Cyclometalation of Primary Benzyl Amines by Ruthenium(II), Rhodium(III), and Iridium(III) Complexes

Jean-Baptiste Sortais,[†] Nicolas Pannetier,[†] Alexandre Holuigue,[†] Laurent Barloy,*[,†] Claude Sirlin,[†] Michel Pfeffer,*[,†] and Nathalie Kyritsakas[‡]

Institut de Chimie de Strasbourg, CNRS-Université Louis Pasteur, Laboratoire de Synthèses Métallo-Induites and Service Commun des Rayons X, 4 rue Blaise Pascal, 67000 Strasbourg, France

Received October 23, 2006

The cyclometalation of chiral and achiral primary amines occurred readily with Ru(II), Rh(III), and Ir(III) derivatives. Thus, the metalation of (*R*)-1-phenylethylamine by $[(\eta^6\text{-benzene})RuCl_2]_2$, $[(\eta^5\text{-Cp*})RhCl_2]_2$, and $[(\eta^5\text{-Cp*})IrCl_2]_2$ was studied. Good yields of the expected cationic products in which the phenyl group was *ortho*-metalated were obtained for the rhodium and the ruthenium derivatives, whereas a mixture of products was formed in the case of the iridium complex. Benzylamine, (*R*)-1-phenylpropylamine, (*R*)-1-(1-naphthyl)ethylamine, and (*R*)-1-aminotetraline afforded also the cycloruthenation products whose general formula is $[(\eta^6\text{-benzene})Ru(N-C)(NCMe)]PF_6$ where N−C represents the *ortho*-metalated ligands. Substitution of the acetonitrile ligand by PMe_2Ph occurred readily on the ruthenium complexes, affording stable compounds that were characterized by X-ray diffraction studies on single crystals, thus ascertaining the existence of the cycloruthenated five-membered rings. Accurate analyses of the structure of the complexes were implemented in solution and in the solid state. The (*S*) configuration at the metal was usually associated with a δ conformation of the metallacycle, and conversely, the (*R*) configuration with the λ conformation. The study of the conformation of the five-membered rings revealed that the orientation of the NH_2 group is such that one NH unit is oriented toward the η^6-benzene ring (roughly parallel to the Ru−centroid benzene vector), whereas the second NH is parallel to the Ru−L bond, L = NCMe or PMe_2Ph.

Introduction

The cyclometalation of ligands by transition metals is one of the oldest, known since the early 1960s, and one of the best developed areas of organometallic chemistry.[1] It was soon recognized to be the easiest way of formation of a transition metal complex with a carbon−metal bond. Moreover as these compounds proved generally to be rather stable, they were easy to characterize. Thus, thousands of papers dealing with this reaction have been published during the last 40 years.[2] The most popular way to achieve the synthesis of the cyclometalated complexes was the route involving CH activation, and therefore this reaction was and still is considered as an important model for the CH activation of hydrocarbons by transitions metals. Several applications of this class of compounds such as the use of cyclometalated compounds as chiral auxiliaries or as mesogenic and photoluminescent compounds, as well as their potential use in biology, contributed significantly to the popularity of this research theme. Palladium is without any doubt the transition metal that has been the most studied, as to date cyclopalladated compounds are known for nearly all classes of ligands.[3] Renewal of interest in these compounds emerged 10 years ago, as some of these compounds were identified as powerful catalysts for C−C or C−Y (Y = heteroatom) bond formation reactions,[4−10] since unprecedented TON or TOF numbers were obtained. However, all attempts made to prove the role of a palladacyclic unit in these catalytic reactions were so far unsuccessful for most of the reactions studied, as it was shown that the first step of the process was a reduction of Pd(II) to Pd(0), this leading to nanoparticles that very likely provided the active species.[11−14] Notable exceptions to this behavior are the aza-Claisen rearrangements, for which Pd(II) catalysts are required.[15−20]

* Corresponding authors. E-mail: pfeffer@chimie.u-strasbg.fr; barloy@chimie.u-strasbg.fr.

[†] Laboratoire de Synthèses Métallo-Induites.

[‡] Service Commun des Rayons X.

(1) For a general review article about cyclometalation see: Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403−424.

(2) 2462 references were found in the database Scifinder using cyclometalation and orthometalation as keywords. Moreover, a large number of review articles have been published on this topic. (a) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327−352. (b) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (c) Omae, I. *Coord. Chem. Rev.* **1979**, *28*, 97−115. (d) Omae, I. *Chem. Rev.* **1979**, *79*, 287−321. (e) Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235−271. (f) Omae, I. *Coord. Chem. Rev.* **1982**, *42*, 245−257. (g) Constable, E. C. *Polyhedron* **1984**, *3*, 1037−1057. (h) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177−200. (i) Steenwinkel, P.; Gossage, R. A.; van Koten, G. *Chem.−Eur. J.* **1998**, *4*, 759−762. (j) Dunina, V. V.; Gorunova, O. N. *Russ. Chem. Rev.* **2004**, *73*, 309−350.

(3) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527−2571.

(4) Herrmann, W. A.; Bohm, V. P. W.; Reisinger, C. P. *J. Organomet. Chem.* **1999**, *576*, 23−41.

(5) Dupont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, 1917−1927.

(6) Bedford, R. B. *Chem. Commun.* **2003**, 1787−1796.

(7) van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759−1792.

(8) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837−1857.

(9) Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coord. Chem. Rev.* **2004**, *248*, 2283−2321.

(10) Beletskaya, I. P.; Cheprakov, A. V. *J. Organomet. Chem.* **2004**, *689*, 4055−4082.

(11) Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553−1582.

(12) Consorti, C. S.; Flores, F. R.; Dupont, J. *J. Am. Chem. Soc.* **2005**, *127*, 12054−12065.

(13) Cassol, C. C.; Umpierre, A. P.; Machado, G.; Wolke, S. I.; Dupont, J. *J. Am. Chem. Soc.* **2005**, *127*, 3298−3299.

(14) Reetz, M. T.; de Vries, J. G. *Chem. Commun.* **2004**, 1559−1563.

(15) Weiss, M. E.; Fischer, D. F.; Xin, Z.-q.; Jautze, S.; Schweizer, W. B.; Peters, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 5694−5698.

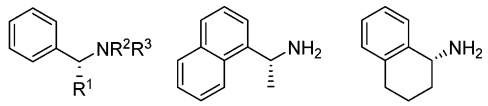
10.1021/om060973t CCC: $37.00
Publication on Web 03/15/2007

Ruthenium complexes as catalysts or catalyst precursors are being increasingly studied.[21] Despite the fact that many cyclometalated compounds involving ruthenium are known, there are only a few examples of such complexes that were shown to be active catalysts, especially in the hydride transfer reaction.[22−27] We have thus embarked on a project aimed at studying the synthesis of new cyclometalated compounds of ruthenium, rhodium, and iridium and their use as potential catalysts for organic reactions in which these metals are known to be efficient. The existing cycloruthenated compounds were either poorly active and selective or active but not selective for the asymmetric reduction of ketones. We had thus to reinvestigate the cyclometalation reactions in order to get better catalysts than those known. In this paper we wish to disclose the synthesis and the characterization of a series of cyclometalated Ru(II), Rh(III), and Ir(III) complexes with primary amines. We have already published preliminary data showing that some cycloruthenated compounds are good catalysts for the asymmetric hydrogen transfer reaction.[28,29]

Results and Discussion

Synthesis of Cyclometalated Complexes. Nitrogen-containing ligands have been cyclopalladated since 1968, but it was long thought that a prerequisite for the reaction to take place was that the nitrogen had to be trisubstituted by alkyl or aryl groups.[30,31] The rational explanation for this was that the steric bulk of the substituents would weaken the N−Pd bond to such an extent that the electrophilicity of Pd(II) would remain high enough to induce the substitution of a proton. An illustration of this was reported by Dunina et al.,[32] who showed that secondary amines could be readily cyclopalladated at an aryl substituent provided that the carbon atom bearing the NHR unit was tertiary (chiral). Later, Fuchita et al.[33−36] and Vicente et al.[37−41] showed that even nonencumbered primary amines could be cyclopalladated by palladium acetate.

