Chiral Olefins as Steering Ligands: Syntheses of C_1-Symmetric Dibenzo[*a*,*e*]cyclooctenes (^{R}dbcot)

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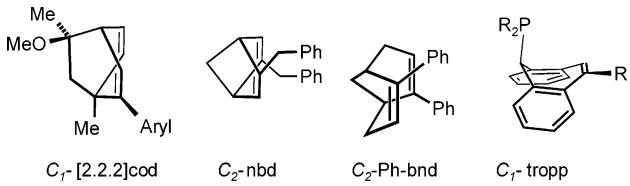
A simple three-step synthesis of chiral dibenzo[*a*,*e*]cyclooctenes (dbcot) starting from commercially available dibenzosuberenone was developed. These compounds give highly stable and robust rhodium(I) and iridium(I) diene complexes of the type [M(^{R}dbcot)(L^1)(L^2)] (M = Rh, Ir; L^1, L^2 = MeCN, Cl, diamine, chloride). The complex [Rh((*R*)-^{Ph}dbcot)((*R*)-(+)-1,1′-binaphthyl-2,2′-diamine)]$^+$OTf$^-$ could be obtained in enantiomerically pure form and catalyzes the enantioselective 1,2-addition of $PhB(OH)_2$ to α,β-unsaturated ketones with good activity and acceptable enantiomeric excess (62%). The iridium complex [Ir(^{Ph}dbcot)-$(MeCN)_2$]$^+$OTf$^-$ catalyzes the hydrogenation of dimethylitaconate with good activity, while the rhodium complexes are almost inactive. Likewise, the complex [Ir(^{Ph}dbcot)(H_2NCH_2-CH_2NH_2)]$^+$OTf$^-$ serves as a rather efficient catalyst precursor with an activity 4 orders of magnitude higher than for the analogous rhodium complex. These experiments further establish the use of dienes as steering ligands in catalysis.

Introduction

Many diene complexes described in the literature contain a η^4-1,5-cyclooctadiene (cod) ligand,[1] which is mostly employed as a placeholder for so-called "vacant" coordination sites. Only recently have dienes became recognized as valuable steering ligands for homogeneously catalyzed reactions. Lemaire et al. found strong evidence that amide complexes derived from C_2-symmetric [Rh^I(cod)(diamine)] complexes are involved in the catalytic cycle: that is, neither the amine nor the olefin is displaced in the catalytically active species.[2] Likewise, van Leeuwen et al. proposed chiral aminosulfide or aminosulfoxide diene complexes [Ir^I(cod)(RHNnSOR)] as efficient catalyst precursors in the transferhydrogenation of aryl alkyl ketones.[3] Dahlenburg et al. reported rhodium and iridium cod complexes with β-aminophosphanes as further ligands as catalysts for the hydrogenation of ketones.[4] Several chiral dienes such as C_1-[2.2.2]cod, C_2-nbd, and C_2-Ph-bnd (Chart 1) have been introduced recently as steering ligands in enantioselective catalytic processes[5] through the work of Carreira et al.[6] and Hayashi et al.[7] In related work, we synthesized chiral C_1-tropp ligands (tropp = tropylidenylphosphanes) and used the unsymmetric substitution pattern at the $C{=}C_{trop}$ bond of the central seven-membered ring for stereochemical induction. Values of up to 86% ee were achieved in the catalyzed hydrogenation of imines using [Ir(C_1-tropp)] complexes.[8]

Chart 1. Chiral Dienes and Olefin Ligands Used in Enantioselective Catalyses



Replacement of the phosphanyl donor function, R_2P, in these tropp-type ligands[9] by a CH=CH unit leads to related dibenzo[*a*,*e*]cyclooctenes (dbcot). The parent hydrocarbon, $C_{16}H_{12}$, was prepared about 60 years ago,[10] and its structure, determined by X-ray diffraction, shows a boat conformation.[11] First coordination compounds with dbcot as ligand contained silver and palladium as metals,[12] followed by reports on complexes

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(1) (a) Rhodium cod complexes: Sharp, P. R. *Comprehensive Organometallic Chemistry*, 2nd ed.; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 8, pp 245−268. (b) Iridium cod complexes: Sharp, P. R. *Comprehensive Organometallic Chemistry*, 2nd ed.; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds., Pergamon: Oxford, U.K., 1995; Vol. 8, pp 365−270.

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(5) For a short review see: Glorius, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3364.

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(8) (a) Grützmacher, H.; Deblon, S.; Maire, P.; Schönberg, H. Ger. Offen. DE 101 59 015.6, 2002. (b) Maire, P.; Deblon, S.; Breher, F.; Geier, J.; Böhler, C.; Rüegger, H.; Grützmacher, H. *Chem. Eur. J.* **2004**, *10*, 4198.

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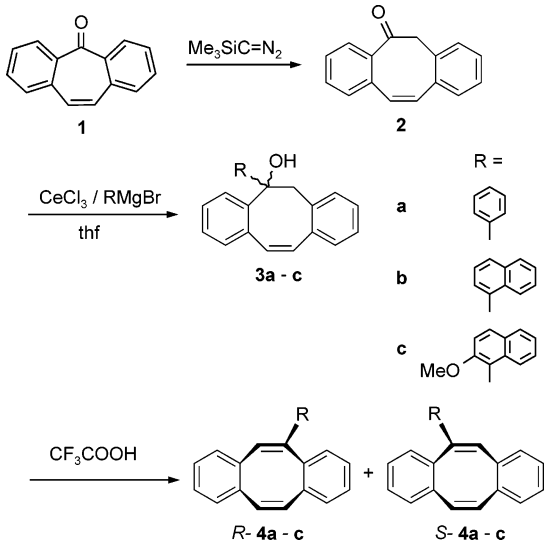
Scheme 1. Syntheses of Chiral Dibenzo[*a,e*]cyclooctene (dbcot) Derivatives



with chromium or molybdenum.[13] With chromium, coordination via the benzo groups was also observed.[14] Crabtree et al. demonstrated the remarkable stability of various molybdenum, rhodium, and iridium complexes,[15,16] and the inertness of $[MH_2(dbcot)L_2]^+$ (M = Rh, Ir; L = phosphane) is especially noteworthy; that is, no hydrogenation of the dbcot ligand is observed. Moreover, dbcot was employed as a catalyst poison. A tetranuclear copper dbcot complex was also described.[17] In this paper we report the facile syntheses of chiral ^{R}dbcot derivatives as ligands for tetracoordinated 16-electron rhodium(I) and iridium(I) complexes (R denotes a substituent in the 5-position). Furthermore, we describe first results concerning the application of these complexes in homogeneously catalyzed reactions.

Results and Discussion

Syntheses. The rather laborious synthesis of dbcot is the likely reason that the investigation of its coordination chemistry stopped about 20 years ago. We found a simple and straightforward synthesis of chiral ^{R}dbcot derivatives[18] which show an unsymmetrical substitution pattern at the C=C bonds of the central eight-membered ring. As reported in the literature[19] and shown in Scheme 1, dibenzosuberenone (**1**) is easily ring-expanded with (trimethylsilyl)diazomethane to give the ketone **2**, having an eight-membered ring in its center. The reaction of **2** with a phenylcerium reagent prepared in situ from phenylmagnesium bromide and $Ce^{III}Cl_3$ in thf[20] yields the tertiary alcohol 5-phenyl-5,6-dihydrodibenzo[*a,e*]cyclooctene-5-ol (**3a**) in 88% isolated yield.

With the same procedure, naphthyl and 2-methoxynaphthyl groups were introduced, and the alcohols **3a**−**c** were easily prepared in gram quantities. With the sterically more demanding 2-methoxynaphthyl group, the yield of **3c** (60%) was lower, and this compound was always contaminated with small amounts of the ketone **2**. However, this impurity did not interfere with the subsequently performed elimination reaction. Addition of 20 mol % CF_3COOH to CH_2Cl_2 solutions of **3a**−**c** and stirring of the reaction mixtures for about 20 h at room temperature led almost quantitatively (yields >95%) to racemic mixtures of the desired 5-substituted dibenzo[a,e]cyclooctenes (*R*)-**4a** and (*S*)-**4a** (^{ph}dbcot), (*R*)-**4b** and (*S*)-**4b** (^{naph}dbcot), and (*R*)-**4c** and (*S*)-**4c** ($^{2MeO-naph}$dbcot). We will denote the racemic mixture as *R*(*S*) hereafter; details concerning the assignment of the stereochemistry are given in the Experimental Section. The impurity **2** is easily separated from (*R*(*S*))-**4c** by flash chromatography. The rotation of the 2-methoxynaphthyl group in (*R*(*S*))-**4c** is hindered at room temperature, causing a doubling of all NMR resonances.

The syntheses of rhodium(I) and iridium(I) complexes with ^{R}dbcot as ligands were accomplished in straightforward ligand substitution reactions (Scheme 2). $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$ is a suitable precursor for rhodium complexes and reacts with the racemic mixture of (*R*(*S*))-**4a**,**b** to give the chloro-bridged dimeric complexes **5a**,**b**. These compounds form complex mixtures containing various stereoisomers which were not isolated or investigated in detail.

Subsequent reactions with silver salts AgX (X^- = $CF_3SO_3^-$, OTf^-, SbF_6^-) in acetonitrile as solvent give the mononuclear bis(acetonitrile) complexes $[Rh(^{R}dbcot)(MeCN)_2]^+X^-$ ((*R*(*S*))-**6a**,**b**) as orange (X^- = OTf^-) and yellow-brown (X^- = SbF_6^-) microcrystalline powders in high yields. Reactions with the sterically more hindered ligand $^{2-MeO-naph}$dbcot (**4c**) were less successful, and no pure compound was obtained. In one experiment, we could however isolate by accident a crystalline substance of composition $[Rh(^{2-MeO-naph}dbcot)(MeCN)(H_2O)]OTf$ ((*R*(*S*))-**6c**) when solutions of $[Rh_2(\mu_2\text{-}Cl_2)(CO)_4]$ and (*R*(*S*))-**4c** were kept in presence of silver triflate for several days in acetonitrile solution.

