c**) as a red solid that decomposes at 263 °C. IR (KBr): 3105 w, 3085 w, 3052 w, 3036 w, 1955 vs, 1932 vs, 1599 w, 1585 w, 1501 s, 1444 m, 1413 w, 1376 w, 1308 w, 1260 w, 1231 w, 1212 w, 1198 w, 1183 w, 1155 m, 1137 w, 1072 m, 1028 m, 1001 w, 986 w, 965 w, 939 w, 922 w, 833 m, 800 m, 785 w, 770 s, 746 s, 727 s, 696 vs, 585 m, 570 m, 551 m, 538 m cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.92−7.12 (m, 14 H), 7.14−7.18 (m, 2 H), 7.19−7.22 (m, 2 H), 7.30 (dd, J = 5.1, 8.4 Hz, 1 H, Qui-*H*3), 7.38 (dd, J = 1.8, 7.8 Hz, 2 H, *o*-Ph*H*), 7.49 (dd, J = 7.2, 8.1 Hz, 1 H, Qui-*H*6), 7.62 (dd, J = 1.1, 8.2 Hz, 1 H, Qui-*H*5), 7.83 (dd, J = 1.2, 7.1 Hz, 1 H, Qui-*H*7), 8.00 (dd, J = 1.4, 8.4 Hz, 1 H, Qui-*H*4), 8.93 ppm (dd, J = 1.5, 5.1 Hz, 1 H, Qui-*H*2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 90.3, 96.8, 99.2, 104.4 (all Cp*C*), 110.3 (Cp*C*-Qui), 123.7 (Qui-*C*3), 127.2 (Qui-*C*6), 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0 (no unambiguous assignment possible), 128.1 (Qui-*C*5), 129.2 (Qui-*C*4a), 131.7, 131.8, 132.4 (two overlapping signals) 133.1 (Qui-*C*7), 136.9 (Qui-*C*4),

156.9 (Qui-*C*2), 160.7 ppm (Qui-*C*8a). Six signals are missing due to overlapping and noise. Most quaternary carbons were detected by their cross-peaks in the HMBC spectrum since the poor solubility of the substance impedes a high-quality ^{13}C NMR spectrum. UV−vis (MeCN): λ_{max} (log ε) 229 (4.50), 367 (3.52), 434 nm (3.34). MS (LIFDI): *m*/*z* (%) 661 (100) $[M]^+$.

General Procedure for the Synthesis of Ruthenium(II) Oxazoline Complexes 6f−h. To a solution of the phenyloxazoline or 2-bromophenyloxazoline in THF (10 mL) was added *n*-BuLi (1 equiv) at −78 °C within 10 min, and the mixture was stirred for 30 min. Tetracyclone (**1**) was added in several portions with additional THF until tetracyclone (**1**) is detectable by TLC (approximately 0.6 equiv). The solution was slowly warmed to room temperature and was stirred for 1 h. $LiAlH_4$ (XS) was added in small portions, and the mixture was stirred for 1 h and hydrolyzed with aqueous saturated NH_4Cl. The mixture was extracted with MTBE, and the organic extracts were filtrated over a short plug of silica (MTBE). The filtrate was evaporated to give a sticky residue or foam, which was subjected to flash column chromatography. The fractions with the desired cyclopentadiene contained the oxazolinylbenzene as an impurity, which could be removed by Kugelrohr distillation (100 °C, 1 mbar). The residue was directly subjected to the complexation reaction. The cyclopentadienes **4f−h** and $Ru_3(CO)_{12}$ (0.33 equiv) were suspended in a mixture of toluene (1.5 mL) and decane (3 mL) in a screw-capped flask and placed in a preheated oil bath at 175 °C. The mixture was stirred for 3 days. After cooling to room temperature, $CHCl_3$ (0.5 mL) was added and the mixture was stirred for 1.5 h at 175 °C. After cooling to room temperature the reaction mixture was directly subjected to column chromatography (silica, toluene). The red fraction yielded the ruthenium oxazolinyl complexes, which could be recrystallized from CH_2Cl_2/MeOH if necessary.