Chart 1



1 R^1 = H, R^2 = R^3 = Me
2 R^1 = R^2 = R^3 = H
3 R^1 = Me, R^2 = R^3 = H
4 R^1 = Et, R^2 = R^3 = H

5 **6**

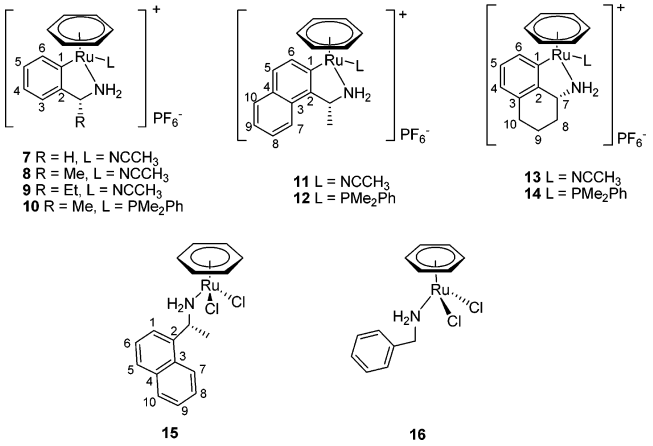
In marked contrast to palladium, ruthenium has been rarely used with success for metalation of ligands with an sp^3-hybridized nitrogen atom.[42−44] The vast majority of the N-containing ligands with sp^2-hybridized nitrogen atoms are heterocyclic compounds such as pyridine derivatives (quinoline or imine). We found that $[(\eta^6\text{-benzene})RuCl_2]_2$ was also a good starting material, as we described that the ready cycloruthenation could be observed with either tertiary amines, pyridine, or quinoline derivatives.[43,45]

We have now modified the established experimental conditions for cyclometalation of tertiary amines to achieve the cycloruthenation of primary benzyl amines, by lowering the amine/ruthenium ratio and the reaction temperature and by increasing the reaction time. These modifications avoided the formation of byproducts.[46] Thus, the treatment of 1 equiv of an amine **2**−**6** (Chart 1) with 1 equiv of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ at room temperature (20 °C) for 3 days led to the ruthenacyclic complexes **7**−**9**, **11**, and **13** (Chart 2) with yields ranging from 33% to 82% (Scheme 1). Under these conditions, we did not detect any byproduct where an extra chiral amine has substituted the acetonitrile ligand. Analysis of the crude reaction mixture by ^{1}H NMR indicated a ca. 100% conversion of the amine to the product. In spite of these almost quantitative conversions, the isolated yields were lower because of the purification step by chromatography over aluminum oxide. Evidence for the metalation of the aryl unit was given by the ^{1}H NMR spectra, which showed the disappearance of one aromatic proton, and also by the important high-frequency chemical shift of the CH *ortho* to the Ru−C bond.

It has often been speculated that the cyclometalation reaction should take place after coordination of the heteroatom of the ligand to the metal center (this was indeed demonstrated in the

(16) Anderson, C. E.; Overman, L. E. *J. Am. Chem. Soc.* **2003**, *125*, 12412−12413.
(17) Kirsch, S. F.; Overman, L. E.; Watson, M. P. *J. Org. Chem.* **2004**, *69*, 8101−8104.
(18) Prasad, R. S.; Anderson, C. E.; Richards, C. J.; Overman, L. E. *Organometallics* **2005**, *24*, 77−81.
(19) Anderson, C. E.; Donde, Y.; Douglas, C. J.; Overman, L. E. *J. Org. Chem.* **2005**, *70*, 648−657.
(20) Overman, L. E.; Owen, C. E.; Pavan, M. M.; Richards, C. J. *Org. Lett.* **2003**, *5*, 1809−1812.
(21) Murahashi, S.-I. *Ruthenium in Organic Synthesis*; Wiley-VCH: Weinheim, 2004; p 383.
(22) Dani, P.; Karlen, T.; Gossage, R. A.; Gladiali, S.; van Koten, C. *Angew. Chem., Int. Ed.* **2000**, *39*, 743−745.
(23) Albrecht, M.; Kocks, B. M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2001**, *624*, 271−286.
(24) Amoroso, D. J. A.; Yap, P. A.; Gusev, D. G.; dos Santos, E. N.; Fogg, D. E. *Organometallics* **2004**, *23*, 4047−4054.
(25) Baratta, W.; Da Ros, P.; Del Zotto, A.; Sechi, A.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3584−3588.
(26) Baratta, W.; Bosco, M.; Chelucci, G.; DelZotto, A.; Siega, K.; Toniutti, M.; Zangrando, E.; Rigo, P. *Organometallics* **2006**, *25*, 4611−4620.
(27) Baratta, W.; Chelucci, G.; Gladiali, S.; Siega, K.; Toniutti, M.; Zanette, M.; Zangrando, E.; Rigo, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 6214−6219.
(28) Sortais, J.-B.; Ritleng, V.; Voelklin, A.; Holuigue, A.; Smail, H.; Barloy, L.; Sirlin, C.; Verzijl, G. K. M.; Boogers, J. A. F.; de Vries, A. H. M.; de Vries, J. G.; Pfeffer, M. *Org. Lett.* **2005**, *7*, 1247−1250.
(29) Sortais, J. B.; Barloy, L.; Sirlin, C.; de Vries, A. H. M.; de Vries, J. G.; Pfeffer, M. *Pure Appl. Chem.* **2006**, *78*, 457−462.
(30) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272−3273.
(31) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909−913.
(32) Dunina, V. V.; Kuzmina, L. G.; Kazakova, M. Y.; Gorunova, O. N.; Grishin, Y. K.; Kazakova, E. I. *Eur. J. Inorg. Chem.* **1999**, *1999*, 1029−1039.
(33) Fuchita, Y.; Tsuchiya, H. *Polyhedron* **1993**, *12*, 2079−2080.
(34) Fuchita, Y.; Tsuchiya, H. *Inorg. Chim. Acta* **1993**, *209*, 229−230.
(35) Fuchita, Y.; Tsuchiya, H.; Miyafuji, A. *Inorg. Chim. Acta* **1995**, *233*, 91−96.
(36) Fuchita, Y.; Yoshinaga, K.; Ikeda, Y.; Kinoshita-Kawashima, J. *J. Chem. Soc., Dalton Trans.* **1997**, 2495−2499.
(37) Vicente, J.; Saura-Llamas, I.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1993**, 3619−3624.
(38) Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 2535−2547.
(39) Vicente, J.; Saura-Llamas, I.; Ramirez de Arellano, M. C. *J. Chem. Soc., Dalton Trans.* **1995**, 2529−2533.
(40) Vicente, J.; Saura-Llamas, I.; Palin, M. G.; Jones, P. G.; Ramirez de Arellano, M. C. *Organometallics* **1997**, *16*, 826−833.
(41) Vicente, J.; Saura-Llamas, I.; Cuadrado, J.; Ramirez de Arellano, M. C. *Organometallics* **2003**, *22*, 5513−5517.
(42) Abbenhuis, H. C. L.; Pfeffer, M.; Sutter, J. P.; de Cian, A.; Fischer, J.; Ji, H. J.; Nelson, J. H. *Organometallics* **1993**, *12*, 4464−4472.
(43) Fernandez, S.; Pfeffer, M.; Ritleng, V.; Sirlin, C. *Organometallics* **1999**, *18*, 2390−2394.
(44) Koike, T.; Ikariya, T. *Organometallics* **2005**, *24*, 724−730.
(45) Ryabov, A. D.; Sukharev, V. S.; Alexandrova, L.; Le Lagadec, R.; Pfeffer, M. *Inorg. Chem.* **2001**, *40*, 6529−6532.
(46) A substoichiometry of 1:2 in amine versus ruthenium was used in order to avoid the coordination of a second amine at the ruthenium center taking place after the cyclometalation has occurred. When this adduct was formed, we were not able to separate these two cycloruthenated complexes.

Chart 2



Scheme 1

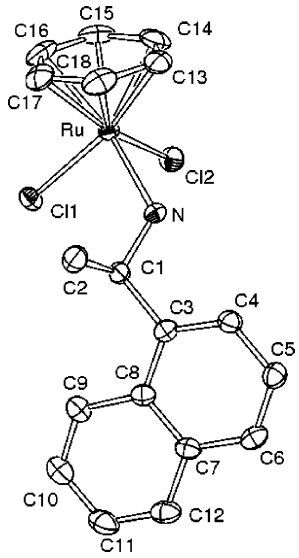


Figure 1. ORTEP style plot of compound **15**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ru−N 2.164(2), Ru−Cl1 2.4114(7), Ru−Cl2 2.4191(7), Ru−Centroid 1.651(3), N−Ru−Cl1 89.35(7), N−Ru−Cl2 82.74(7), Cl1−Ru−Cl2 86.80(3), N1−Ru−Centroid 128.57(15).

case of palladium[47−50]). In a preliminary study,[29] we have checked that (*R*)-1-(1-naphthyl)ethylamine reacts with $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ in the absence of KPF_6 and base to afford the N-monocoordinated complex **15** in CH_2Cl_2. An ORTEP representation of this compound and some key data are given in Figure 1. Its conversion into the cationic species **15′** at room temperature within 2 h by abstraction of one chloro ligand with a large excess of KPF_6 in CD_3CN was followed by NMR (Chart 2, Scheme 2). This species is related to the one that had been postulated as the genuine intermediate formed prior to CH activation by ruthenium.[43] Indeed, NMR signals characteristic of the cycloruthenated complex **11** arose upon addition of NaOH after 72 h stirring at RT.

Following a similar procedure, we have synthesized the N-coordinated complex **16** from benzylamine and analyzed it by X-ray crystallography (Chart 2, Figure 2). Comparison of the structures of **15** and **16** shows that the ruthenium−nitrogen bond is slightly shorter in **16** (2.16 vs 2.12 Å, respectively), probably on steric grounds. The absence of the methyl group on the benzylic carbon in **16** did apparently not induce any significant change in the orientation of the aryl group with respect to the ruthenium center. For instance, the hydrogen atom at C4 does not present any specific interaction with Cl2 in the X-ray structure of **15**.

The acetonitrile ligand in compounds **8**, **11**, and **13** could be substituted in good yields (76−80%) by a phosphine ligand (Scheme 3), as was found recently for the corresponding cycloruthenated compounds obtained with tertiary amines.[51]

The successful cycloruthenation of primary amines encouraged us to try analogous reactions with Rh(III) and Ir(III) derivatives. Recently, Davies et al.[52] showed that $[(\eta^5\text{-Cp*})IrCl_2]_2$ was a good starting material for the cyclometalation of $PhCH_2NMe_2$. We have checked that under the general conditions described for Ru(II) with tertiary benzylic amines,[43] viz., under stoichiometric conditions (metal:amine = 1:1) for 4 h at 45 °C, this ligand could indeed be cyclometalated by both $[(\eta^5\text{-Cp*})RhCl_2]_2$ and $[(\eta^5\text{-Cp*})IrCl_2]_2$ to afford **17** (68% yield) and **20** (58% yield), respectively (Chart 3, Scheme 4).