The neutral 16-electron iridium complex $[IrCl(^{Ph}dbcot)(MeCN)]$ ((*R*(*S*))-**7a**) was obtained as orange crystals when $[Ir_2(\mu_2\text{-}Cl)_2(cod)_2]$ was reacted with (*R*(*S*))-**4a** in an acetonitrile/CH_2Cl_2 mixture at room temperature. In CD_3CN, only one isomer with the chloro ligand in a position trans to the 5-phenyl substituent of the ^{Ph}dbcot ligand is observed. In $CDCl_3$ or CD_2Cl_2, several species are observed (some showing exchange broadened signals), which are tentatively attributed to the various possible stereoisomers of the chloro-bridged dinuclear compounds $[Ir_2(\mu_2\text{-}Cl)_2(^{Ph}dbcot)_2]$ and a mixture of the mononuclear complexes (*R*(*S*))-**7a** with a cis- and trans-orientation of the chloro ligand with respect to PhC=CH unit. Reaction of (*R*(*S*))-**7a** with AgOTf again gives cleanly the cationic bis(acetonitrile) complex $[Ir(^{Ph}dbcot)(MeCN)_2]^+OTf^-$ ((*R*(*S*))-**8a**) as orange microcrystalline powder (X^- = $CF_3SO_3^-$, SbF_6^-) in high yield. In the reaction with the naphthyl-substituted ligand ^{naph}dbcot (**4b**) in benzene at 80 °C, we used $[Ir_2(\mu_2\text{-}Cl)_2(coe)_4]$ as a precursor (coe = cyclooctene). The chloro-bridged dinuclear complex **9b** precipitates during the

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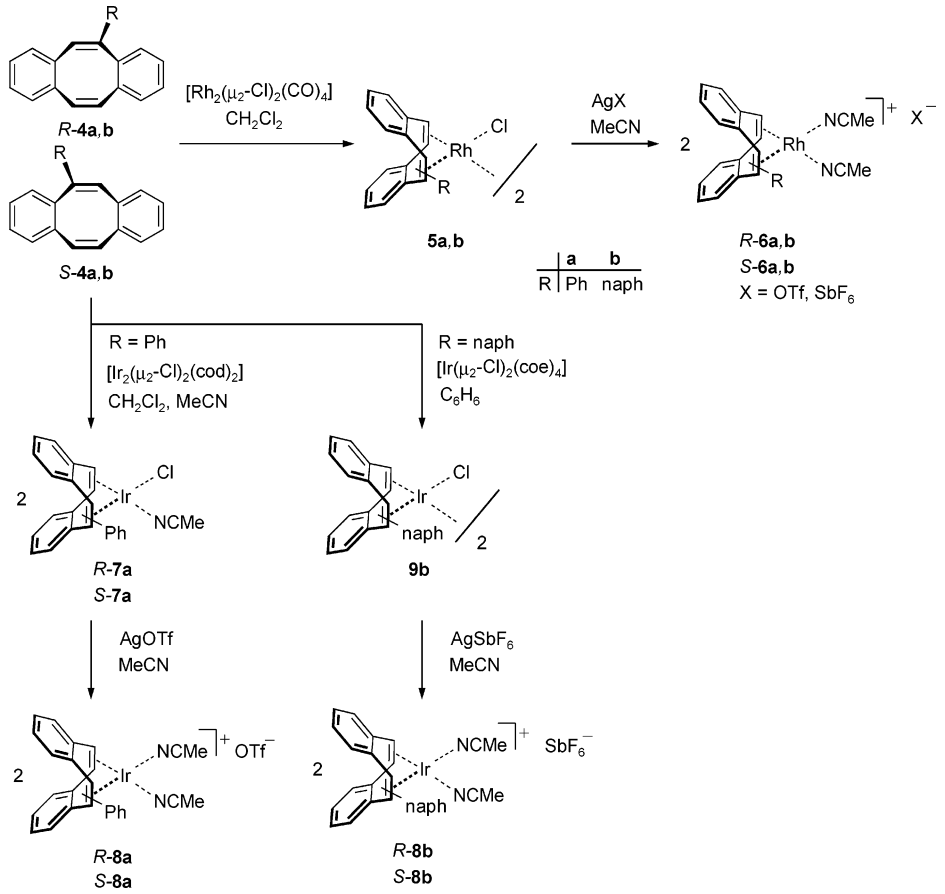
Scheme 2. Syntheses of Rhodium(I) and Iridium(I) ^{R}dbcot Complexes (R = Ph, naph)



reaction time (24 h) as a yellow microcrystalline substance which is only sparingly soluble in common deuterated solvents. The reaction with $AgSbF_6$ in acetonitrile converts **9b** cleanly into the orange crystalline mononuclear bis(acetonitrile) complex [Ir(^{naph}dbcot)-$(MeCN)_2]^+SbF_6^-$ ((*R*(*S*))-**8b**).

In ^{1}H NMR spectra of the complexes [M(^{Ph}dbcot)-$(MeCN)_2]^+X^-$ (M = Rh, (*R*(*S*))-**6a**; M = Ir, (*R*(*S*))-**8a**), the ortho and meta protons of the phenyl group appear as exchange-broadened signals, indicating hindered rotation on the NMR time scale. In the corresponding ^{naph}dbcot-substituted complexes (*R*(*S*))-**6b** (M = Rh) and (*R*(*S*))-**8b** (M = Ir), sharp resonances are observed for all protons of the naphthyl group. Of special diagnostic value is the resonance of the proton at the 8-position of the naphthyl substituent, which is shifted to unusually high frequencies (δ 10.07 ppm (M = Rh), 9.34 ppm (M = Ir)). An X-ray diffraction study of [Ir(^{naph}dbcot)-$(MeCN)_2]^+SbF_6^-$ shows (vide infra) that this proton (H24) points toward the metal center. We therefore conclude that the naphthyl group resides in a frozen position which corresponds to that seen in the solid state.

In Table 1, the coordination shifts, $\Delta\delta = \delta_{ligand} - \delta_{complex}$ (δ_{ligand} is the chemical shift in the uncomplexed ^{R}dbcot molecule; $\delta_{complex}$ is the corresponding chemical shift in the complex), for the four coordinated carbon atoms C5, C6, C11, and C12 are listed for selected compounds. The $\Delta\delta$ values (46−59 ppm for M = Rh; 59−72 ppm for M = Ir) are in the usual range for rhodium(I) or iridium(I) complexes.[21]

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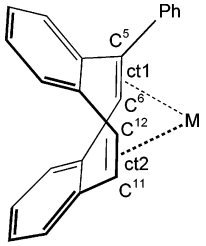
Table 1. Coordination Shifts, $\Delta\delta = \delta_{ligand} - \delta_{complex}$, Determined for the ^{13}C Chemical Shifts (δ in ppm), of the Olefinic Carbons C5, C6, C11, and C12[a] and the M−ct Distances (Å; ct = Centroid of the Coordinated C=C Bond) in the Complexes (*R*(*S*))-7a, (*R*(*S*))-8b, and (*R*)-[(*R*)-(+)]-11a

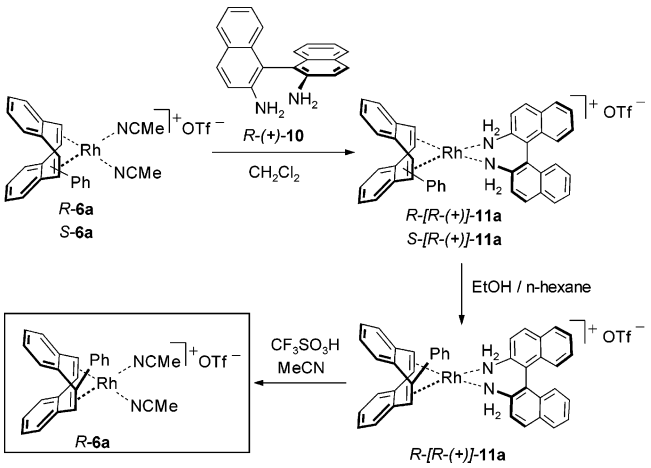


		Δδ(^{13}C)					
	M	C5	C6	C11	C12	M−ct1	M−ct2
(*R*(*S*))-**7a**	Ir	70.6	72.2	64.3	60.8	2.004(4)	1.997(5)
(*R*(*S*))-**8b**	Ir	57.6	65.3	62.5	64.6	1.990(7)	1.993(8)
(*R*)-[(*R*)-(+)]-**11a**	Rh	46.0	53.7	53.2[b]	54.2[b]	2.016(5)	2.001(5)

[a] δ_{ligand} for **4a**: 145.12 (C5), 129.51 (C6), 134.19 (C11), 133.21 (C12). δ_{ligand} for **4b**: 142.97 (C5), 133.85 (C6), 134.87 (C11), 133.50 (C12). [b] For (*R*)-[(*R*)-(+)]-**11a** the unambiguous assignment of C11 and C12 was impossible.

It is generally assumed that with increasing $\Delta\delta$ the interaction energy between the metal and the coordinated olefins increases as well. Remarkably then, these data indicate in combination with the distances M−ct from the metal to the centroid of the coordinated C=C bond (determined by X-ray diffraction; vide supra), that both C=C units interact almost equally and rather strongly with the metal center in all [M(^{R}dbcot)] com-

Scheme 3. Synthesis of the Diastereomerically Pure Complexes (*R*)-[(*R*)-(+)]-11a and (*R*)-6a



plexes, despite the fact that trisubstituted olefins are usually considered to be significantly more weakly bound ligands. The coordination shifts $\Delta\delta$ are, as expected, somewhat larger in the iridium complexes than in the rhodium complexes, indicating a higher degree of metal-to-ligand back-bonding. Therefore, the ^{R}dbcot ligand should be more tightly bound in the iridium complexes, which is confirmed by the following experiments. When the rhodium complex [Rh(^{Ph}dbcot)(MeCN)$_2$]$^+$OTf$^-$ ((*R*(*S*))-**6a**) is reacted with 4 equiv of PPh_3 in acetonitrile solution at room temperature, a quantitative displacement of the ^{Ph}dbcot ligand and the formation of [Rh(PPh_3)$_3$(MeCN)]$^+$ is observed.[22] On the other hand, the complete displacement of the ^{R}dbcot ligands from the iridium complexes by PPh_3 or even chelating diphosphanes such as dppe requires temperatures above 70 °C and prolonged reaction times (~24 h).

All complexes described so far were obtained as racemic mixtures containing both enantiomers of the ^{R}dbcot ligands. Our attempts to find conditions allowing a separation of either the free ^{R}dbcot or the complexes failed. However, the reaction of the rhodium complex [Rh(^{Ph}dbcot)(MeCN)$_2$]$^+$OTf ((*R*(*S*))-**6a**) with (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine ((*R*)-(+)-**10**) gave the diastereomeric diamine rhodium complexes (*R*)-[(*R*)-(+)]-**11a** and (*S*)-[(*R*)-(+)]-**11a** (Scheme 3) as pure compounds, which show clearly separated signals for each diastereomer in the ^{1}H NMR spectrum. Also, the reaction of racemic (*R*(*S*))-**6a** with a the *R*,*R*-configured enantiomer of 1,2-diaminocyclohexane ((*R*,*R*)-dach) gave a mixture of diastereomeric diamine complexes which show clearly separated sets of NMR resonances; however, these could not be separated by fractional crystallization. On the other hand, recrystallization of the mixture of (*R*)-[(*R*)-(+)]-**11a** and (*S*)-[(*R*)-(+)]-**11a** from ethanol/*n*-hexane gave one diastereomer in 32% isolated yield, as determined by ^{1}H NMR spectroscopy. The absolute configuration of this compound was determined by X-ray analysis as the (*R*)-[(*R*)-(+)]-**11a** isomer (vide infra). No further diastereomerically pure complex could be isolated from the mother liquor. All attempts to use this method with the other ^{R}dbcot ligands failed (R = naph, 2-MeO-naph). Also, analogous reactions with the iridium complexes (*R*(*S*))-**8a** and (*R*(*S*))-**8b** with enantiomerically pure diamines gave dark brown insoluble materials only.

The addition of trifluorosulfonic acid, CF_3SO_3H, to the diastereomer (*R*)-[(*R*)-(+)]-**11a** in acetonitrile allowed the displacement of the binaphthyldiamine ligand as chiral auxiliary, and the bis(acetonitrile) complex (*R*)-[Rh(^{Ph}dbcot)(MeCN)$_2$]$^+$OTf$^-$ ((*R*)-**6a**) was obtained in enantiomerically pure form (determined by adding (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine, (*R*)-(+)-**10,** which furnished the single diastereomer (*R*)-[(*R*)-(+)]-**11a** quantitatively within the detection limits of ^{1}H NMR spectroscopy).