(S_{Ru})-Carbonylchloro-η^5-[1-(2-((*S*)-4-isopropyloxazolinyl-phenyl)-2,3,4,5-tetraphenylcyclopentadienyl]ruthenium(II) (6f). According to the general procedure (*S*)-2-(2-bromophenyl)-4-isopropyl-4,5-dihydrooxazole (618 mg, 2.30 mmol), *n*-BuLi (1.6 M in hexane, 1.44 mL, 2.30 mmol), tetracyclone (**1**) (647 mg, 1.68 mmol), and $LiAlH_4$ (230 mg, 6.08 mmol) yielded "crude" cyclopentadiene **4f** (590 mg, 62%) after chromatography (TLC: silica, PE/EtOAc, 10:1; R_f = 0, 0.18−0.33 (**4f**), 0.42, 0.53, 0.61, 0.70). EI (70 eV): *m*/*z* 557 (100) $[M]^+$. The reaction of **4f** (380 mg, 0.68 mmol) with $Ru_3(CO)_{12}$ (149 mg, 0.18 mmol) yielded chelated ruthenium oxazoline complex **6f** as a red solid (245 mg, 48% based on the assumption of pure **4f**), which decomposes at 258 °C. IR (KBr): 3111 w, 3058 w, 3033 w, 2963 m, 2932 m, 2901 w, 2873 w, 1954 vs, 1608 m, 1501 m, 1479 w, 1459 w, 1444 w, 1430 w, 1391 w, 1368 m, 1334 w, 1300 w, 1286 w, 1265 w, 1240 m, 1181 w, 1147 w, 1079 w, 1054 w, 1028 w, 1003 w, 963 w, 919 w, 847 w, 803 w, 783 w, 765 w, 748 m, 738 m, 700 s, 679 w, 621 w, 578 s cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.73 (d, J = 6.9 Hz, 3 H, CH_3), 0.88 (d, J = 7.0 Hz, 3 H, CH_3), 2.47−2.63 (dhept, J = 3.2, 6.7 Hz, 1 H, CH(CH_3)$_2$), 3.77 (dd, J = 8.9, 10.0 Hz, 1 H, CH_2(Oxaz)), 4.34 (dd, J = 4.4, 8.7 Hz, 1 H, CH_2(Oxaz)), 4.73−4.83 (m, 1 H, CH(Oxaz)), 6.87 (dd, J = 1.3, 8.5 Hz, 2 H, *o*-Ph*H*), 6.91−7.03 (m, 19 H, Ph*H*, (Oxaz)Ph-*H*6), 7.29−7.39 (m, 2 H, (Oxaz)Ph-*H*4, (Oxaz)Ph-*H*5), 7.71−7.79 ppm (m, 1 H, (Oxaz)Ph-*H*3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.91, 18.66 (both *C*H_3), 28.21 (*C*(CH_3)$_2$), 67.62 (*C*H_2(Oxaz)), 69.15 (*C*H(Oxaz)), 85.38 (Cp*C*-Ph(Oxaz)), 88.76, 94.36, 96.62, 120.30 (all Cp*C*), 127.24, 127.42, 127.49, 127.56, 127.71, 127.78, 128.13 (all d), 128.16 ((Oxaz)Ph-*C*4), 130.17 (s), 130.41 ((Oxaz)Ph-*C*3), 130.91 (s), 131.63, 131.65, 131.89, 132.02 (all d), 132.31 ((Oxaz)Ph-*C*5), 132.43, 132.83, 133.35, 133.53 (no unambiguous assignments possible), 163.83 (*C*═N), 204.35 ppm (Ru-*C*O), two carbons are missing due to overlapping. UV−vis (MeCN): λ_{max} (log ε) 217 (4.61), 368 (3.32), 468 nm (2.91). MS (FAB): *m*/*z* (%) 721 (4) $[M]^+$, 693 (100) $[M - CO]^+$, 658 (36) $[M - CO - Cl]^+$, 572 (11).