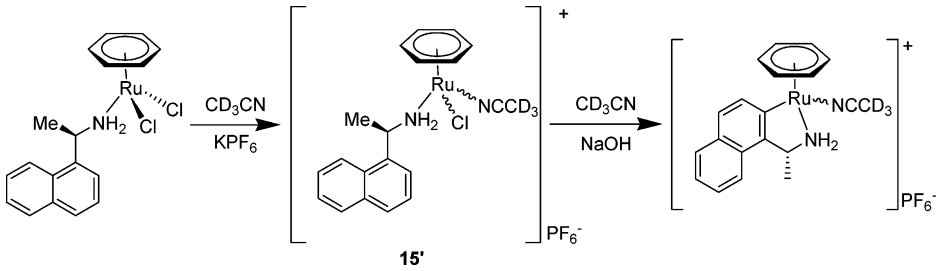
The reaction between $[(\eta^5\text{-Cp*})RhCl_2]_2$ and **3**, using the same reaction conditions as those used above for the cycloruthenation reaction with primary amines, afforded compound **18** (58% yield). As for the ruthenium analogues, the proton *ortho* to the Rh−C bond was significantly shifted to higher frequency. Exchanging the acetonitrile ligand for Cl^- in a biphasic medium ($KCl/H_2O/CH_2Cl_2$) afforded the neutral chloride derivate $[(\eta^5\text{-Cp*})Rh(C_6H_4CH(CH_3)NH_2)Cl]$, **19**.

The cyclometalation of **3** by $[(\eta^5\text{-Cp*})IrCl_2]_2$ did not afford a single reaction product, as the expected $[(\eta^5\text{-Cp*})Ir(C_6H_4CH(CH_3)NH_2)(NCCH_3)](PF_6)$, compound **21**, was mixed with $[(\eta^5\text{-Cp*})Ir(C_6H_4CH(CH_3)NH_2)(C_6H_5CH(CH_3)NH_2)](PF_6)$, in which a primary amine ligand has substituted the acetonitrile ligand despite the very low **3**:Ir ratio (0.5). This somewhat disappointing result indicated that the free amine **3** coordinated the cycloiridated species faster (and most probably irreversibly) than any non-cyclometallated iridium(III) precursor. Hence it would be difficult to obtain a cycloiridated compound that would not contain a κ^1-N-coordinated amine.

Tridimensional Structure of the Complexes. Like other ruthenium, rhodium, and iridium half-sandwich complexes, the geometry of the metal is pseudotetrahedral in our metallacyclic amines; its configuration is determined assuming the following decreasing priority sequence: 1 ($\eta^6\text{-}C_6H_6$ or $\eta^5\text{-}C_5(CH_3)_5$), 2 ($CH_3CN$ or $P(CH_3)_2Ph$), 3 (NR^1R^2), 4 (C_{aryl}).[53,54] We have endeavored to determine the tridimensional structures of com-

(47) Ryabov, A. D.; Sakodinskaya, I. K.; Yatsimirsky, A. K. *J. Chem. Soc., Dalton Trans.* **1985**, 2629−2638.
(48) Khare, G. P.; Little, R. G.; Veal, J. T.; Doedens, R. J. *Inorg. Chem.* **1975**, *14*, 2475−2479.
(49) Davies, D. L.; Donald, S. M. A.; Macgregor, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 13754−13755.
(50) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Poelleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210−4211.
(51) Ritleng, V.; Bertani, P.; Pfeffer, M.; Sirlin, C.; Hirschinger, J. *Inorg. Chem.* **2001**, *40*, 5117−5122.
(52) Davies, D. L.; Al-Duaij, O.; Fawcett, J.; Giardiello, M.; Hilton, S. T.; Russell, D. R. *Dalton Trans.* **2003**, 4132−4138.
(53) Lecomte, C.; Dusausoy, Y.; Protas, J.; Tirouflet, J.; Dormond, A. *J. Organomet. Chem.* **1974**, *73*, 67−76.
(54) Brunner, H. *Enantiomer* **1997**, *2*, 133−134.

Scheme 2



Scheme 3

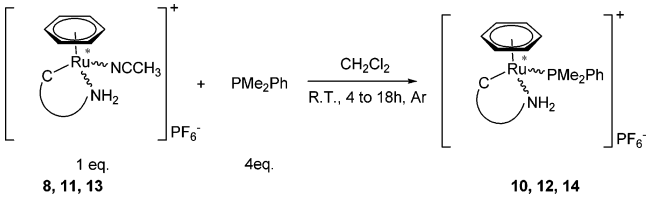
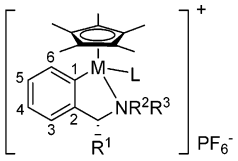
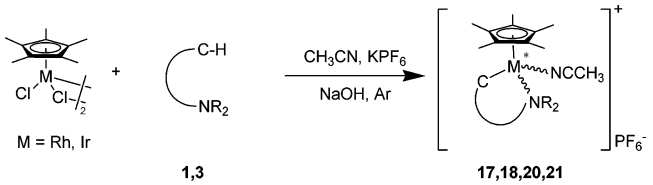


Chart 3



17 M= Rh, R^1 = H, R^2 = R^3 = Me, L = $NCCH_3$
18 M= Rh, R^1 = Me, R^2 = R^3 = H, L = $NCCH_3$
19 M= Rh, R^1 = Me, R^2 = R^3 = H, L = Cl
20 M= Ir, R^1 = H, R^2 = R^3 = Me, L = $NCCH_3$
21 M= Ir, R^1 = Me, R^2 = R^3 = H, L = $NCCH_3$

Scheme 4



plexes **8**−**14** and **17**−**19**, i.e., their configuration and the conformation of the five-membered metallacycles, either in solution or in the solid state.[55] Indeed, it is of paramount importance to know the accurate stereochemistry of the ruthenium complexes in order to be able to rationalize their hydrogen transfer catalytic activities and selectivities.[56]

Their solution NMR analysis showed a NOE effect between the high-frequency aromatic proton H6 and the η^6-benzene or η^5-pentamethylcyclopentadienyl protons, which is characteristic of the existence of the metal−carbon bond.

NMR analysis of the rhodium and iridium complexes **17** and **20** militated in favor of nonrigid enantiomers that interconvert quickly into each other at room temperature by inversion of the configuration of the metal center. Their ^{1}H and ^{13}C{^{1}H} NMR spectra recorded at RT showed two averaged singlets corresponding to the NMe_2 and the CH_2 signals. Lowering the temperature of a solution of complex **17** from 298 to 233 K froze this interconversion, according to its variable-temperature ^{1}H NMR spectra. At 233 K, the CH_2 signal gave rise to an AB pattern and the NMe_2 signal was split into two singlets, as is expected for diastereotopic CH_2 and NMe_2 groups. The energy barrier was estimated as 54.9 kJ·mol^{-1} from the coalescence of the methyl signals.[57]

The ^{1}H−^{1}H ROESY spectrum of complex **17** recorded at 233 K revealed that the (S_{Rh}) enantiomer adopts a somewhat flattened δ conformation and, conversely, that the (R_{Rh}) enantiomer is λ as its mirror image (Scheme 5). This is shown in particular by a strong NOE contact between one of the benzylic protons and the Cp* protons.

The primary amines **2**−**6** are chiral and consequently enantiopure, and complexes **8**−**14**, **18**, and **19** exist as mixtures of diastereoisomers having (R_C,S_M) and (R_C,R_M) configurations in solution. The distinct signals of each diastereoisomer are detectable in the RT NMR spectra of all complexes except **18**. Indeed, it is necessary to lower the temperature to 233 K to observe the narrow signal of the benzylic proton and the methyl signals of both isomers of **18**; at room temperature they have coalesced into broad signals.

Several elements of the NMR analysis provided accurate informations about the conformation of the five-membered

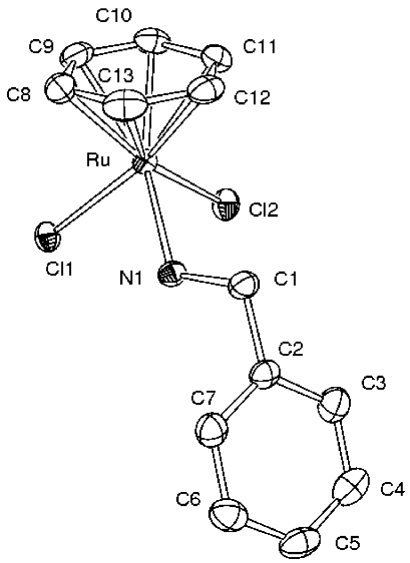


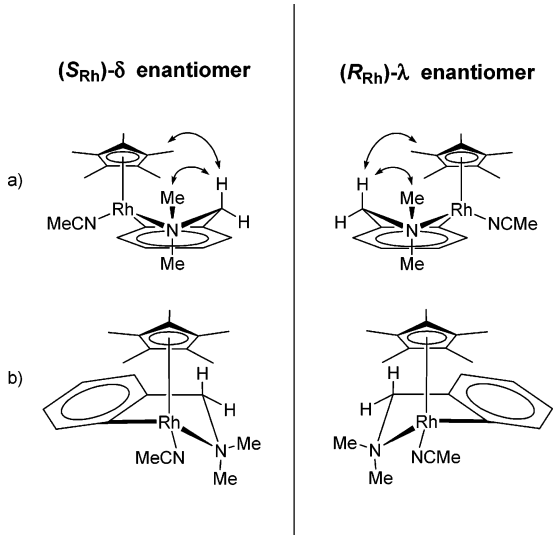
Figure 2. ORTEP style plot of compound **16**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ru−N1 2.1287(17), Ru−Cl1 2.4175(5), Ru−Cl2 2.4068(5), Ru−Centroid 1.649 (2), N1−Ru−Cl1 80.93(5), N1−Ru−Cl2 83.33(5), Cl2−Ru−Cl1 86.653(19), N1−Ru−Centroid 130.76 (10).