As discussed above, addition of phosphanes easily displaces the ^{R}dbcot ligands in the rhodium complexes. Therefore we hoped that we might obtain the enantiomerically pure free ligand (*R*)-^{Ph}dbcot ((*R*)-**4a**) in the reaction of (*R*)-[(*R*)-(+)-**11a** or (*R*)-**6a** with PPh_3. Unfortunately, it turned out that the free ligand (*R*)-^{Ph}dbcot is not conformationally stable but racemizes completely in less than 3 h at room temperature.[23]

Structures. Single crystals of the uncomplexed 5-phenyldibenzo[*a*,*e*]cyclooctene (^{Ph}dbcot (*R*(*S*))-**4a**; Figure 1) and the iridium complexes (*R*(*S*))-[IrCl(^{Ph}dbcot)(MeCN)] ((*R*(*S*))-**7a**; Figure 2) and (*R*(*S*))-[Ir(^{naph}dbcot)(MeCN)$_2$]$^+$SbF$_6^-$ ((*R*(*S*))-**8b**; Figure 3) were investigated by X-ray diffraction. The results are displayed as ORTEP plots for one of the enantiomers in Figures 1−3, respectively. A crystal of the chiral complex (*R*)-[(*R*)-(+)]-[Rh(^{Ph}dbcot)(1,1′-binaphthyl-2,2′-diamine)]$^+$OTf$^-$ ((*R*)-[(*R*)-(+)]-**11a**) was also subjected to an X-ray structure analysis; the result is displayed in Figure 4. Furthermore, we investigated (*R*(*S*))-**6c**. However, the asymmetric unit contains several solvent molecules (that is, *n*-hexane and CH_2Cl_2) on special positions of 2-fold symmetry. Due to strong disorder, the quality of the data set is insufficient to allow for a detailed discussion (a graphical presentation of the complex is given in the Supporting Information).

Selected structural parameters for each compound are given in the corresponding figure caption, and details concerning the data collections and refinements are given in Table 3 in the Experimental Section. In the uncomplexed ^{Ph}dbcot ((*R*(*S*))-**4a**) the central olefinic C5−C6 (1.332(4) Å) and C12−C11 (1.323(5) Å) double bonds have the usual lengths. For the description of the boat conformation in ^{Ph}dbcot, we use the average of the four torsion angles defined by the central olefinic bonds and the adjacent C=C$_{benzo}$ bonds (for instance, C5−C6−C15−C16) which amounts to 62.9° in (*R*(*S*))-**4a**. This value is similar to that for the parent dbcot (59.7°).[11] All structures of the metal complexes

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(23) The inversion barrier of cyclooctatetraene (C_8H_8, cod) is lower than 14 kcal mol^{-1}, and the resolution of the enantiomers of monosubstituted cod derivatives could not be achieved: (a) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576. (b) Cope, A. C.; Meili, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 1883. Also, the inversion barrier of other chiral dibenzo[*a*,*e*]cyclooctenes (dbcot's) with substituents attached to one of the benzo groups is too low to allow isolation in nonracemic form: (c) Senkler, G. H.; Gust, D.; Riccobono, P. X.; Mislow, K. *J. Am. Chem. Soc.* **1972**, *94*, 8626. However, chiral dbcot's showing multiple substitution at the olefinic C=C bonds have inversion barriers >25 kcal mol^{-1}, which is sufficient to allow their isolation in enantiomerically pure form: (d) Mislow, K.; Perlmutter, H. D. *J. Am. Chem. Soc.* **1962**, *84*, 3591. (e) Salisbury, L. E. *J. Org. Chem.* **1978**, *43*, 26.

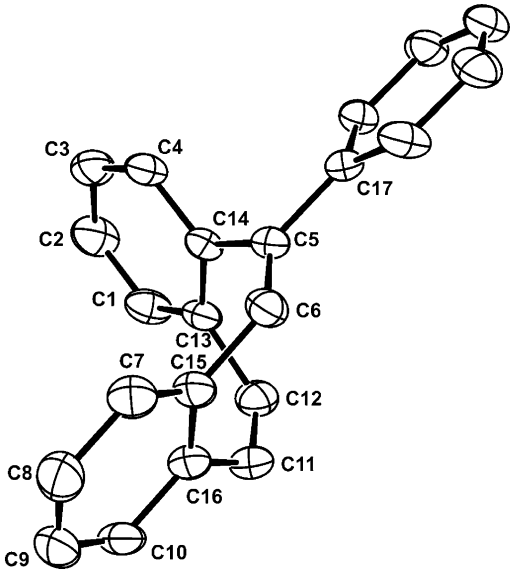


Figure 1. Molecular structure of ^{Ph}dbcot (**4a**). Only the *R*-configured isomer is shown. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C5−C6 = 1.332(4), C11−C12 = 1.323(5), C5−C17 = 1.499(4), C5−C14 = 1.484(4), C12−C13 = 1.485(5), C11−C16 = 1.473(5), C6−C15 = 1.481(4), C13−C14 = 1.403(4), C15−C16 = 1.404(5); C15−C6−C5 = 127.4(3), C6−C5−C14 = 122.4(3), C13−C12−C11 = 124.6(3), C12−C11−C16 = 126.6(3). Torsion angles (deg): C5−C6−C15−C16 = 62.2(5), C15−C16−C11−C12 = −60.6(5), C11−C12−C13−C14 = 62.2(5), C13−C14−C5−C6 = −65.4(4); average 62.9°.

show only minor distortions from a planar coordination sphere (the intersection angles φ of the ct1−M−ct2 plane with the L^1−M−L^2 plane (L^1, L^2 = donor atoms of the other two ligands) are smaller than 12°). The olefinic bonds of the ^{R}dbcot ligands are elongated in the complexes to about 1.41−1.43 Å, which is normal for diene complexes of this type. The bond lengthening in the iridium complexes is slightly more pronounced, which is in accord with the higher degree of metal-to-ligand bonding and back-bonding and with the stability of these complexes. The curvature of the boat form of the central eight-membered ring is in all complexes more pronounced (by about 10°) than in the uncomplexed ^{Ph}dbcot molecule ((*R*(*S*))-**7a**, 70.6°; (*R*(*S*))-**8b**, 70.8°; (*R*)-[(*R*)-(+)]-**11a**, 71.2°). However, the differences are rather small and we believe that the preorganization in the uncomplexed ^{R}dbcot molecules is the decisive factor for the very high stability of these complexes (an extreme example is complex **9b**, which decomposes only above 300 °C).

Noteworthy is the orientation of the naphthyl groups in the complex [Ir(^{naph}dbcot)(MeCN)$_2$]$^+$SbF$_6^-$ ((*R*(*S*))-**8b**). While in [Rh($^{2-MeO-naph}$dbcot)(MeCN)(H$_2$O)]OTf ((*R*(*S*))-**6c**, not shown here; see the Supporting Information) the naphthyl substituent is oriented away from the rhodium center which shows a weak interaction (~3 Å) with the oxygen center of the methoxy group, the naphthyl group in (*R*(*S*))-**8b** points toward the iridium center. This brings the hydrogen atom H24 at the 8-position into contact with the metal center at 2.83 Å. Similar weak interactions at 2.3−2.9 Å have been detected in Pt compounds, for instance, and are noticeable by significant high-frequency shifts in the ^{1}H NMR spectra, as we also see in (*R*(*S*))-**8b** (vide supra).[24,25]

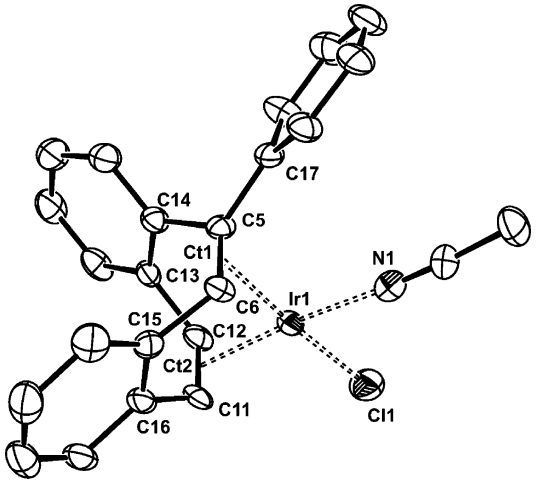


Figure 2. Molecular structure of [IrCl(^{Ph}dbcot)(MeCN)] **7a**. Only the *R*-configured isomer is shown. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−C5 = 2.148(4), Ir1−C6 = 2.107(4), Ir1−ct1 = 2.004(4), Ir1−C11 = 2.110(4), Ir1−C12 = 2.134-(5), Ir1−ct2 = 1.997(5), Ir1−N1 = 2.059(5), Ir1−Cl1 = 2.344(1), C5−C6 = 1.431(6), C11−C12 = 1.432(6); N1−Ir1−Cl1 = 88.7(1), N1−Ir1−Ct1 = 91.4(2), Cl1−Ir1−Ct2 = 92.1-(2), Ct1−Ir1−Ct2 = 88.4(2). ct = centroids of the coordinated C=C units); φ = 8.8° is the intersection angle of the ct1−Ir1−ct2 plane and the Cl1−Ir1−N1 plane. Torsion angles (deg): C5−C6−C15−C16 = 75.8(5), C15−C16−C11−C12 = −69.2(5), C11−C12−C13−C14 = 66.1(6), C13−C14−C5−C6 = −71.7(5); average 70.6°.

Catalyses. Crabtree et al. observed that the addition of dibenzo[*a*,*e*]cyclooctene (dbcot) to solutions containing ruthenium, rhodium, or iridium phosphane complexes impedes or even blocks their catalytic activity in hydrogenation reactions.[16,17] Presumably, the formation of highly inert [M(dbcot)(PR$_3$)$_2$] complexes is responsible for this finding. We tested the complexes [M(^{Ph}dbcot)-(MeCN)$_2$]$^+$X$^-$ ((*R*(*S*))-**6a** (M = Rh), (*R*(*S*))-**8a** (M = Ir)) and [M(^{naph}dbcot)(MeCN)$_2$]$^+$X$^-$ ((*R*(*S*))-**6b** (M = Rh), (*R*(*S*))-**8b** (M = Ir)) as catalyst precursors. Because the complex (*R*)-**6a** is enantiomerically pure, reactions aimed at achieving enantioselective transformations were of special interest. All complexes are phosphane-free and contain a firmly bound ^{R}dbcot ligand and two labile acetonitrile ligands. Homogeneously catalyzed (i) hydrogenations with H$_2$, (ii) transfer hydrogenations with 2-propanol, (iii) additions of arylboronic acids to α,β-unsaturated ketones, (iv) hydroborations, and (v) hydrosilylations were investigated (Scheme 4). Dimethylitaconate (**12**) is a frequently used substrate in enantioselective hydrogenations.[26] However, attempts to hydrogenate **12** under 4 bar of H$_2$ using 1 mol % of [Rh(^{Ph}dbcot)(MeCN)$_2$]$^+$OTf$^-$ ((*R*)-**6a**) as catalyst precursor yielded only 3−4% of **13** after 20 h (stereochemistry not determined). With the analogous iridium complex

(24) Albinati, A.; Arz, C.; Pregosin, P. S. *Inorg. Chem.* **1987**, *26*, 508.
(25) Albinati, A.; Pregosin, P. S.; Wombacher, F. *Inorg. Chem.* **1989**, *29*, 1812.
(26) Selected examples: (a) Tappe, K.; Knochel, P. *Tetrahedron: Asymmetry* **2004**, *15*, 91 and literature cited therein. (b) Reetz, M. T.; Mehler, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 3889, and literature cited therein. (c) Burk, M. J.; Gross, M. F. *Tetrahedron Lett.* **1994**, *35*, 9363.