(S_{Ru})-Carbonylchloro-η^5-[1-(2-((*S*)-4-isobutyloxazolinyl)-phenyl)-2,3,4,5-tetraphenylcyclopentadienyl]ruthenium(II) (6g). According to the general procedure (*S*)-2-phenyl-4-isopropyl-4,5-dihydrooxazole (457 mg, 2.25 mmol), *n*-BuLi (1.6 M in hexane, 1.50 mL, 2.40 mmol), tetracyclone (**1**) (600 mg, 1.56 mmol), and $LiAlH_4$ (220 mg, 5.81 mmol) yielded "crude" cyclopentadiene **4g** (365 mg, 41%) after chromatography (TLC, silica: PE/EtOAc, 10:1 R_f = 0, 0.24−0.38 (**4g**), 0.51, 0.69). MS (FAB): *m*/*z* 572 (100) $[M + 1]^+$. The reaction of **4g** (210 mg, 0.37 mmol) with $Ru_3(CO)_{12}$ (80 mg, 0.13 mmol) yielded the chelated ruthenium oxazolinyl complex **6g** as a red solid (160 mg, 58% based on the assumption of pure **4g**), which decomposes at 210 °C. IR (KBr): 3084 w, 3056 w, 3032 w, 2955 m, 2901 w, 2869 w, 1964 vs, 1952 vs, 1611 m, 1576 w, 1500 m, 1444 m, 1420 w, 1404 w, 1371 m, 1348 w, 1314 w, 1269 w, 1246 m, 1231 m, 1181 w, 1148 w, 1138 w, 1058 m, 1073 m, 1055 w, 1028 m, 973 w, 958 w, 922 w, 805 w, 785 w, 767 w, 747 m, 736 s, 698 s, 622 w, 581 s, 568 m, 537 w cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 0.97 (d, J = 6.6 Hz, 3 H, CH_3), 1.01 (d, J = 6.6 Hz, 3 H, CH_3), 1.27 (ddd, J = 4.1, 11.4, 13.0 Hz, 1 H, CH_2CH(CH_3)$_2$), 1.58−1.66 (m, 1 H, CH(CH_3)$_2$), 2.04 (ddd, 1 H, J = 2.6 Hz, 10.1, 12.8 Hz, 1 H, CH_2CH(CH_3)$_2$), 3.93 (t, J = 8.8 Hz, 1 H, CH_2(Oxaz)), 4.31 (dd, J = 4.3, 8.4 Hz, 1 H, CH_2(Oxaz)), 4.82−4.89 (m, 1 H, CH(Oxaz)), 6.88 (d, J = 8.6 Hz, 2 H, *o*-Ph*H*), 6.93−7.16 (m, 19 H, Ph*H*, (Oxaz)Ph-*H*6), 7.31−7.37 (m, 2 H, (Oxaz)Ph-*H*5, (Oxaz)Ph-*H*4), 7.76−7.78 ppm (m, 1 H, (Oxaz)Ph-*H*3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.69, 24.23 (both *C*H_3), 25.75 (*C*H(CH_3)$_2$), 42.14 (*C*H_2CH(CH_3)$_2$), 64.38 (*C*H(Oxaz)), 71.96 (*C*H_2(Oxaz)), 86.33 (Cp*C*-Ph(Oxaz)), 89.45, 94.93, 95.57, 118.23 (all Cp*C*), 127.21, 127.44, 127.47, 127.64, 127.71, 127.96, 128.03, 128.07 (all d), 128.15 ((Oxaz)Ph-*C*4/5), 130.27 ((Oxaz)Ph-*C*2), 130.41 ((Oxaz)Ph-*C*3), 130.91, 131.47 (both s), 131.64, 131.88, 132.04, 132.28, 132.31 (no unambiguous assignment possible), 132.77, 133.12, 133.44 (all d), 163.28 (*C*═N), 204.58 ppm (Ru−*C*O), one signal is missing due to overlapping. UV−vis (MeCN): λ_{max} (log ε) 240 (4.17), 368 (3.29), 484 nm (2.86). MS (FAB): *m*/*z* (%) 735 (2) $[M]^+$, 707 (100) $[M - CO]^+$, 700 (23) $[M - Cl]^+$, 686 (5), 670 $[M - CO - Cl - 2]^+$.