(55) The conformations determined in solution and discussed hereafter are the overwhelmingly major ones; it is of course possible that very minor conformations exchanging rapidly coexist in solution.

(56) Noyori, R.; Yamakawa, M.; Hashiguchi, S. *J. Org. Chem.* **2001**, *66*, 7931−7944.

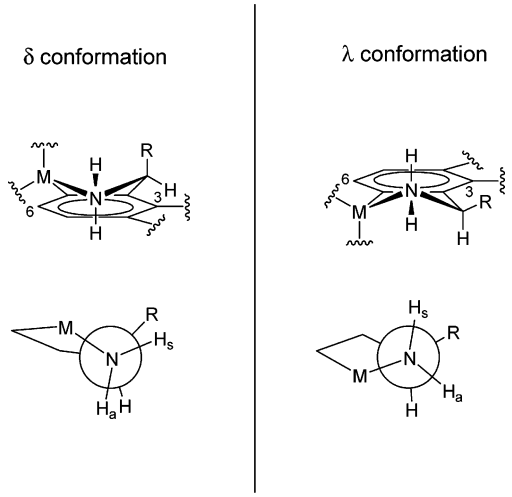
(57) The $\Delta G^{\ddagger}$ value was calculated with the Eyring equation $\Delta G^{\ddagger} = RT_c(22.96 + \ln T_c/\Delta\nu)$ [J·mol^{-1}] where T_c (K) is the temperature of coalescence of two given signals and $\Delta\nu$ (Hz) is the difference in their chemical shifts at low exchange temperature; the error is estimated to be ±0.4 kJ·mol^{-1}; see: Günther, H. *La Spectroscopie de RMN*; Masson: Paris, France, 1993.

Scheme 5. Conformations of Complex 17: (a) Front Views; (b) Side Views[a]



[a] Double arrows represent key NOE contacts. For the sake of clarity, the positive charge of the complex has been omitted.

Scheme 6. Conformations of the Five-Membered Metallacycles in Complexes 8−12, 18, and 19; R = Me or Et; M = Ru or Rh



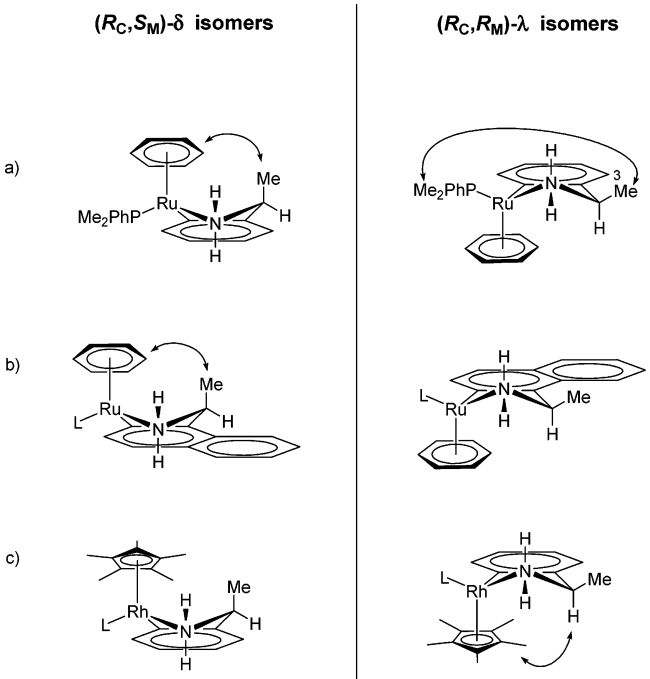
metallacycles. They indicated that for all cyclometalated complexes (except **13**, which derived from (*R*)-1,2,3,4-tetrahydro-1-naphthylamine, **6**), viz., complexes **8**, **9**, **10**, **11**, **12**, **18**, and **19**, the conformation is envelope, δ (R group in axial position), for one of the stereoisomers, whereas it is envelope, λ (R group in equatorial position), for the other (Scheme 6). This could be demonstrated with the help of Newman projections (Scheme 9), using a Karplus-like relationship applied to HCNH structural units.[58−60] The δ conformation is characterized by (i) a very low value of $^3J_{HCNH}$ (0−3 Hz) for the *syn* proton H_s, in agreement with a torsion angle close to 90°; (ii) a moderate value of $^3J_{HCNH}$ (4−7 Hz) for the *anti* proton H_a, indicative of a low torsion angle (generally a strong CH−H_a NOE effect is also detected); (iii) for complexes **8**, **9**, and **10**, a strong NOE

(58) Fraser, R. R.; Renaud, R. N.; Saunders, J. K.; Wigfield, Y. Y. *Can. J. Chem.* **1973**, *51*, 2433−2437.

(59) Glaser, R.; Adin, I.; Shiftan, D.; Shi, Q.; Deutsch, H. M.; George, C.; Wu, K.-M.; Froimowitz, M. *J. Org. Chem.* **1998**, *63*, 1785−1794.

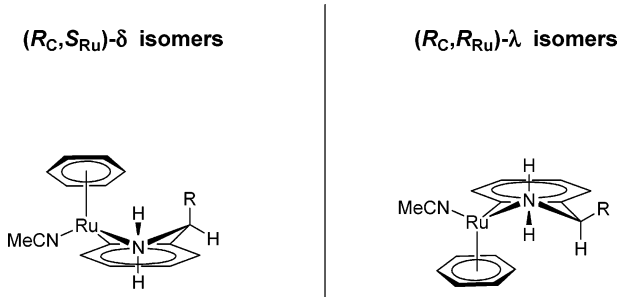
(60) Rey, A.; Pirmettis, I.; Pelecanou, M.; Papadopoulos, M.; Raptopoulou, C. P.; Mallo, L.; Stassinopoulou, C. I.; Terzis, A.; Chiotellis, E.; León, A. *Inorg. Chem.* **2000**, *39*, 4211−4218.

Scheme 7. Diastereoisomers of Complexes (a) 10; (b) 11 (L = MeCN) and 12 (L = PMe_2Ph); (c) 18 (L = MeCN) and 19 (L = Cl)[a]

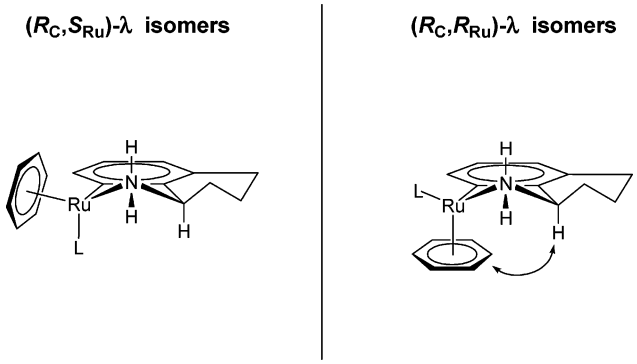


[a] Double arrows represent key NOE contacts.

Scheme 8. Diastereoisomers of Complexes 8 (R = Me) and 9 (R = Et)



Scheme 9. Diastereoisomers of Complexes 13 (L = MeCN) and 14 (L = PMe_2Ph)[a]



[a] Double arrow represents a key NOE contact.

contact between the benzylic proton and H3, related with the equatorial position of the former. Conversely, the spectroscopic data that are typical of a λ conformation are (i) a very high value of $^3J_{HCNHs}$ (10−12 Hz) and a weak or nonexistent

Table 1. Characteristics of the Diastereomers of the Cyclometalated Complexes 8−14, 18, and 19[a]

	(S_M) isomer		(R_M) isomer		major/minor
compound	conformation	proportion (%)	conformation	proportion (%)	isomer ratio
8[b]	δ	46	λ	54	1.2
9[b]	δ	57	λ	43	1.3
10[c]	δ	55	λ	45	1.2
11[b]	δ	97	λ	3	32
12[c]	δ	85	λ	15	5.7
13[d]	λ	17	λ	83	4.9
14[c]	λ	22	λ	78	3.5
18[b,e]	δ	8	λ	92	11.5
19[d]	δ	27	λ	73	2.7

[a] Determined by ^{1}H NMR in solution at room temperature unless otherwise stated; M = Ru or Rh. [b] In CD_3CN. [c] In CD_2Cl_2. [d] In $CDCl_3$. [e] At 233 K.

CH−H_S NOE effect, in agreement with a high torsion angle close to 180°; (ii) a medium value of $^3J_{HCNHa}$ (5−6 Hz), associated of a low torsion angle; (iii) for complexes **8**, **9**, and **10**, a weak NOE contact between the axial benzylic proton and H3.