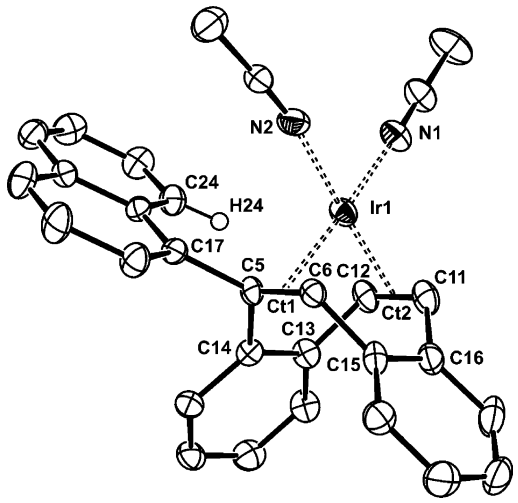


Figure 3. Structure of the cation $[Ir(^{Naph}dbcot)(MeCN)_2]^+$ in **8b**. Only the *R*-configured isomer is shown. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms, the SbF_6^- anion, and a MeCN solvent molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir1−C5 = 2.131(6), Ir1−C6 = 2.102(7), Ir1−ct1 = 1.990(7), Ir1−C11 = 2.126(8), Ir1−C12 = 2.103(8), Ir1−ct2 = 1.993(8), Ir1−N1 = 2.030(6), Ir1−N2 = 2.041(6), C5−C6 = 1.443(9), C11−C12 = 1.41(1); N1−Ir1−N2 = 90.3(3), N2−Ir1−Ct1 = 90.2(3), Ct1−Ir1−Ct2 = 88.6(3), Ct2−Ir1−N1(3) = 91.3. ct = centroids of the coordinated C=C units; φ = 6.7° is the intersection angle of the ct1−Ir1−ct2 plane with the N1−Ir1−N2 plane. Torsion angles (deg): C5−C6−C15−C16 = 71.1(9), C15−C16−C11−C12 = −69(1), C11−C12−C13−C14 = 74(1), C13−C14−C5−C6 = −68.8(9); average 70.8°.

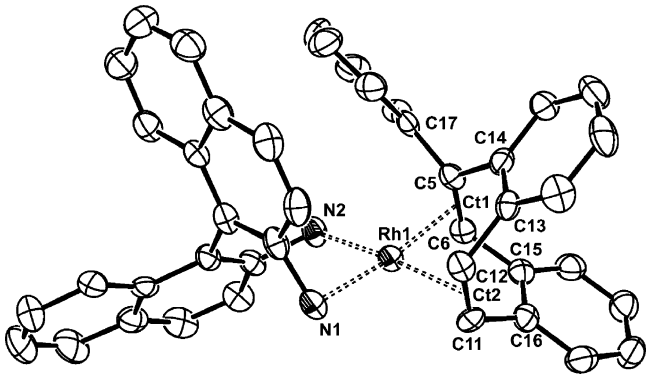


Figure 4. Structure of the cation $[Rh((R)-^{Ph}dbcot)((R)-(+)-1,1'-binaphthyl-2,2'-diamine)]^+$ in (*R*)-[(*R*)-(+)]-**11a**. Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms and the $CF_3SO_3^-$ anion are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1−C5 = 2.148(4), Rh1−C5 = 2.123(5), Rh1−ct1 = 2.016(5), Rh1−C11 = 2.121(4), Rh1−C12 = 2.121(5), Rh1−ct2 = 2.001(5), Rh1−N1 = 2.138(4), Rh1−N2 = 2.193(4), C5−C6 = 1.407(7), C11−C12 = 1.403(7); N1−Rh1−N2 = 87.7(1), N2−Rh1−Ct1 = 92.7(2), Ct1−Rh1−Ct2 = 88.0(2), Ct2−Rh1−N1 = 92.6(2) ct = centroids of the coordinated C=C units; φ = 11.5° is the intersection angle of the ct1−Rh1−ct2 plane with the N1−Rh1−N2 plane. Torsion angles (deg): C5−C6−C15−C16 = 74.9(6), C15−C16−C11−C12 = −69.3(6), C11−C12−C13−C14 = 72.2(6), C13−C14−C5−C6 = −68.4(6): average 71.2°.

(*R*(*S*))-**8a** complete conversion was achieved under the same conditions. Note that we have no indications that the ^{Ph}dbcot ligand ((*R*(*S*))-**4a**) is hydrogenated either as a ligand in the iridium catalyst or when (*R*(*S*))-**4a** is added as substrate instead of **12**.

η^4-1,5-Cyclooctadiene complexes such as [Rh(cod)(RHN∩*NHR)]$^+$ and [Ir(cod)(RHN∩*SOR)]$^+$ with chiral chelating diamine[2] or β-amino sulfoxide ligands[3] (∩* denotes a chiral ligand backbone) are rather effective catalyst precursors for the transfer hydrogenation of acetophenone **14** with 2-propanol to 1-phenylethanol (**15**) and ee's >90% can be achieved for one of the enantiomers. We explored the combination of a chiral diene with an achiral diamine in the ligand sphere of the catalyst precursor. The complex (*R*(*S*))-$[Rh(^{Ph}dbcot)(MeCN)_2]^+OTf^-$ ((*R*(*S*))-**6a**) was reacted with various simple ethylenediamines $RHNCH_2CH_2NHR$ (R = H, Me, Et) to give the complexes (*R*(*S*))-$[Rh(^{Ph}dbcot)(diamine)]^+OTf^-$. The iridium complex (*R*(*S*))-$[Ir(^{Ph}dbcot)(H_2NCH_2CH_2NH_2)]^+OTf^-$ was prepared in an analogous way. Furthermore, the enantiomerically pure complex (*R*)-$[Rh(^{Ph}dbcot)(EtHNCH_2CH_2NHEt)]^+OTf^-$ was synthesized. All these diamine complexes give yellow powders after evaporation of the solvent and were used without further purification or characterization as crude reaction products. In addition, the complex $[Rh(^{Ph}dbcot)(1,1'-binap-2,2'-NH_2)]^+OTf^-$ ((*R*)-[(*R*)-(+)]-**11a**) was investigated as catalyst precursor. The results are compiled in Table 2.

Unfortunately, the rhodium complexes, the only ones we had at hand enantiomerically pure, showed low activity again. The best result was obtained with *N*,*N*-diethylethylenediamine (entry 3), and this diamine was therefore tested in an enantioselective hydrogenation with (*R*)-$[Rh(^{Ph}dbcot)(EtHNCH_2CH_2NHEt)]^+OTf^-$. The enantiomeric excess (ee) was reproducible within 10% but was disappointingly low. Even worse is the performance of (*R*)-[(*R*)-(+)]-**11a**, which shows both low activity and selectivity (entry 4). That sterically more demanding diamines perform better in transfer hydrogenations has been observed before.[27] Remarkably, the iridium complex (*R*(*S*))-$[Ir(^{Ph}dbcot)(H_2NCH_2CH_2NH_2)]^+OTf^-$ serves as a rather efficient catalyst precursor (entry 5), with an activity 4 orders of magnitude higher than that of the analogous rhodium complex (entry 1). Future work will therefore concentrate on the isolation of enantiomerically pure iridium complexes.

The catalytic addition of aryl- and alkenylboronic acids to α,β-unsaturated ketones has been developed by Miyaura and Hayashi,[28] giving examples for the application of chiral dienes as steering ligands in catalysis.[6c] We used (*R*)-$[Rh(^{Ph}dbcot)(MeCN)_2]^+OTf^-$ ((*R*)-**6a**) as a catalyst precursor for the 1,2-addition of $PhB(OH)_2$ to cyclohexen-2-one (**16**) under the reported conditions[6c] and obtained (3*R*)-phenylcyclohexanone ((*R*)-**17**) in 92% yield and 62% ee (the configuration of the major isomer was determined by comparison with the reported optical rotation for (*R*)-**17**[29]). While the activity of (*R*)-**6a** is comparable to that of the Hayashi catalyst, the ee is lower (99% is given in ref 6c). As previously proposed for the preferred formation of (*R*)-**17**, we likewise assume that the α-*re* face of cyclohexen-2-one (**16**) is

(27) Gamez, P.; Fache, F.; Lemaire, M. *Tetrahedron: Asymmetry* **1995**, *6*, 705.

(28) Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579.

(29) Schultz, A. G.; Harrington, R. E. *J. Am. Chem. Soc.* **1991**, *113*, 4926.

Scheme 4. Catalytic Transformation with [M(Rdbcot)] Complexes

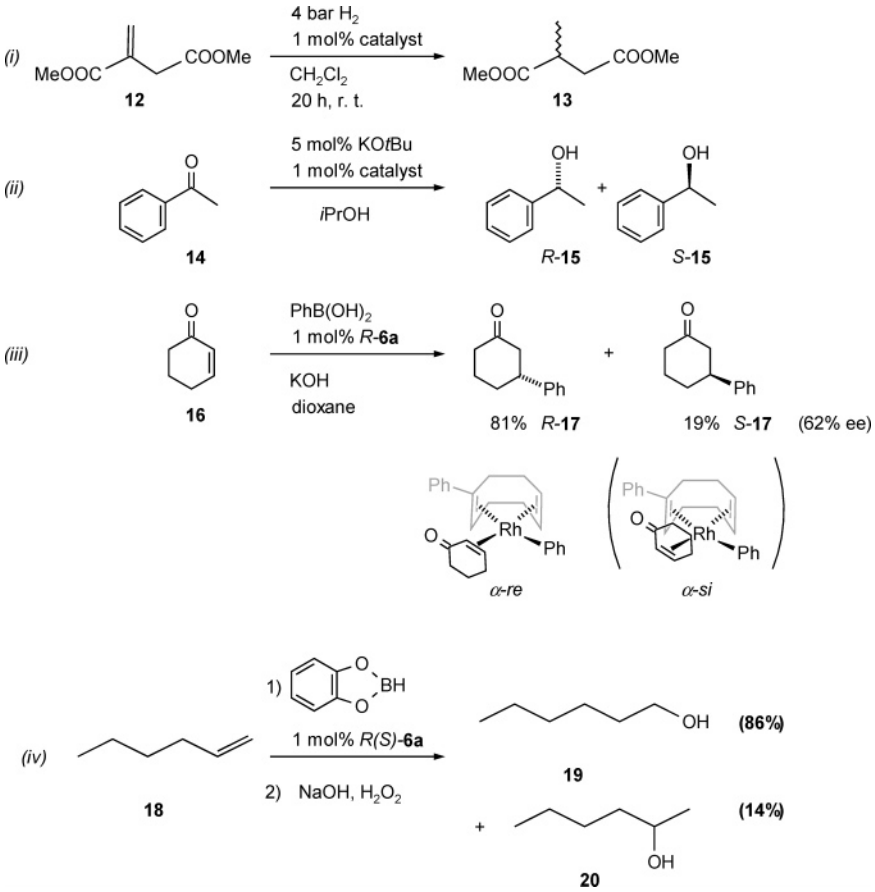


Table 2. Results in Transfer Hydrogenations of Acetophenone with Isopropyl Alcohol with 1 mol % [M(Phdbcot)(diamine)]$^+$OTf$^-$ as Catalyst Precursor and 5 Mol % KOH as Base (T = 80 °C)

	M/diamine	t (h)	conversn (%)	TOF (h^{-1})	ee (%)
1	$Rh/H_2NCH_2CH_2NH_2$	20	4	0.2	
2	$Rh/MeHNCH_2CH_2NHMe$	22	42	1.9	
3	$Rh/EtHNCH_2CH_2NHEt$	4	71	17.7	10
4	Rh/(*R*)-(+)-1,1′-binap-2,2′-NH_2	24	80	3.3	4
5	$Ir/H_2NCH_2CH_2NH_2$	0.3	92	307	

coordinated to the metal center, leading to a sterically less encumbered transition state for the insertion of **16** into Rh−Ph bond (see Scheme 4). The relatively low steric demand of the phenyl substituent may then explain the rather low ee.