(S_{Ru})-Carbonylchloro-η^5-[1-(2-((*S*)-4-benzyloxazolinyl)phenyl)-2,3,4,5-tetraphenylcyclopentadienyl]ruthenium(II) (6h). According to the general procedure (*S*)-2-(2-bromophenyl)-4-benzyl-4,5-dihydrooxazole (1.06 g, 3.35 mmol), *n*-BuLi (1.6 M in hexane, 2.10 mL, 3.36 mmol), tetracyclone (**1**) (1.01 g, 2.63 mmol), and $LiAlH_4$ (280 mg, 7.40 mmol) yielded "crude" cyclopentadiene **4h** (730 mg, 46%) after chromatography (TLC, silica: PE/EtOAc, 10:1; R_f = 0, 0.16−0.32 (**4h**), 0.48, 0.53, 0.77). MS (FAB): *m*/*z* 606 (100) $[M + 1]^+$. The reaction of **4h** (400 mg, 0.66 mmol) with $Ru_3(CO)_{12}$ (157 mg, 0.24 mmol) yielded the chelated ruthenium oxazolinyl complex **6h** as a red solid (210 mg, 42% based on the assumption of pure **4h**), which decomposes at 254−257 °C. IR (KBr): 3105 w, 3083 w, 3057 w, 3029 w, 3001 w, 2971 w, 2961 w, 2951 w, 2925 w, 2909 w, 2852 w, 1960 vs, 1610 m, 1589 w, 1576 w, 1499 m, 1444 w, 1473 w, 1453 w, 1444 m, 1422 w, 1405 w, 1380 m, 1332 w, 1268 w, 1239 m, 1226 w, 1198 w, 1177 w, 1169 w, 1157 w, 1136 w, 1110 w, 1088 w, 1077 w, 1069 w, 1054 w, 1028 w, 1001 w, 975 w, 931 w, 915 w, 890 w, 857 w, 842 w, 803 w, 786 w, 765 w, 749 m, 739 m, 698 s cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.41 (dd, J = 11.0, 12.8 Hz, 1 H, Ph−CH_2), 3.67−3.72 (m, 2 H, Ph−CH_2, CH_2(Oxaz)), 4.30 (dd, J = 8.7, 4.2 Hz, 1 H, CH_2-(Oxaz)), 5.09−5.16 (m, 1 H, CH(Oxaz)), 6.93−6.99 (m, 6 H), 7.02−7.23 (m, 16 H), 7.26−7.29 (m, 2 H), 7.36−7.41 (m, 4 H, Ph-*H*4(Oxaz), *o*-Ph*H*-CH_2), 7.75−7.77 ppm (m, 1 H, Ph-*H*3-(Oxaz)). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 39.2 (Ph-*C*H_2), 66.3 (*C*H(Oxaz)), 71.1 (*C*H_2(Oxaz)), 85.4 (Cp*C*-Ph(Oxaz)), 88.8, 94.1, 96.6, 120.0 (all Cp*C*), 126.8, 127.2, 127.4, 127.4, 127.7, 127.7, 128.1, 128.1, 128.7 (all d), 129.8 (*o*-Ph*C*H−CH_2), 130.0 (s), 130.4 (d), 130.7 (Ph-*C*3(Oxaz)), 131.4 (both s), 131.5, 131.8, 131.9 (all d), 132.3 (s), 132.4 (Ph-*C*5(Oxaz)), 132.7 (s), 133.2, 133.4 (both d), 137.4 (s), 164.5 (*C*═N), 204.4 (Ru−*C*O) ppm, seven carbons are missing due to overlapping. UV−vis (MeCN):

λ_{max} (log ε) 235 (4.44), 368 (3.32), 468 nm (2.89). MS (FAB): m/z (%) 793 (2) $[M + Na + 1]^+$, 769 (5) $[M]^+$, 741 (100) $[M - CO]^+$, 734 $[M - Cl]^+$ (35), 706 $[M - CO - Cl]^+$ (60).

Representative Procedure for Transferhydrogenation of Phenyl Ketones 9. A mixture of the phenyl ketone **9** (0.29 mmol), KOH (0.26 mmol), and the ruthenium complex (1−2 mol %) in dry 2-propanol (0.5 mL) in a screw-capped vessel was placed in a preheated oil bath (82 °C) and stirred for 3 h. The internal standard (see Table 2) was added, and the mixture was filtrated over a short plug of silica (2-propanol). GC[24] of the filtrate revealed the formation of the benzylic alcohol **10**. The residue was distilled bulb-to bulb to give the benzylic alcohol, depending on the conversion of the catalysis together with unreacted starting material. This distillate was used without further manipulation for the preparation of Mosher's ester in the next step to determine the ee.

Representative Procedure for the Formation of the Mosher Ester from Benzylic Alcohols 10. To a solution of (*R*)-(+)-α-methoxy-α-trifluoromethylphenylacetic acid (20 mg, 0,085 mmol), DCC (27 mg, 0.13 mmol), and 4-DMAP (5 mg, 0.04 mmol) in dry CH_2Cl_2 (0.8 mL) was added the benzylic alcohol **10** (ca. 0.06 mmol). The mixture was sonicated in the ultrasonic bath for 5 min and allowed to stand for 12 h. The urea was filtered off. GC without further manipulation of the filtrate directly gave the ratio of the diastereomeric esters, reflecting the ratio of enantiomers in the benzylic alcohols **10**. In the case of the starting alcohols **10d** and **10e** the filtrate was washed with 1 N HCl (2 mL), saturated aqueous $NaHCO_3$ (2 mL), and brine (2 mL). The organic layer was filtrated over a short plug of silica (CH_2Cl_2) and evaporated. The crude product was not purified; NMR afforded the ratio of the diastereomeric esters by integration of the diagnostic benzylic hydrogens (around 6 ppm). In all cases complete conversion was additionally controlled since the diastereomeric esters exhibit different rates of formation.

(24) In case of the transfer hydrogenation of cyclohexyl phenyl ketone the yield was determined by ^{1}H NMR of the distillate.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new compounds and X-ray data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.