For complexes **10**, **11**, and **12**, we could unambiguously determine the configuration of the diastereomer with the δ conformation as S_{Ru}, as shown by a key NOE contact between the η^6-arene protons and the benzylic methyl protons in *cis*-1,3-diaxial position (Scheme 7). Consequently, the configuration of the other diastereoisomer is R_{Ru}; in the case of complex **10**, it could also be identified by a NOE cross-peak between the methyl belonging to the phosphine and the benzylic methyl. Similarly, the major (R_{Rh}) isomers of **18** and **19** in λ conformations were characterized by strong NOE cross-peaks between the η^5-Cp* proton signal and the benzylic proton signal.

Unfortunately, such decisive NOE interactions were not detected in the spectra of complexes **8** and **9**. However, it is highly probable that the δ diastereomer has the (S_{Ru}) configuration, and the λ diastereomer the (R_{Ru}) configuration as depicted in Scheme 8, first because these compounds are akin to **10** and second because this is in agreement with the crystallographic data (*vide infra*).

The complexes **13** and **14** are exceptions within the family of cycloruthenated primary amines. Obviously both diastereomers must be in a constrained λ conformation, because the benzylic substituent is embedded in a six-membered ring (Scheme 9) and is thus always equatorial. Unfortunately, many signals of both complexes overlap, and H−H coupling constants could not be determined, as they had been with other complexes. However, NOE contacts were found between CH and H_a but not between CH and H_s, which is an indication in favor of the λ conformation. The major (R_{Ru}) isomer of **13** was characterized by a NOE cross-peak between the η^6-arene proton signal and the benzylic proton signal in *cis*-1,3-diaxial position. No such distinct cross-peak was observed in the ROESY spectrum of its homologue **14**, but it is probable that the (R_{Ru}) isomer (also characterized by X-ray diffraction, *vide infra*) is also the major one.

The proportion of each diastereomer of complexes **8**−**14**, **18**, and **19** is reported Table 1, and will be discussed below.

Single crystals of complexes (R_C,S_{Ru})-**8**, (R_C,R_{Ru})-**10**, (R_C,S_{Ru})-**12**, and (R_C,R_{Ru})-**14** were analyzed by X-ray diffraction. Their ORTEP representations are shown in Figures 3, 4, 5, and 6, respectively. The following measured bond distances fall within the expected range: Ru−(centroid of η^6-C_6H_6) (1.70−1.74 Å); Ru−C_{aryl} (2.06−2.09 Å); Ru−N_{amine} (2.12−2.14 Å); Ru−P (2.31−2.32 Å).[61]

(61) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.

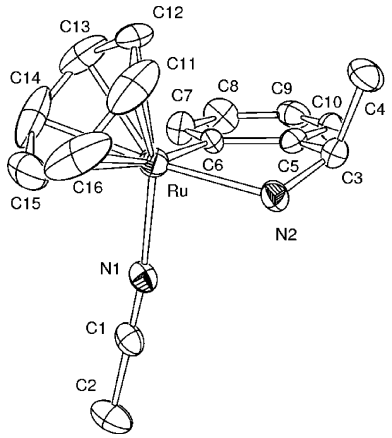


Figure 3. ORTEP style plot of compound (R_C,S_{Ru})-**8**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ru−Centroid 1.698 (6), Ru−N1 2.066(4), Ru−N2 2.120(4), Ru−C6 2.064(4), N1−Ru−N2 85.6(1), N1−Ru−C6 86.3-(1), N2−Ru−C6 78.2(2), N2−Ru−Centroid 132.59(4).

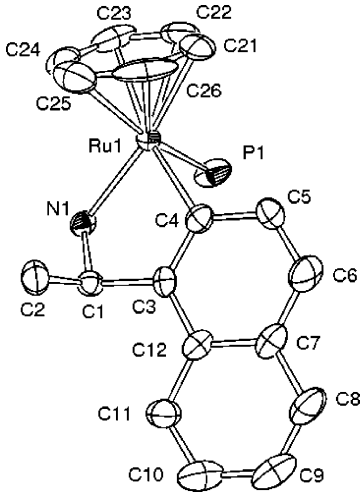


Figure 4. ORTEP style plot of one of the two inequivalent molecules of (R_C,S_{Ru})-**12**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms, PF_6, and substituents of PMe_2Ph are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ru1−Centroid 1.734(8), Ru1−C4 2.068(7), Ru1−N1 2.139(5), Ru1−P1 2.3090(18), C4−Ru1−N1 77.7(2), C4−Ru1−P1 83.7(2), N1−Ru1−P1 88.81(16), N1−Ru1−Centroid 130.21(4).

Overall, these solid-state analyses confirm what we had observed by NMR for these complexes in solution. The conformation of the five-membered ruthenacycles is envelope; the carbon atoms and the metal atom are nearly coplanar, with very small Ru−C_{aryl}−C_{aryl}−C_{benzyl} torsion angles (absolute

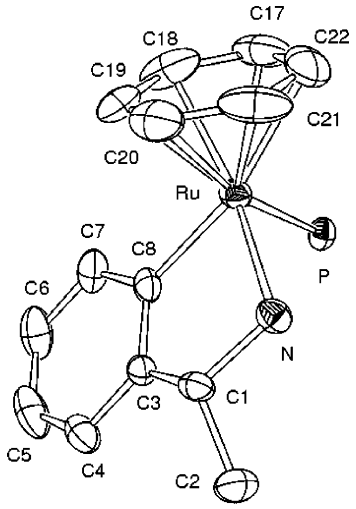


Figure 5. ORTEP style plot of compound (R_C,R_{Ru})-**10**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms, PF_6, and substituents of PMe_2Ph are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ru−Centroid 1.734(6), Ru−C8 2.070(4), Ru−N 2.133(3), Ru−P 2.3165(10), C8−Ru−N 78.08(15), N−Ru−P 90.99(10), C8−Ru−P 85.48(11), N−Ru−Centroid 127.83(3).

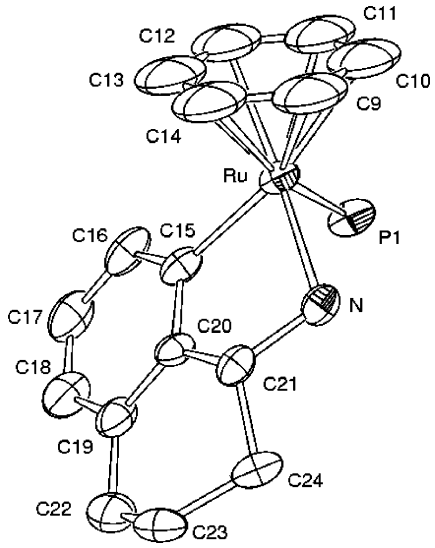
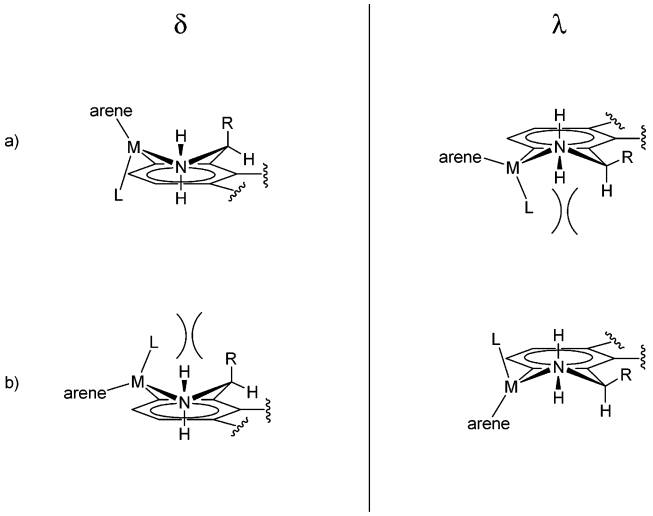


Figure 6. ORTEP style plot of compound (R_C,R_{Ru})-**14**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms, PF_6, and substituents of PMe_2Ph are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ru−Centroid 1.744(9), Ru−C15 2.087(10), Ru−N 2.126(7), Ru−P1 2.313(2), C15−Ru−N 78.0(3), C15−Ru−P1 84.6(2), N−Ru−P1 90.6(2), N−Ru−Centroid 127.36(4).

values 2−6°), and the nitrogen atom deviates more or less from that plane (absolute values of $N-C_{benzyl}-C_{aryl}-C_{aryl}$ angles: 19−30°). An (S_{Ru}) configuration is always associated with a δ conformation of the ruthenacycle, and conversely an (R_{Ru}) configuration is associated with a λ conformation. As a consequence, the benzylic methyl is axial in the first case and equatorial in the second. Moreover, the η^6-C_6H_6 ligand always lies in a pseudoaxial position; however, this position differs from a true axial position, as revealed by the very large centroid−$Ru-C_{aryl}-C_{aryl}$ torsion angles (absolute values 114−125°). By comparison, in the crystal structures of (R_C,S_{Ru})-**8** and (R_C,S_{Ru})-**12**, where the methyl group is also in axial position, the $C_{methyl}-C_{benzyl}-C_{aryl}-C_{aryl}$ angles reach −97° to −101°. Conversely, the pseudoequatorial position of the L ligand (MeCN in **8**, PMe_2Ph in **12**, **10**, and **14**) is characterized by small $N-Ru-C_{aryl}-C_{aryl}$ or $P-Ru-C_{aryl}-C_{aryl}$ angles (94−107°).