Finally, we tested in preliminary experiments the rhodium complex (*R*(*S*))-[Rh(Phdbcot)$(MeCN)_2]^+$OTf$^-$ ((*R*(*S*))-**6a**) as a catalyst precursor (1 mol %) for hydroborations and hydrosilylations. When styrene is used as substrate and catecholborane (catBH) as borane, no hydroboration is observed but polymerization of styrene occurred instead. With 1-hexene (**18**) as the more reactive substrate, complete conversion is achieved and 1-hexanol (**19**) and 2-hexanol (**20**) are obtained after the usual workup[30] with H_2O_2 in a 6:1 ratio. Since the internal alcohol is the minor product in this reaction, we employed the enantiomerically pure catalyst precursor (*R*)-**6a**.

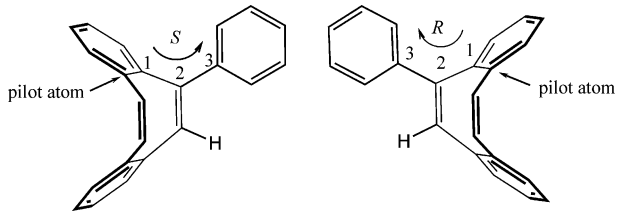
The enantioselectively catalyzed hydrosilylation of norborene with $HSiCl_3$ has been reported by Togni et al.[31] Under the same conditions using 1 mol % of (*R*)-**6a** as catalyst precursor, we find less than 5% conversion, however.

Conclusions

A simple synthesis of unsymmetrically chiral dibenzo[*a*,*e*]cyclooctenes, Rdbcot, has been developed. Remarkably, this protocol includes fewer reaction steps (only three) and gives higher yields than the best synthesis of the parent dibenzo[*a*,*e*]cyclooctene reported so far.[19] With these dienes, tetracoordinated 16-electron rhodium(I) and, especially, iridium(I) complexes could be prepared. Importantly, the NMR and X-ray data show that these complexes are very stable, despite the high degree of substitution of the coordinated C=C double bonds. Unfortunately, only one complex, (*R*)-[Rh(Phdbcot)$(MeCN)_2]^+$OTf$^-$ ((*R*)-**6a**), could be obtained in enantiomerically pure form. The first investigations of [M(Rdbcot)$(MeCN)_2]^+$ and [M(Rdbcot)-(RHNnNHR)]$^+$complexes show, especially for M = Ir, promising properties as catalyst precursors in hydrogenations with H_2 and in transfer hydrogenations. The enantiomerically pure rhodium complex (*R*)-**6a** catalyses the enantioselective 1,2-addition of $PhB(OH)_2$ to α,β-unsaturated ketones with good activity and acceptable enantiomeric excess. Thereby, the use of dienes as steering ligands for a wide range of reactions, including even catalyzed hydrogenations of unsaturated functionalities, is firmly established.[8] Clearly, these first experi-

(30) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671.
(31) Pioda, G.; Togni, A. *Tetrahedron: Asymmetry* **1998**, *9*, 3903.

Chart 2. Description of the Stereochemical Assignment in ^{R}dbcot Molecules



ments show that chiral dibenzo[*a*,*e*]cyclooctenes and related cyclooctatetraenes have a high potential for the development of robust phosphane-free catalyst precursors.

Experimental Section

General Remarks. All syntheses were performed in flame-dried glassware under an atmosphere of argon using standard Schlenk techniques. Solvents were freshly distilled from sodium/benzophenone (THF), from sodium/tetraglyme/benzophenone (hexane, toluene), or calcium hydride (dichloromethane) prior to use. Air-sensitive compounds were stored and weighed in an argon-filled glovebox (Braun MB 150 B-G system), and reactions on a small scale were performed directly in the glovebox. (*Z*)-6*H*-Dibenzo[*a*,*e*]cycloocten-5-one (**2**) was prepared from dibenzosuberenone (**1**) by a literature method.[19] $CeCl_3 \cdot 7H_2O$ was dried by the procedure of Dimitrov et al.[32]

NMR spectra were taken at room temperature on an AMX-500, Avance DRX-400, Avance DPX-300, or Avance DPX-250 system. The chemical shifts are given as dimensionless δ values and were referenced against tetramethylsilane (tms) for ^{1}H and ^{13}C, 85% H_3PO_4 for ^{31}P, and $CFCl_3$ for ^{19}F NMR spectra. Coupling constants J are given in hertz (Hz) as positive values, regardless of their absolute signs. The multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets, respectively. Quaternary carbons are indicated as C_{quat} and aromatic carbons as C_{ar}, when not noted otherwise. Broadened signals are indicated as "br". The assignments of C11 and C12 in free ligands **4a**−**c** as well as in complexes **6a**,**b**, **7a**, **8b**, and **11a** are established by CH-COSY and CH-long-range experiments. Mass spectra were taken on a Finnigan MAT SSQ 7000 in the EI (70 eV) mode.

Assignment of the Stereochemistry. The stereochemistry of the ^{R}dbcot ligands was assigned according to the rules for molecules showing "planar chirality" given by Chan, Ingold, and Prelog in ref 33. In our case, the element of planar chirality is defined by the carbon atoms of the unsymmetrically substituted C=C bond and the atoms directly attached to it. The "pilot atom" is then the atom of highest priority next to these atoms sticking out of the plane. In our case, this is the quaternary carbon atom of one benzo group, as indicated in Chart 2. Looking from this atom onto the plane and ranking the atoms in the element of planar chirality according to their priority leads to an *S* conformation for the molecule on the left and a *R* conformation for the molecule on the right side in Chart 2.

5-Phenyl-5,6-dihydrodibenzo[*a*,*e*]cycloocten-5-ol (3a). A suspension of dry $CeCl_3$ (1.57 g, 6.36 mmol) in 20 mL of THF was treated dropwise with a solution of PhMgBr (5.6 mL of a 1.13 M solution in Et_2O, 6.36 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h, and then a solution of (*Z*)-6*H*-dibenzo-[*a*,*e*]cycloocten-5-one **(2;** 1.00 g, 4.54 mmol) was added. After 3 h of stirring at room temperature, the mixture was quenched with 30 mL of 0.1 M HCl and extracted three times with 30 mL of *tert*-butyl methyl ether (tbme). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to yield a sticky, slightly yellow solid. Recrystallization from hexane afforded the pure product as a colorless solid (1.20 g, 88%). Mp: 97−98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.85 (s, 1H, O*H*), 3.09 (d, J_{HH} = 13.6, 1H, CH_2), 4.08 (d, J_{HH} = 13.6, 1H, CH_2), 6.86 (d, J_{HH} = 12.2, 1H, CH_{alkene}), 7.04−7.36 (m, 10H, CH_{ar}, CH_{alkene}), 7.40−7.53 (m, 3H, CH_{ar}), 7.60−7.66 (m, 1H, CH_{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 48.70 (*C*H$_2$), 80.04 (*C*(OH)), 124.96 (2C, *C*H$_{phenyl}$), 126.45 (*C*H), 126.65 (*C*H), 126.83 (*C*H), 127.33 (*C*H), 127.38 (*C*H), 128.05 (2C, *C*H$_{phenyl}$), 128.06 (*C*H), 130.03 (*C*H), 130.53 (*C*H), 130.84 (*C*H), 131.11 (*C*H), 133.57 (*C*H), 133.97 (C_{quat}), 136.46 (C_{quat}), 138.10 (C_{quat}), 143.82 (C_{quat}), 149.42 (C_{quat}). MS (70 eV, *m*/*z*, %): 298.1 (100) [M$^+$], 280.1 (24) [M$^+$ − H_2O], 207.1 (37), 178.0 (44), 165.0(39), 77.1 (61).

5-Phenyldibenzo[*a*,*e*]cycloocten (4a). A mixture of the alcohol **3a** (0.88 g, 2.95 mmol) and CF_3COOH (0.07 mL) in 40 mL of CH_2Cl_2 was stirred at room temperature for 22 h. The reaction solution was washed with 20 mL of water and then two times with 20 mL of saturated Na_2CO_3 solution. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to give a colorless, foamy solid. Recrystallization from hexane yielded the pure product as a colorless, crystalline solid (0.77 g, 93%). Mp: 91−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.90 (d, J_{HH} = 11.8, 1H, C(11)H_{alkene}), 6.97 (d, J_{HH} = 11.8, 1H, C(12)H_{alkene}), 6.99 (dm, J_{HH} = 7.9, C(4)H_{benzo}), 7.12−7.27 (m, 8H, CH_{benzo}, C(6)H_{alkene}), 7.28−7.38 (m, 5H, CH_{phenyl}). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 126.97 (*C*H$_{benzo}$), 127.17 (*C*H$_{benzo}$), 127.20 (*C*H$_{benzo}$), 127.34 (*C*H$_{benzo}$), 127.76 (s, 1C, *C*H$_{phenyl}$), 128.13 (2C, *C*H$_{phenyl}$), 128.53 (*C*H$_{benzo}$), 128.63 (2C, *C*H$_{phenyl}$), 128.86 (*C*H$_{benzo}$), 128.98 (*C*H$_{benzo}$), 129.51 (*C*(6)H$_{alkene}$), 133.21 (*C*(12)H$_{alkene}$), 134.19 (*C*(11)H$_{alkene}$), 137.84 (*s*, 1C, $C_{quat\ benzo}$), 138.55 ($C_{quat\ benzo}$), 138.56 ($C_{quat\ benzo}$), 140.00 ($C_{quat\ benzo}$), 143.42 ($C_{quat\ phenyl}$), 145.12 (*C*(5)$_{quat\ alkene}$). MS (70 eV, *m*/*z*, %): 280.0 (100) [M$^+$], 202.0 (76) [M$^+$ − Ph], 177.9 (59). Anal. Calcd for $C_{22}H_{16}$: C, 94.24; H, 5.75. Found: C, 93.99; H, 5.69.

5-Naphthalen-1-yl-5,6-dihydrodibenzo[*a*,*e*]cycloocten-5-ol (3b). The preparation was performed as described for **3a** by reacting $CeCl_3$ (0.61 g, 2.5 mmol) with NaphMgBr (5 mL of a 0.5 M solution, 2.5 mmol) and **2** (0.40 g, 1.81 mmol) in 17 mL of THF for 17 h at room temperature. The crude product was contaminated with naphthalene, which was removed by sublimation (40 °C, 0.05 mbar). After recrystallization from hexane the pure product was obtained as a colorless powder (0.52 g, 82%). Mp: 165−169 °C dec. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.88 (s, 1H, O*H*), 3.42 (d, J_{HH} = 13.7, 1H, CH_2), 4.37 (d, J_{HH} = 13.7, 1H, CH_2), 6.90−7.64 (m, 13H, C$_{ar}$, CH_{alkene}), 7.73−7.92 (m, 3H, CH_{ar}), 8.57 (m, br, 1H, CH_{ar}). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 45.60 (*C*H$_2$), 80.75 (*C*(OH)), 123.90 (*C*H), 124.90 (*C*H), 125.15 (*C*H), 125.20 (*C*H), 126.37 (*C*H), 126.89 (*C*H), 127.26 (*C*H), 127.32 (*C*H), 128.33 (*C*H), 129.07 (*C*H), 130.21 (C_{quat}), 131.12 (*C*H), 131.21 (*C*H), 132.01 (*C*H), 132.34 (*C*H), 132.75 (*C*H), 133.92 (C_{quat}), 134.64 (C_{quat}), 136.51 (C_{quat}), 137.92 (C_{quat}), 144.13 (C_{quat}), 144.88 (C_{quat}). MS (70 eV, *m*/*z*, %): 348.2 (100) [M$^+$], 330.2 (44) [M$^+$ − H_2O], 207.1 (56), 128.1 (69) [naphH$^+$].