Scheme 10. Comparison of Intramolecular Steric Interactions in λ or δ Conformations in Complexes 8−12, 18, and 19; M = Ru, Rh; R = Me, Et; L = MeCN, PMe_2Ph, Cl; (a) (R_C,S_M) Diastereomers; (b) (R_C,R_M) Diastereomers



Another common feature of the X-ray structures of **12**, **10**, and **14** is the position of the substituents of the phosphine ligand with regard to the ruthenacycle. Indeed, the phenyl group is always located below the ruthenacycle, as illustrated by the low values of the $C_{ipso}-P-Ru-N$ torsion angles (1−46°) (see Supporting Information). It may be due to favorable CH−π or NH−π interactions; it clearly indicates that there is no steric hindrance between the phosphine ligand and the metallacycle. This contrasts with the closely related complex $[(\eta^6\text{-}C_6H_6)Ru(C_6H_4\text{-}2\text{-}(R)\text{-}CHMe\text{-}NMe_2)(PMe_2Ph)]^+$ derived from a tertiary amine:[51] the $C_{ipso}-P-Ru-N$ angle reaches −177°, indicating that the phenyl group is repelled from the metallacycle (see discussion below).

Overall, the NMR and X-ray analyses of the cycloruthenated chiral primary amines reported in this paper are convergent. They show that in general the envelope conformation of the ruthenacycle is such that the η^6-C_6H_6 ligand lies in a pseudoaxial position, whereas the acetonitrile or phosphine ligand is pseudoequatorial. Similarly, the Cp* ligand of the cyclorhodated complexes **18** and **19** is also pseudoaxial. In other words, the conformation of the (R_C,S_M) diastereomer is δ and the conformation of the (R_C,R_M) diastereomer is λ. Exceptions are the minor (R_C,S_{Ru}) diastereomers of **13** and **14**, where the benzene is forced in a pseudoequatorial position because of the constraining backbone of the tetraline ligand (Scheme 9).

We believe that the origin of this general rule is a strong steric hindrance between the L ligand and the metallacycle in the (R_C,S_M)-λ and (R_C,R_M)-δ stereochemistries (Scheme 10). In addition, this unfavorable interaction accounts for the high (R_{Ru})/(S_{Ru}) ratios measured for complexes **13** and **14** (Table 1).

It is striking that the reverse configuration−conformation associations, viz., (S_{Ru})-λ and (R_{Ru})-δ, were found in previously reported η^6-arene cycloruthenated tertiary amines.[51,62−67] Our

(62) Attar, S.; Nelson, J. H.; Fischer, J.; de Cian, A.; Sutter, J.-P.; Pfeffer, M. *Organometallics* **1995**, *14*, 4559−4569.
(63) Attar, S.; Catalano, V. J.; Nelson, J. H. *Organometallics* **1996**, *15*, 2932−2946.
(64) Gul, N.; Nelson, J. H. *Polyhedron* **1999**, *18*, 1835−1843.
(65) Gul, N.; Nelson, J. H. *Organometallics* **1999**, *18*, 709−725.
(66) Hansen, H. D.; Maitra, K.; Nelson, J. H. *Inorg. Chem.* **1999**, *38*, 2150−2156.

interpretation for this latter case is that the repulsive interaction between L and the ruthenacycle mentioned above is then overwhelmed by a stronger one between the methyls borne by the nitrogen atom and the η^6-arene.

It is also believed that the high $(S_{Ru})/(R_{Ru})$ ratios found for complexes **11** and **12** (Table 1) are due to a destabilizing steric interaction between the naphthyl backbone (at H7) and the equatorial benzylic methyl in the minor (R_{Ru})-δ isomer (Scheme 10). Conversely, in complexes **8**, **9**, and **10**, the steric interactions between the phenyl backbone of the amine and the R group in benzylic position [in the (R_{Ru})-λ isomer] and between R and η^6-C_6H_6 [in the (S_{Ru})-δ isomer] must be of the same order of magnitude. This explains why the [major isomer]/[minor isomer] ratio is low for those compounds. If we now consider the cyclorhodated complexes **18** and **19**, which are derived from the same amine (viz., **3**) as the cycloruthenated **8** and **10**, the η^5-Cp* ligand is bulkier than η^6-C_6H_6; therefore the (S_{Rh})-δ isomer is destabilized and its proportion is rather low (respectively 8% and 27%).

Configurational Stability of Cyclometalated Primary Amines. The coalescence of several ^{1}H NMR signals of the rhodium complex **18** between 233 and 298 K (*vide supra*) indicated that its diastereoisomers rapidly exchange at room temperature. However, the RT NMR spectra of the cycloruthenated complexes **8**−**14** and of the cyclorhodated complex **19** exhibited the well-resolved resonances of both diastereoisomers, and therefore the question of their configurational stability at the metal arose. The (R_C,R_{Ru})-**8**/(R_C,S_{Ru})-**8** ratio was 63:37 in $CDCl_3$, whereas it was 54:46 in CD_3CN. Adding D_2O to the latter solution did not lead to disappearance of the NH signals. A ^{13}C CP-MAS NMR spectrum of **8** with good resolution was recorded, which displayed the same number of resonances as the $^{13}C\{^1H\}$ spectrum; according to this spectrum, the diastereomeric ratio was 53:47. Furthermore, a 2D phase-sensitive ^{1}H NMR ROESY experiment carried out at room temperature in CD_3CN showed only negative NOE cross-peaks. Yet the same NMR experiment carried out at 348 K showed positive exchange cross-peaks between the proton signals of each diastereomer. These NMR data reveal that the diastereoisomers of **8** are in equilibrium, which illustrates the nonrigidity of the chirality at the ruthenium through decoordination/recoordination of the labile acetonitrile ligand.[68] It is noteworthy that, according to the ROESY spectrum, the *anti* NH_a proton of a given isomer selectively exchanged only with the *anti* NH_a proton of the corresponding isomer; conversely, the *syn* NH_s protons exchange selectively. This indicates that no inversion of the N atom is taking place during the process and thus that the NH_2 unit remains coordinated to the Ru atom during the fast epimerization process of the organoruthenium compound. A similar behavior was found for cycloruthenated tertiary amine derivatives,[51] and the ^{1}H ROESY spectrum of **19** recorded at RT in CD_3CN also displayed such selective exchange cross-peaks. The exchange rates related to the epimerization of **8** were determined by performing a selective inversion−recovery experiment in CD_3CN at 343 K on the methyl protons at 1.22 and 1.46 ppm.[69] A rate constant of 1.17 ± 0.06 s^{-1} is estimated for the (minor isomer) → (major isomer) conversion, which corresponds to $\Delta G^{\ddagger} = 84.0 \pm 0.4$ kJ·mol^{-1}. For the reverse reaction, respective values of the rate constant and the energy barrier at 343 K were determined as 1.01 s^{-1} and 84.4 kJ·mol^{-1}. Noteworthy, the $\Delta G^{\ddagger}$ value (79 kJ·mol^{-1}) for related cycloruthenated tertiary amines is comparable to that determined here.

Conclusion

These results establish unambiguously that the *ortho*-metalation of benzyl amines by Ru(II), Rh(III), or Ir(III) displays a high degree of chemo- and regioselectivity. This is remarkable as, to our knowledge, no other process is known to functionalize the *ortho* position of the aryl ring of these ligands, which does not require any protection of the amine function and which occurs without epimerization of the chiral carbon center. The structure of these compounds is also remarkable both in solution and in the solid phase, as it reflects the small size of the NH_2 unit as compared with the NMe_2 unit. This induces a pseudoaxial position for the η^6-arene ligand in the former complexes instead of a pseudoequatorial position for the latter complexes. The orientation of the NH_2 group will be of paramount importance in order to rationalize the catalytic selectivity for the reduction of ketones displayed by these complexes.[70,71]

Experimental Section

Experiments were carried out under an argon atmosphere using a vacuum line. Diethyl ether and pentane were distilled over sodium and benzophenone, dichloromethane and acetonitrile over calcium hydride, and methanol over magnesium under argon immediately before use. Column chromatography was carried out on Merck aluminum oxide 90 standardized. The following commercial reagents were used as received. Aldrich: (*R*)-(+)-1-phenylethylamine 98% (96% ee), (*R*)-(+)-1-(1-naphthyl)ethylamine (99+%), 1,3-cyclohexadiene, benzylamine, sodium hydroxide. Lancaster: (*R*)-1,2,3,4-tetrahydro-1-naphthylamine 99+% (99+% ee), (*R*)-(+)-1-phenylpropylamine 99+% (ee 99+%), potassium hexafluorophosphate. Alfa Aesar: (*R*)-(+)-1-(1-naphthyl)ethylamine, ChiPros. Avocado: dimethylphenylphosphine. The compounds listed hereafter were synthesized following reported procedures: $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$,[72] $[Ir(\eta^5\text{-}C_5(CH_3)_5)Cl_2]_2$,[73] $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$.[73] The NMR spectra were obtained at room temperature (unless otherwise indicated) on Bruker spectrometers. ^{1}H NMR spectra were recorded at 300.13 MHz (AC-300), 400.13 MHz (AM-400), or 500.13 MHz (ARX-500) and referenced to $SiMe_4$. $^{13}C\{^1H\}$ NMR spectra (broadband decoupled) were recorded at 75.48 MHz (AC-300), 100.62 MHz (AM-400), or 125.76 MHz (ARX-500) and referenced to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra (broadband decoupled) were recorded at 121.51 MHz (AC-300) or 202.46 MHz (ARX-500) and referenced to 85% aqueous H_3PO_4. For variable-temperature spectra, the probe temperature was controlled (±1 K) by a B-VT 2000 unit calibrated with a methanol (low temperature) or ethylene glycol (high temperature) NMR tube. The NMR assignments were supported by COSY, NOESY, or ROESY spectra or irradiations for ^{1}H NMR, and DEPT-135° and/or HSQC, HMQC, and HMBC spectra for $^{13}C\{^1H\}$ NMR. For the adopted numbering scheme, see Charts 2 and 3. Multiplicity: s = singlet, d = doublet, t = apparent triplet, m = multiplet, br = broad signal, q = quadruplet, sept = septuplet. ES-MS spectra and elemental analyses were carried out

(67) Hansen, H. D.; Nelson, J. H. *Organometallics* **2001**, *20*, 5257−5257.
(68) Robitzer, M.; Ritleng, V.; Sirlin, C.; Dedieu, A.; Pfeffer, M. *C. R. Chim.* **2002**, *5*, 467−472.
(69) The rate constants were determined by using a selective 180° pulse. For closely related experiments see: Barloy, L.; Gauvin, R. M.; Osborn, J. A.; Sizun, C.; Graff, R.; Kyritsakas, N. *Eur. J. Inorg. Chem.* **2001**, 1699−1707, and references therein.
(70) Alonso, D. A.; Brandt, P.; Nordin, S.; Andersson, P. G. *J. Am. Chem. Soc.* **1999**, *121*, 9580−9588.
(71) Petra, D. G. I.; Reek, J. N. H.; Handgraaf, J.-W.; Meijer, E. J.; Dierkes, P.; Kamer, P. C. J.; Brussee, J.; Schoemaker, H. E.; van Leeuwen, P. W. N. M. *Chem.−Eur. J.* **2000**, *6*, 2818−2829.
(72) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063−3072.
(73) White, C.; Yates, A.; Maitlis, P. M.; Heinekey, D. M. *Inorg. Synth.* **1992**, *29*, 228−234.

by the corresponding facilities at the Institut de Chimie, Université Louis Pasteur, Strasbourg, and at the Service Central d'Analyse du CNRS, Vernaison.

[(η^6-C_6H_6)Ru(C_6H_4-2-CH_2NH_2)($NCCH_3$)](PF_6) (7). To a suspension of [Ru(η^6-C_6H_6)Cl_2]$_2$ (0.1 g, 0.2 mmol), NaOH (0.016 g, 0.4 mmol), and KPF_6 (0.147 g, 0.8 mmol) in CH_3CN (5 mL) was added the amine **2** (0.021 g, 0.2 mmol), and the mixture was stirred at 20 °C under argon during 72 h. The resulting dark yellow suspension was filtered over Celite, concentrated *in vacuo*, and filtered over standardized Al_2O_3 (12 × 3 cm) using CH_3CN as eluent. A yellow fraction was collected and concentrated *in vacuo*. The yellow residue was then redissolved in a minimum of CH_2Cl_2, and a yellow solid precipitated (0.031 g, 33% yield) upon addition of *n*-pentane. Anal. Calcd for $C_{15}H_{17}F_6N_2PRu\cdot 1/4CH_3CN$: C, 38.66; H, 3.71; N, 6.54. Found: C, 38.16; H, 3.79; N, 6.86. ES-MS: *m*/*z* (%) 327.0438 (41) $[M]^+$, 286.0161 (100) $[M - CH_3CN]^+$. ^{1}H NMR (300 MHz, CD_3CN, 300 K): δ 7.81 (d, 1H, H6, $^3J_{HH}$ = 7.8 Hz), 7.02−6.87 (m, 3H, H5 + H4 + H3), 5.57 (s, 6H, η^6-C_6H_6), 4.99 (br, 1H, NH_2), 3.92 (m, 1H, CH_2), 3.60−3.80 (m, 2H, NH_2 + CH_2). ^{13}C{^{1}H} NMR (75 MHz, CD_3CN, 300 K): 166.0 (C1), 148.7 (C2), 139.9 (C6), 127.0 (C5), 124.2 (C4), 121.8 (C3), 87.4 (η^6-C_6H_6), 55.6 (CH_2).

[(η^6-C_6H_6)Ru(C_6H_4-2-(*R*)-$CH(CH_3)NH_2$)($NCCH_3$)](PF_6) (8). The procedure was the same as for **7**: [Ru(η^6-C_6H_6)Cl_2]$_2$ (2.04 g, 4.12 mmol), NaOH (0.33 g, 8 mmol), KPF_6 (2.98 g, 16.1 mmol), CH_3CN (70 mL), and the chiral amine **3** (0.51 g, 4.12 mmol) gave after 3 days **8** (1.5 g, 75% yield). Anal. Calcd for $C_{16}H_{19}F_6N_2PRu$: C 39.59, H 3.95, N 5.77. Found: C 39.10, H 3.96, N 5.76. ^{1}H NMR (400 MHz, CD_3CN, 300 K): major isomer (54%), δ 7.75 (dd, 1H, H6, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz), 6.87−7.05 (m, 2H, H4 + H5), 6.82 (d, 1H, H3, $^3J_{HH}$ = 7.4 Hz), 5.55 (s, 6H, η^6-C_6H_6), 5.43 (br, 1H, NH_a), 3.75 (dqd, 1H, CH, $^3J_{HH}$ = 11.2 Hz, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 4.8 Hz), 3.08 (br, 1H, NH_s), 1.44 (d, 3H, CH_3, $^3J_{HH}$ = 6.6 Hz); minor isomer (46%), δ 7.83 (d, 1H, H6, $^3J_{HH}$ = 7.4 Hz), 6.87−7.00 (m, 3H, H3 + H4 + H5), 5.60 (s, 6H, η^6-C_6H_6), 4.62 (br, 1H, NH_s), 4.25 (br, 1H, NH_a), 4.09 (qdd, 1H, CH, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 6.0 Hz, $^3J_{HH}$ = 3.2 Hz), 1.96 (s, 3H, CH_3CN), 1.17 (d, 3H, CH_3, $^3J_{HH}$ = 6.7 Hz). ^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 300 K): major isomer, δ 167.3 (C1), 150.1 (C2), 139.9 (C6), 127.4 (C5), 124.2 (C4), 122.9 (C3), 87.4 (η^6-C_6H_6), 63.4 (*C*HCH_3), 21.7 (CH_3); minor isomer, 164.1 (C1), 153.3 (C2), 140.1 (C6), 127.0 (C5), 124.2 (C4), 122.2 (C3), 87.4 (η^6-C_6H_6), 60.1 (*C*HCH_3), 23.1 (CH_3).

[(η^6-C_6H_6)Ru(C_6H_4-2-(*R*)-$CH(CH_2CH_3)NH_2$)($NCCH_3$)](PF_6) (9). The procedure was the same as for **7**: [Ru(η^6-C_6H_6)Cl_2]$_2$ (0.500 g, 1 mmol), NaOH (0.08 g, 2 mmol), KPF_6 (0.74 g, 4 mmol), CH_3CN (15 mL), and the chiral amine **4** (0.135 g, 1 mmol) gave after 3 days **9** (180 mg, 36% yield). Anal. Calcd for $C_{17}H_{21}F_6N_2PRu\cdot 1/4CH_2Cl_2$: C, 39.80; H, 4.16; N, 5.38. Found: C, 39.72; H, 4.26; N, 5.79. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): major isomer (55%), δ 7.78 (dd, 1H, H6, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz), 7.10−7.01 (m, 1H, H5), 6.99 (td, 1H, H4, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.2 Hz), 6.94 (dd, 1H, H3, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.6 Hz), 5.59 (s, 6H, η^6-C_6H_6), 4.29 (br d, 1H, NH_s, $^2J_{HH}$ = 11 Hz), 4.06 (br, 1H, NH_a), 3.94 (m, 1H, C*H*(CH_2CH_3)), 2.25 (s, 3H), 1.53 (m, 1H, CH_2CH_3), 1.47 (m, 1H, CH_2CH_3), 1.04 (t, 3H, CH_2CH_3, $^3J_{HH}$ = 7.4 Hz); minor isomer (45%), δ 7.73 (dd, 1H, H6, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.4 Hz), 7.10−7.01 (m, 2H, H4 + H5), 6.87 (d, 1H, H3, $^3J_{HH}$ = 7.4 Hz), 5.58 (s, 6H, η^6-C_6H_6), 5.21 (br, 1H, NH_a), 3.74 (m, 1H, C*H*(CH_2CH_3)), 2.86 (br t, 1H, NH_s, $^2J_{HH}$ = $^3J_{HH}$ = 11 Hz), 2.26 (s, 3H, CH_3CN), 2.13 (m, 1H, CH_2CH_3), 1.68 (m, 1H, CH_2CH_3), 1.09 (t, 3H, CH_2CH_3, $^3J_{HH}$ = 7.4 Hz). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$, 300 K): major isomer, δ 163.2 (C1), 150.3 (C2), 139.1 (C6), 126.7 (C5), 124.1 (CH_3CN), 123.7 (C4), 122.6 (C3), 86.7 (η^6-C_6H_6), 65.7 (*C*$H(CH_2CH_3)$), 30.0 ($CH(CH_2CH_3)$), 10.1 ($CH(CH_2CH_3)$), 4.0 (*C*H_3CN); minor isomer, δ 165.8 (C1), 149.0 (C2), 139.1 (C6), 127.0 (C5), 124.1 (CH_3CN), 123.9 (C4), 122.9 (C3), 86.7 (η^6-C_6H_6), 68.1 (*C*$H(CH_2CH_3)$), 28.1 ($CH(CH_2CH_3)$), 8.8 ($CH(CH_2CH_3)$), 4.0 (*C*H_3CN).