5-Naphthalen-1-yldibenzo[*a*,*e*]cyclooctene (4b). The preparation was as described for **4a** by reacting alcohol **3b** (0.52 g, 1.49 mmol) with CF_3COOH (0.05 mL) in 10 mL of CH_2Cl_2 for 20 h at room temperature. The pure product is obtained after recrystallization from *n*-hexane as colorless crystals (0.45 g, 91%). Mp: 138−139 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.94−7.01 (m, 2H, CH_{benzo}), 7.04 (s, 1H, C(6)H_{alkene}), 7.05 (d, J_{HH} = 11.3, 1H, C(11)H_{alkene}), 7.11−7.32 (m, 7H, CH_{benzo}, C(12)H_{alkene}), 7.47−7.61 (m, 4H, C$H_{naphthyl}$), 7.83−7.90 (m, 2H, C$H_{naphthyl}$), 8.25−8.30 (m, 1H, C(24)$H_{naphthyl}$). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 127.75 (*C*H$_{naphthyl}$), 126.06 (*C*H$_{benzo}$), 126.46 (*C*H$_{naphthyl}$), 126.61 (*C*H$_{naphthyl}$), 127.19 (*C*H$_{benzo}$), 127.21 (*C*H$_{benzo}$), 127.28 (*C*H$_{benzo}$), 127.36 (*C*H$_{benzo}$), 127.88 (*C*H$_{naphthyl}$),

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128.33 ($CH_{naphthyl}$), 128.68 ($CH_{naphthyl}$), 129.07 (CH_{benzo}), 129.14 (CH_{benzo}), 129.39 (CH_{benzo}), 129.62 (CH_{benzo}), 131.99 ($C_{quat\ naphthyl}$), 133.50 ($C(12)H_{alkene}$), 133.85 ($C(6)H_{alkene}$), 134.32 (*s*, 1C, $C_{quat\ naphthyl}$), 134.87 ($C(11)H_{alkene}$), 137.42 ($C_{quat\ benzo}$), 137.60 ($C_{quat\ benzo}$), 138.07 ($C_{quat\ benzo}$), 140.96 ($C_{quat\ benzo}$), 142.97 ($C(5)_{alkene}$). MS (70 eV, *m/z*, %): 330.0 (M^+, 100%), 202.0 (M^+ − naph), 177.9. Anal. Calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 94.43; H, 5.20.

5-(2-Methoxynaphthalen-1-yl)-5,6-dihydrodibenzo[*a,e*]-cycloocten-5-ol (3c). The preparation was as described for **3a** from $CeCl_3$ (1.20 g, 4.9 mmol), (2-methoxynaphthyl)MgBr (15 mL of a 0.32 M solution in THF, 4.9 mmol), and **2** (0.75 g, 3.4 mmol) in 15 mL of THF. The mixture was stirred at room temperature for 24 h and then heated under reflux for 6 h. The crude product was purified by flash chromatography (FC) on silica gel with *n*-hexane/AcOEt (4:1) as eluent to give the product (1.41 g, ca. 55%) together with about 40 mol % (determination by NMR) of the starting ketone. The two products could not be separated, and the mixture was directly applied in the following transformation.

5-(2-Methoxynaphthalen-1-yl)dibenzo[*a,e*]cyclooctene (4c). To a solution of the mixture **3c/2** (0.30 g, containing ca. 0.4 mmol of alcohol **3c**) in 10 mL of CH_2Cl_2 was added CF_3COOH (0.02 mL). The reaction mixture was stirred at room temperature for 20 h. After workup in a way analogous to that described for **4a**, the crude product (a slightly pink oil) containing the unreacted ketone was purified by FC (silica gel, hexane/AcOEt (10:1)) to yield the pure product as a colorless solid (0.13 g, 90%). Due to hindered rotation around the C5−C17 bond, the compound **4c** consists of solution of two rotational isomers (ratio 1:2.5) which exchange at room temperature. The NMR signals are therefore doubled and broadened. Signals of the minor isomer are given and assigned only where possible. Mp: 165−166 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 3.69 (*s*, 3H, OCH_3(maj)), 4.16 (*s*, 3H, OCH_3(min)), 6.82−7.01 (m, 3H, CH_{alkene}(min,maj)), 7.03−7.51 (m, 11H, CH_{ar}), 7.41 (m, 1H, $CH_{naphthyl}$(min)), 7.47 (m, 1H, $CH_{naphthyl}$(maj,min)), 7.67 [*m*, 1H, $CH_{naphthyl}$(maj)), 7.77 (m, br, 1H, $C_{naphthyl}$(min)), 7.85 (m, br, 1H, $CH_{naphthyl}$(maj)], 7.88 (m, br, 1H, $CH_{naphthyl}$(min)), 8.20 (m, br, 1H, $CH_{naphthyl}$(min)), 8.56 (m, br, 1H, $CH_{naphthyl}$(maj)). ^{13}C NMR (100.6 MHz, C_6D_6): δ 57.29 (OCH_3(maj)), 57.42 (OCH_3(min)), 114.86 ($CH_{naphthyl}$), 124.07 ($CH_{naphthyl}$), 125.47 ($CH_{naphthyl}$), 126.74 (CH_{benzo}), 127.13 (CH_{benzo}), 127.17 (CH_{benzo}), 127.34 (CH_{benzo}), 128.42 ($CH_{naphthyl}$), 128.55 (CH_{benzo}), 128.56 (CH_{benzo}), 128.93 ($C_{quat\ naphthyl}$), 129.03(CH_{benzo}), 129.17 (CH_{benzo}), 129.48 ($CH_{naphthyl}$), 129.95 ($C_{quat\ naphthyl}$), 133.09 ($C(12)H_{alkene}$), 133.95 ($C_{quat\ naphthyl}$), 134.27 ($C(11)H_{alkene}$), 134.31 ($C(6)H_{alkene}$), 137.83 (C_{quat}), 138.22 (C_{quat}), 139.76 ($C5_{quat\ alkene}$), 141.09 (C_{quat}), 153.24 ($COCH_3$(min)), 154.24 ($COCH_3$(maj)). MS (70 eV, *m/z*, %): 360.0 (100) [M^+], 328.9 (33), 202.0 (81), 178.0 (94).

[Rh(^{Ph}dbcot)(MeCN)$_2$]$^+$OTf$^-$ (6a). A mixture of [Rh$_2$(μ_2-Cl)$_2$(CO)$_4$] (0.20 mg, 0.56 mmol) and ligand **4a** (0.288 g, 1.02 mmol) in 10 mL of CH_2Cl_2 and 5 mL of MeCN was stirred at room temperature for 16 h. To the orange solution was added AgOTf (0.26 g, 1.02 mmol), and the suspension was stirred for 1 h at room temperature. The precipitated silver chloride was removed by filtration through a pad of Celite, and the filtrate was concentrated under high vacuum to give an orange, foamy solid. Precipitation from CH_2Cl_2 and hexane afforded the product as an orange powder (0.45 g, 73%). Mp: >175 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.12 (s, 6H, CH_3), 5.37 (d, J_{HH} = 8.3, 1H, C(12)H_{alkene}), 5.56 (dd, J_{HH} = 8.3, J_{RhH} = 1.6, 1H, C(11)H_{alkene}), 5.69 (s, br, 1H, C(6)H_{alkene}), 6.60 (dm, J_{HH} = 7.7 Hz, 1H, C(4)H_{benzo}), 6.88−6.94 (m, 1H, CH_{benzo}), 6.99−7.10 (m, 6H, CH_{benzo}), 7.39 (m, br, 3H, CH_{phenyl}), 7.8 (s, br, 2H, CH_{phenyl}). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 3.03 (2C, CH_3), 74.43 (d, J_{RhC} = 13.5, 1C, $C(6)H_{alkene}$), 81.17 (d, J_{RhC} = 12.3, $C(12)H_{alkene}$), 84.50 (d, J_{RhC} = 14.1, $C(11)H_{alkene}$), 97.72 (d, J_{RhC} = 12.9, $C(5)_{quat\ alkene}$), 121.82 (2C, C_{quat}, CN), 126.32 (2C, CH_{benzo}), 126.38 (CH_{benzo}), 127.26 (CH_{benzo}), 127.35 (CH_{benzo}), 127.38 (CH_{benzo}), 127.74 (CH_{benzo}), 128.54 (CH_{benzo}), 129.0 (br, 2C, $CH_{phenyl(meta)}$), 129.47 (2C, $CH_{phenyl(ortho)}$), 142.90 ($C_{quat\ benzo}$), 142.93 ($C_{quat\ benzo}$), 142.99 ($C_{quat\ benzo}$), 143.78 ($C_{quat\ phenyl}$), 145.13 ($C_{quat\ benzo}$). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −77.9 (s). ^{103}Rh NMR (12.7 MHz, $CDCl_3$): δ 1530 (m). MS (70 eV, *m/z*, %): 532.0 (13) [Rh(**4a**) (OTf)]$^+$, 382.1 (12) [Rh(**4a**)]$^+$, 280.1 (100) (**4a**)$^+$. Anal. Calcd for $C_{27}H_{22}F_3N_2O_3RhS$: C, 52.78; H, 3.61; N, 4.56. Found: C, 53.04; H, 3.82; N, 4.24.

[Rh(^{Naph}dbcot)(MeCN)$_2$]$^+$SbF$_6^-$ (6b). A solution of [Rh$_2$(μ_2-Cl)$_2$(CO)$_4$] (28 mg, 72 μmol) and ligand **4b** (47 mg, 244 μmol) in 2 mL of CH_2Cl_2 and 2 mL of MeCN was stirred at room temperature for 16 h. $AgSbF_6$ (49 mg, 142 μmol) was then added, and the reaction mixture was stirred for 1 h. The precipitate was removed by filtration through Celite, and the filtrate was concentrated under vacuum to give a dark yellow solid. Recrystallization from CH_2Cl_2/hexane yields the product as yellow-brown, thin needles (62 mg, 57%). Mp: >235 °C dec. ^{1}H NMR (300 MHZ, CD_3CN): δ 2.07 (*s*, 6H, CH_3), 5.65 (d, J_{HH} = 8.4, 1H, C(12)H_{alkene}), 5.73 (dd, J_{HH} = 8.4, J_{RhH} = 1.7, 1H, C(11)H_{alkene}), 5.90 (s, br, 1H, C(6)H_{alkene}), 6.48 (d, J = 7.7, 1H, CH_{benzo}), 6.69 (d, J = 7.7, 1H, CH_{benzo}), 7.02 (dt, J = 7.6, J = 1.1, 1H, CH_{benzo}), 7.06−7.17 (m, 4H, CH_{benzo}), 7.23 (m, 1H, CH_{benzo}), 7.45−7.57 (m, 2H, CH_{naph}), 7.60−7.68 (m, 2H, CH_{naph}), 7.93 (d, J = 8.3, 1H, CH_{naph}), 7.96 (d, J = 8.4, 1H, CH_{naph}), 10.07 (d, J = 8.4, 1H, CH_{naph}). ^{13}C NMR (75.5 MHz, CD_3CN): δ 0.93 (2C, CH_3), 80.5 (br, $C(6)H_{alkene}$), 81.1 (br, $C(12)H_{alkene}$), 85.5 (br, $C(11)H_{alkene}$), 124.98 (CH_{naph}), 126.24 (CH_{naph}), 126.5 (2C, CH_{naph}), 126.53 (CH_{benzo}), 126.82 (CH_{benzo}), 127.08 (CH_{benzo}), 127.23 (CH_{benzo}), 127.26 (CH_{benzo}), 127.29 (CH_{benzo}), 127.33 (CH_{benzo}), 127.44 (CH_{benzo}), 127.84 (CH_{naph}), 128.90 (CH_{naph}), 130.38 (CH_{naph}), 132.66 ($C_{quat\ naph}$), 134.39 ($C_{quat\ naph}$) 140.09 ($C(17)_{quat\ naph}$), 141.3 ($C(13)_{quat\ benzo}$), 142.23 ($C(15)_{quat\ benzo}$), 142.44 ($C(16)_{quat\ benzo}$), 146.0 ($C(14)_{quat\ benzo}$). ^{19}F NMR (188.3 MHz, CD_3CN): δ −125 (sext, br, J_{SbF} = 1950). MS (ESI, *m/z*, %): 465.2 (15), 451.2 (14), 433.2 (100) [Rh(**4b**)]$^+$. Anal. Calcd for $C_{30}H_{24}N_2F_6RhSb$: C, 47.97; H, 3.22; N, 3.73; Found: C, 48.03; H, 3.33; N, 3.49.

[IrCl(^{Ph}dbcot)(MeCN)] (7a). To a solution of [Ir$_2$(μ_2-Cl)$_2$(cod)$_2$] (0.170 g, 0.25 mmol) in 2 mL of CH_2Cl_2 and 2 mL of MeCN was added a solution of ligand **4a** (0.142 g, 0.51 mmol) in 2 mL of CH_2Cl_2. The solution was stirred for 18 h at room temperature and was then concentrated to a volume of 2 mL. When the orange-brown solution was layered with hexane, the product precipitated as orange crystals suitable for X-ray analysis (0.21 g, 76%). Mp: 215−220 °C. ^{1}H NMR (500 MHz, CD_3CN): δ 1.96 (*s*, 3H, CH_3), 5.43 (d, J_{HH} = 8.0, 1H, C(12)-H_{alkene}), 5.54 (s, 1H, C(6)H_{alkene}), 5.58 (d, J_{HH} = 8.0, 1H, C(11)-H_{alkene}), 6.53 (dm, J_{HH} = 7.70, 1H, CH_{benzo}), 6.77 (tm, J_{HH} = 7.70, 1H, CH_{benzo}), 6.85−6.95 (m, 3H, CH_{benzo}), 7.00−7.07 (m, 2H, CH_{benzo}), 7.11−7.17 (m, 1H, CH_{benzo}), 7.25−7.34 (m, br, 3H, CH_{phenyl}), 7.55 (s, br, 1H, CH_{phenyl}), 7.72 (s, br, 1H, CH_{phenyl}). ^{13}C NMR (125.7 MHz, CD_3CN): δ 2.19 (CH_3), 57.33 (br, $C(6)H_{alkene}$), 69.85 (br, $C(12)H_{alkene}$), 72.39 (br, $C(11)H_{alkene}$), 74.55 (br, $C(5)_{quat\ alkene}$), 117.00 (C_{quat}, CN), 125.91 (CH_{benzo}), 125.92 (CH_{benzo}), 125.99 (CH_{benzo}), 126.2 (br, $CH_{phenyl(ortho)}$), 126.21 (CH_{benzo}), 126.28 (CH_{benzo}), 126.43 (CH_{benzo}), 126.45 (CH_{benzo}), 127.37 ($CH_{phenyl(para)}$), 127.88 (br, $CH_{phenyl(meta)}$), 127.93 (CH_{benzo}), 129.18 (br, $CH_{phenyl(para)}$), 133.93 (br, $CH_{phenyl(ortho)}$), 145.53 ($C_{quat\ benzo}$), 145.82 ($C_{quat\ benzo}$), 146.62 ($C_{quat\ benzo}$), 147.21 ($C_{quat\ phenyl}$), 149.22 ($C_{quat\ benzo}$). Anal. Calcd for $C_{24}H_{19}ClNIr$: C, 52.50; H, 3.49; N, 2.55. Found: C, 52.63; H, 3.58; N, 2.61.

[Ir$_2$(μ_2-Cl)$_2$(^{Naph}dbcot)$_2$] (9b). A mixture of [Ir$_2$(μ_2-Cl)$_2$(coe)$_4$] (90 mg, 0.10 mmol) and ligand **4b** (49 mg, 0.15 mmol) in 3 mL of benzene was kept at 80 °C for 24 h. The yellow, crystalline precipitate **9b** was filtered, washed with 2 mL of benzene und dried under high vacuum. It is only sparingly soluble in common deuterated solvents. The crystals contain 0.5 equiv of benzene, which could not be removed upon prolonged drying under high vacuum (80 mg, 90% with respect to **4b**). Mp: > 310 °C dec. ^{1}H NMR (300 MHz, CD_3CN): δ 5.62 (d, br, J = 7.2, 1H, CH_{alkene}), 5.68 (d, br, J = 7.2, 1H, CH_{alkene}), 5.76 (s, br, 1H, C(6)H_{alkene}), 6.30 (d, J = 7.8, 1H, CH_{benzo}), 6.51 (dt, J1

= 7.8, *J*2 = 1.0, 1H, C*H*$_{benzo}$), 6.77 (dt, *J*1 = 7.8, *J*2 = 1.2, 1H, C*H*$_{benzo}$), 6.82−6.89 (m, 2H, C*H*$_{benzo}$), 7.00−7.06 (m, 2H, C*H*$_{benzo}$), 7.20 (m, 1H, C*H*$_{benzo}$), 7.30−7.40 (m, 3H, C*H*$_{naph}$), 7.73−7.88 (m, 3H, C*H*$_{naph}$), 9.42 (m, 1H, C*H*$_{naph}$). MS (70 eV, *m/z*, %): 1116.0 (16) [M$^+$], 518.1 (29), 330.1 (25) [M$^+$ (**4b**)] (100%), 191.0 (22), 149.0 (44). Anal. Calcd for $C_{52}H_{36}Cl_2Ir_2 \times 0.5\ C_6H_6$: C, 57.18; H, 3.40. Found: C, 57.13; H, 3.28.

[Ir(Naphdbcot)(MeCN)$_2$]$^+$SbF$_6^-$ (8b). A suspension of compound **9b** (35 mg, 31 μmol) in 2 mL of MeCN and 1 mL of CH_2Cl_2 was treated with $AgSbF_6$ (22 mg, 64 μmol) and stirred at room temperature for 2 h. Filtration of the reaction mixture through Celite and removal of the solvent left an orange solid. Precipitation from CH_2Cl_2/hexane yielded the pure product as an orange, microcrystalline solid (45 mg, 89%). Mp: > 185 °C dec. ^{1}H NMR (300 MHz, CD_3CN): δ 1.99 (s, 6H, C*H*$_3$), 5.60 (d, *J* = 7.8, 1H, C(12)*H*$_{alkene}$), 5.68 (d, *J* = 7.8, 1H, C(11)*H*$_{alkene}$), 5.93 (s, 1H, C(6)*H*$_{alkene}$), 6.41 (d, *J* = 7.5, 1H, C*H*(4)$_{benzo}$), 6.63 (td, *J* = 7.5, *J* = 0.9, 1H, C*H*(3)$_{benzo}$), 6.87 (td, *J* = 7.5, *J* = 1.1, 1H, C*H*(2)$_{benzo}$), 6.91−7.00 (m, 2H, C*H*$_{benzo}$), 7.08 (m, 2H, C*H*$_{benzo}$), 7.17 (m, 1H, C*H*$_{benzo}$), 7.35−7.52 (m, 3H, C*H*$_{naph}$), 7.65 (d, *J* = 7.2, 1H, C*H*$_{naph}$), 7.82 (d, *J* = 8.2, 1H, C*H*$_{naph}$), 7.87 (d, *J* = 8.2, 1H, C*H*$_{naph}$), 9.34 (d, *J* = 8.3, 1H, C(24) *H*$_{naph}$). ^{13}C NMR (75.5 MHz, CD_3CN): δ 1.56 (2C, *C*H$_3$), 68.56 (*C*(6)H$_{alkene}$), 68.61 (*C*(12)H$_{alkene}$), 72.37 (*C*(11)H$_{alkene}$), 85.34 (*C*(5)$_{quat\ alkene}$), 116.85 (2C, *C*N), 124.78 (*C*H$_{naphthyl}$), 125.50 (*C*H$_{benzo}$), 125.7−126.2 (6C, 2 × *C*H$_{naphthyl}$, 4 × *C*H$_{benzo}$), 126.31 (*C*H(4)$_{benzo}$), 126.32 (*C*H$_{naphthyl}$), 126.57 (*C*H(3)$_{benzo}$), 126.74 (*C*H$_{benzo}$), 128.27 (*C*H$_{naphthyl}$), 128.43 (*C*H$_{naphthyl}$), 129.70 (*C*H$_{naphthyl}$), 132.73 (*C*(25)$_{quat\ naphthyl}$), 134.48 (*C*(26)$_{quat\ naphthyl}$), 140.50 (*C*(17)$_{quat\ naphthyl}$), 142.49 (*C*(13)$_{quat\ benzo}$), 143.53 (*C*(15)$_{quat\ benzo}$), 143.69 (*C*(16)$_{quat\ benzo}$), 147.44 (*C*(14)$_{quat\ benzo}$). MS (ESI, *m/z*, %): 647.4 (69), 619.4 (94), 548.0 (100) [Ir(**4b**)]$^+$, 521.0 (30), 437.2 (44). Anal. Calcd for $C_{30}H_{24}F_6N_2IrSb$: C, 42.87; H, 2.88; N, 3.33. Found: C, 42.62; H, 3.04; N, 3.35.

(*R*)-[Rh(Phdbcot)(*R*-(+)-1,1′-binaphthyl-2,2′-diamine)]$^+$OTf$^-$ ((*R*)-[(*R*)-(+)]-11a). A racemic mixture of the complex (*R,S*)-**6a** (0.185 mg, 0.30 mmol) and (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine (**10**; 0.086 g, 0.30 mmol) in 5 mL of CH_2Cl_2 was stirred at room temperature for 3 h. The solvent was removed under high vacuum to give the product as a mixture of diastereomers in the form of an orange powder. The product was dissolved in 2.5 mL of EtOH and layered with 5 mL of hexane. After 1 week at 4 °C, the product (*R*)-[(*R*)-(+)]-**11a** was obtained as orange crystals which were suitable for X-ray analysis (0.080 mg, 32%). The compound is only slightly soluble in common nonpolar solvents. In polar solvents (that is, d_3-acetonitrile or d_6-acetone) exchange with the diamine ligand is observed. Additionally, the ^{13}C NMR signals are strongly broadened. It was therefore not possible to detect and assign all ^{13}C signals. Mp: > 250 °C dec. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 2.1 (m, br, 2H, N*H*), 3.7 (m, br, 2H, N*H*), 5.43 (d, J_{HH} = 8.3, C*H*$_{alkene}$), 5.52 (*s*, 1H, C(6)*H*$_{alkene}$), 5.81 (d, J_{HH} = 8.3, 1H, C*H*$_{alkene}$), 6.38 (t, br, J_{HH} = 7.0, 1H, C*H*$_{benzo}$), 6.57 (d, br, J_{HH} = 7.7, 1H, C*H*$_{benzo}$), 6.75−7.71 (m, 18 H, C*H*$_{ar}$), 7.87−8.37 (m, br, 5H, C*H*$_{ar}$). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ 75.8 (C(6)H$_{alkene}$), 79.0 (CH$_{alkene}$), 81.0 (CH$_{alkene}$), 99.1 (C$_{quat\ alkene}$), 119.7 (*C*H$_{ar}$), 120.6 (*C*H$_{ar}$), 124.8 (*C*H$_{ar}$), 125.3 (*C*H$_{ar}$), 125.4 (*C*H$_{ar}$), 126.5 (2C, *C*H$_{ar}$), 126.6 (*C*H$_{ar}$), 126.9 (*C*H$_{ar}$), 127.0−127.1 (m, br, 3C, *C*H$_{ar}$), 127.7 (*C*H$_{ar}$), 127.8 (*C*H$_{ar}$), 128.1 (*C*H$_{ar}$), 128.8 (*C*H$_{ar}$), 128.9 (*C*H$_{ar}$), 129.0 (*C*H$_{ar}$), 129.2 (*C*H$_{ar}$), 129.3 (*C*H$_{ar}$), 131.8 (br, 2C, *C*H$_{ar}$), 132.3 (*C*H$_{ar}$), 132.7 (C$_{quat}$), 142.4 (C$_{quat}$), 142.6 (C$_{quat}$), 143.5 (C$_{quat}$), 143.7 (C$_{quat}$), 145.1 (C$_{quat}$). ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ −78.7 (s). ^{103}Rh NMR (15.7 MHz, CD_2Cl_2): δ 1517. Anal. Calcd for $C_{42}H_{32}F_3N_2O_3SRh$: C, 62.69; H, 4.01; N, 3.48. Found: C, 62.97; H, 4.28; N, 3.55.

(*R*)-[Rh(Phdbcot)(MeCN)$_2$]$^+$OTf$^-$ ((*R*)-6a). To a solution of (*R*)-[(*R*)-(+)]-**11a** (20 mg, 24 μmol) in 1.5 mL of MeCN was added CF_3SO_3H (0.05 mL of a 1 M solution in MeCN, 50 μmol). The mixture was stirred at room temperature for 3 h, and then the solvent was removed under high vacuum. The oily residue was dried under high vacuum for 12 h and then dissolved in 3 mL of CH_2Cl_2 and the solution filtered through Celite. Precipitation of the crude material from CH_2Cl_2/hexane gave the enantiomerically pure complex (*R*)-**6a** (19 mg, 95%). The analytical data are identical with those for the racemic mixture of **6a**. Optical rotation $[\alpha]^{20}_D = -93.0°$ (*c* = 0.55, $CHCl_3$).

Displacement of Phdbcot from (*R*)-6a. A mixture of (*R*)-**6a** (47 mg, 58 μmol) and PPh_3 (67 mg, 230 μmol) in 2 mL of CH_2Cl_2 and 1 mL of MeCN was stirred at room temperature for 1 h. The solvent was removed under high vacuum. To the solid residue was added 5 mL of hexane, and the mixture was treated with ultrasonic radiation for 15 min and then filtered through Celite. The clear solution was concentrated under high vacuum and dissolved in 2 mL of toluene, and 3 drops of H_2O_2 (30%) were added in order to oxidize the remaining PPh_3. Subsequently, the mixture was stirred for 1.5 h and then filtered through $MgSO_4$ and silica gel. After removal of the solvent, the pure ligand **4a** was obtained (14 mg, 86%). Immediate treatment of this ligand with $[Rh_2(\mu_2\text{-}Cl)_2(CO)_4]$, AgOTf, and (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine (**10**) gave a 1:1 mixture of the two diastereomeric complexes (*R*)-[(*R*)-(+)]-**11a** and (*S*)-[(*R*)-(+)]-**11a**.

Catalyses: Hydrogenations. A Schlenk tube containing a solution of dimethylitaconate (**12**; 1.8 mmol) and catalyst (0.018 mmol) in 3 mL of CH_2Cl_2 was frozen in liquid nitrogen, evacuated, and purged with 1 bar of hydrogen. The closed vessel was brought to room temperature and stirred for 20 h. The reaction mixture was analyzed by GC.

Transfer Hydrogenation of Acetophenone. (a) Preparation of the Catalysts. For [Rh((*R*)-Phdbcot)(EtHNCH$_2$CH$_2$-NHEt)]$^+$OTf$^-$, a mixture of enantiomerically pure (*R*)-**6a** and 1 equiv of *N*,*N*′-diethylethane-1,2-diamine was stirred in CH_2Cl_2 for 3 h. The solvent was evaporated, and the product was precipitated from CH_2Cl_2/hexane as a yellow powder. In the same manner the racemic complexes [Rh((*R,S*)-Phdbcot)-(NH$_2$CH$_2$CH$_2$NH$_2$)]$^+$OTf$^-$ and [Rh((*R,S*)-Phdbcot)(MeHNCH$_2$-CH$_2$NHMe)]$^+$OTf$^-$ were prepared from (*R,S*)-**6a** and the corresponding diamine. For, [Ir((*R,S*)-Phdbcot)(NH$_2$CH$_2$CH$_2$-NH$_2$)]$^+$OTf$^-$, a mixture of **7a** and ethylene-1,2-diamine in CH_2Cl_2 was reacted with AgOTf and stirred for 1 h at room temperature. The solvent was removed under high vacuum, which left the product as a yellow solid.

(b) Typical Procedure Employed in Catalyses. In a closed Schlenk tube, a mixture of acetophenone **14** (96 mg, 800 μmol), KO^{t}Bu (5 mg, 40 μmol), and catalyst (8 μmol) in 2.5 mL of ^{i}PrOH was heated to 80 °C. The progress of the reaction was monitored by GC analysis, taking aliquots of the reaction solution. The enantiomeric excess (ee) was determined by GC on a chiral capillary (Machery-Nagel Lipodex-E).

Asymmetric 1,4-Addition. The procedure was adapted from ref 34. A mixture of 2-cyclohexenone (**16**; 158 mg, 1.62 mmol), phenylboronic acid (397 mg, 3.25 mmol), KOH (0.54 mL, 1.5 M in H_2O, 0.88 mmol), and catalyst (*R*)-**6a** was stirred for 2 h at room temperature (20 °C). The reaction was quenched with saturated $NaHCO_3$, and the mixture was extracted with 3 × 10 mL of tbme. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified with flash chromatography (silica gel, hexane/AcOEt (2:1)) to give the product 3-phenylcyclohexanone (**17**) as a slightly yellow oil (250 mg, 92%). The enantiomeric excess was determined with chiral HPLC (Chiracel OD-H, *n*-hexane/^{i}PrOH (98:2)), being 62%. The absolute configuration of the stereogenic center of the major enantiomer is *R* (by comparison with the reported optical rotation of (3*R*)-3-phenyl-cyclohexanone:[29] $[\alpha]^{20}_D = +11.8°$ (*c* = 0.55, $CHCl_3$).

Crystal Data and Structure Determination of ((*R*(*S*))-4a, (*R*(*S*))-8b, (*R*(*S*))-7a, and **(*R*)-[(*R*)-(+)]-11a.** Data collection for the X-ray structure determinations were performed on a Bruker SMART Apex ((*R*(*S*))-**4a**, (*R*(*S*))-**8b,** (*R*)-[(*R*)-(+)]-

(34) Hayashi, T.; Ueyama, K.; Tokunaga, N.; Yoshida, K. *J. Am. Chem. Soc*. **2003**, *125*, 11508.

Table 3. Details Concerning the Data Collection and Refinement of the Structures of (*R*(*S*))-4a, (*R*(*S*))-7a, (*R*(*S*))-8b, and (*R*)-[(*R*)-(+)]-11a

	(*R*(*S*))-**4a**	(*R*(*S*))-**7a**	(*R*(*S*))-**8b**·CH_3CN	(*R*)-[(*R*)-(+)]-**11a**
empirical formula	$C_{22}H_{16}$	$C_{24}H_{19}NClIr$	$C_{30}H_{24}Cl_6IrN_2Sb$·CH_3CN	$C_{43}H_{32}F_3N_2O_3SRh$
M_r	280.35	549.05	980.22	816.68
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	Cc (No. 9)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
a/Å	13.392(1)	17.941(1)	13.904(4)	10.758(1)
b/Å	7.869(1)	8.959(1)	9.393(2)	14.537(1)
c/Å	15.579(2)	12.430(1)	23.682(6)	22.981(1)
β/deg	113.685(2)	103.128(1)	96.004(5)	
V/Å^3	1503.5(3)	1945.7(2)	3075.9(1)	3594.0(3)
μ/mm^{-1}	0.070	7.008	5.752	0.593
D_{calcd}/g cm^{-3}	1.239	1.874	2.117	1.509
cryst dimens/mm	0.60 × 0.39 × 0.39	0.42 × 0.20 × 0.20	0.65 × 0.22 × 0.14	0.13 × 0.11 × 0.11
Z	4	4	4	4
T/K	250	room temp	200	250
$2\theta_{max}$/deg	46.50	52.70	56.56	49.42
no. of rflns measd	9730	5312	21 899	28 511
no. of unique rflns	2152 (R_{int} = 0.0462)	3360	7625 (R_{int} = 0.0423)	6131 (R_{int} = 0.0597)
no. of params/restraints	199/0	245/2	391/0	478/1
R1 ($I \geq 2\sigma(I)$)	0.0768	0.0169	0.0483	0.0424
wR2 (all data)	0.1771	0.0381	0.1420	0.0952
max/min resid electron dens/e Å^{-3}	0.240/−0.211	0.305/−0.929	3.381/−1.959	1.396/−0.712

11a) or Siemens CCD1k ((*R*(*S*))-**7a**) diffractometer system with CCD area detector by using graphite-monochromated Mo Kα (0.710 73 Å) radiation and a low-temperature device if available (Table 3).

Crystals suitable for X-ray diffraction of (*R*(*S*))-**4a** were obtained by crystallization of a concentrated *n*-hexane solution at room temperature; those of (*R*(*S*))-**7a** and (*R*(*S*))-**8b** were obtained from a methylene chloride/acetonitrile solution layered with *n*-hexane at 0 °C. Crystals of (*R*)-[(*R*)-(+)]-**11a** were grown at 0 °C from a ethanol solution layered with *n*-hexane. The asymmetric unit of (*R*(*S*))-**8b** contains one acetonitrile solvent molecule. To avoid quality degradation, most single crystals were mounted in perfluoropolyalkyl ether oil on top of a glass fiber and then brought into the cold nitrogen stream of a low-temperature device so that the oil solidified. All calculations were performed by using the programs SHELXTL (version 6.12) and SHELXL-97. The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). Moreover, an empirical absorption correction using SADABS (version 2.03) was applied to all structures, except for (*R*)-[(*R*)-(+)]-**11a**. All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures of (*R*(*S*))-**4a** and (*R*(*S*))-**7a** showed no significant peaks. For (*R*)-[(*R*)-(+)]-**11a**, some residual electron density was located close to the sulfur atom of the triflate counteranion (∼1.00 Å) or the heavy atom rhodium (∼1.00 Å); for (*R*(*S*))-**8b** residual electron density was found around the $[SbCl_6]^-$ counteranion (∼0.80 Å) or the heavy atom iridium (∼0.80 Å) even when an absorption correction was applied.

Relevant data concerning crystallographic data, data collection, and refinement details are summarized in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 267929 (**4a**), CCDC 267930 (**7a**), CCDC 267931 (**8b**), and CCDC 267932 ((*R*)-[(*R*)-(+)]-**11a**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Cell constants and a structure plot of the complex [Rh($^{2-MeO-naph}$dbcot)(MeCN)-(H_2O)]OTf ((*R*(*S*))-**6c**). This material is available free of charge via the Internet at http://pubs.acs.org.

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