[(η^6-C_6H_6)Ru(C_6H_4-2-(*R*)-$CH(CH_3)NH_2$)($P(CH_3)_2Ph$)](PF_6) (10). A yellow solution of **8** (49 mg, 0.1 mmol) was stirred with $P(CH_3)_2Ph$ (0.059 mL, 0.4 mmol) in CH_2Cl_2 (4 mL) for 15 h at room temperature. The resulting reaction mixture was dried *in vacuo* and washed with *n*-pentane (3 × 5 mL) to remove excess $P(CH_3)_2Ph$. The yellow residue was then redissolved in a minimum of CH_2Cl_2 (1 mL), and a yellow solid (45 mg, 78% yield) precipitated upon addition of *n*-pentane. Anal. Calcd for $C_{22}H_{27}F_6NP_2Ru\cdot 1/2\ CH_2Cl_2$: C, 43.24; H, 4.52; N, 2.24. Found: C, 43.22; H, 4.61; N, 2.41. ES-MS: *m*/*z* (%) 438.0959 (100) $[M - PF_6]^+$. ^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 300 K): major isomer, δ 16.18 (s, $P(CH_3)_2Ph$), −143.13 (sept, $^1J_{PF}$ = 710 Hz); minor isomer, δ 16.83 (s, $P(CH_3)_2Ph$), −143.13 (sept, $^1J_{PF}$ = 710 Hz). ^{1}H NMR (300 MHz, CD_2Cl_2, 300 K): major isomer (57%), δ 7.45−7.20 (m, 4H, H6 + H_m + H_p), 7.05−6.84 (m, 4H, H4 + H5 + H_o), 6.72−6.58 (m, 1H, H3), 5.65 (d, 6H, η^6-C_6H_6, $^3J_{HP}$ = 0.9 Hz), 3.80 (br d, 1H, NH_s, $^2J_{HH}$ = 11 Hz), 3.42 (dq, 1H, C*H*CH_3, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6.9 Hz), 3.07 (br, 1H, NH_a), 1.94 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP}$ = 9.6 Hz), 1.46 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP}$ = 9.9 Hz), 1.14 (d, 3H, $CHCH_3$, $^3J_{HH}$ = 6.9 Hz); minor isomer (43%), δ 7.45−7.20 (m, 4H, H6 + H_m + H_p), 7.05−6.84 (m, 2H, H4 + H5), 6.72−6.58 (m, 3H, H3 + H_o), 5.67 (d, 6H, η^6-C_6H_6, $^3J_{HP}$ = 0.9 Hz), 4.69 (br, 1H, NH_a), 3.69 (ddq, 1H, C*H*CH_3, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz), 2.05 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP}$ = 9.3 Hz), 1.61 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP}$ = 10.2 Hz), 1.59 (br, 1H, NH_s), 0.81 (d, 3H, $CHCH_3$, $^3J_{HH}$ = 6.3 Hz). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 300 K): major isomer, δ 158.6 (s, C1), 153.2 (s, C2), 140.9 (d, C6, $^3J_{CP}$ = 4 Hz), 132.4 (d, C_i, $^1J_{CP}$ = 40 Hz), 130.9 (s, C_p), 130.1 (d, C_o, $^2J_{CP}$ = 8 Hz), 129.3 (d, C_m, $^3J_{CP}$ = 9 Hz), 126.4 (s, C4), 123.9 (s, C5), 122.5 (s, C3), 90.3 (d, η^6-C_6H_6, $^2J_{CP}$ = 3 Hz), 60.0 (s, *C*HCH_3), 23.8 (s, CH_3), 18.3 (d, $P(CH_3)_2Ph$, $^1J_{CP}$ = 32 Hz), 15.7 (d, $P(CH_3)_2Ph$, $^1J_{CP}$ = 35 Hz); minor isomer, δ 160.7 (s, C1), 150.0 (s, C2), 140.5 (d, C6, $^3J_{CP}$ = 5 Hz), 131.1 (d, C_i, $^1J_{CP}$ = 40 Hz), 130.9 (s, C_p), 130.4 (d, C_o, $^2J_{CP}$ = 8 Hz), 129.3 (d, C_m, $^3J_{CP}$ = 9 Hz), 126.6 (s, C4), 123.9 (s, C5), 123.3 (s, C3), 90.2 (d, η^6-C_6H_6, $^2J_{CP}$ = 3 Hz), 63.3 (s, *C*HCH_3), 22.7 (s, CH_3), 19.2 (d, $P(CH_3)_2Ph$, $^1J_{CP}$ = 32 Hz), 16.4 (d, $P(CH_3)_2Ph$, $^1J_{CP}$ = 35 Hz).

[(η^6-C_6H_6)Ru($C_{10}H_6$-2-(*R*)-$CH(CH_3)NH_2$)($NCCH_3$)](PF_6) (11). The procedure was the same as for **7**: [Ru(η^6-C_6H_6)Cl_2]$_2$ (2.919 g, 5.8 mmol), NaOH (0.47 g, 11.6 mmol), KPF_6 (4.3 g, 23.3 mmol), CH_3CN (87 mL), and the chiral amine **5** (1.0 g, 5.8 mmol) gave after 3 days **11** (2.54 g, 82% yield). Anal. Calcd for $C_{20}H_{21}F_6N_2PRu\cdot 1/4CH_3CN$: C 45.12, H 4.02, N 5.78. Found: C 45.55, H 4.28, N 5.50. ^{31}P{^{1}H} NMR (121 MHz, CD_3CN, 273 K): δ −143.30 (sept, $^1J_{PF}$ = 690 Hz). ^{1}H NMR (300 MHz, CD_3CN, 300 K): major isomer (97%), δ 7.99 (d, 1H, H6, $^3J_{HH}$ = 8.2 Hz), 7.79 (d, 1H, H10, $^3J_{HH}$ = 8.0 Hz), 7.61 (d, 1H, H7, $^3J_{HH}$ = 8.0 Hz), 7.54 (d, 1H, H5, $^3J_{HH}$ = 8.2 Hz), 7.39 (ddd, 1H, H8, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.1 Hz), 7.30 (ddd, 1H, H9, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.1 Hz), 5.67 (s, 6H, η^6-C_6H_6), 4.98 (dq, 1H, C*H*CH_3, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 6.7 Hz), 4.73 (br d, 1H, NH_s, $^2J_{HH}$ = 11 Hz), 4.12 (br, 1H, NH_a), 1.26 (d, 3H, CH_3, $^3J_{HH}$ = 6.7 Hz); minor isomer (3%), 8.22 (d, 1H, H6, $^3J_{HH}$ = 8.0 Hz), 5.61 (s, 6H, η^6-C_6H_6), 1.39 (d, 3H, CH_3, $^3J_{HH}$ = 7.3 Hz). ^{13}C{^{1}H} NMR (125 MHz, CD_3CN, 273 K): major isomer, δ 164.9 (C1), 146.7 (C2), 139.2 (C6), 132.2 (C4), 129.1 (C5), 128.8 (C3), 126.4 (C8/C9), 126.0 (C8/C9), 124.0 (C7/C10), 123.8 (C7/C10), 87.3 (η^6-C_6H_6), 59.3 (*C*HCH_3), 21.5 (CH_3).

[(η^6-C_6H_6)Ru($C_{10}H_6$-2-(*R*)-$CH(CH_3)NH_2$)($P(CH_3)_2Ph$)](PF_6) (12). The procedure was the same as for **10**. **11** (0.2 g, 0.37 mmol) and $P(CH_3)_2Ph$ (0.2 mL, 1.44 mmol) gave after 15 h **12** (0.18 g, 76% yield). Anal. Calcd for $C_{26}H_{29}F_6NP_2Ru\cdot 1/4CH_2Cl_2$: C, 48.23; H, 4.55; N, 2.14. Found: C, 48.28; H, 4.52; N, 2.43. ES-MS: *m*/*z* (%) 488.1120 (100) $[M - PF_6]^+$. ^{31}P{^{1}H} NMR (121 MHz, CD_2-

Cl_2, 300 K): major isomer, 16.48 (s, $P(CH_3)_2Ph$), −143.10 (sept, $^1J_{PF} = 710$ Hz); minor isomer, 15.80 (s, $P(CH_3)_2Ph$), −143.10 (sept, $^1J_{PF} = 710$ Hz). ^1H NMR (300 MHz, CD_2Cl_2, 300 K): major isomer (85%), δ 7.79 (d, 1H, H10, $^3J_{HH} = 7.5$ Hz), 7.57 (dd, 1H, H6, $^3J_{HH} = 9.0$ Hz, $^4J_{HP} = 0.6$ Hz), 7.53 (d, 1H, H5, $^3J_{HH} = 8.4$ Hz), 7.39−7.22 (m, 4H, H7 + H8 + H9 + H_p), 7.09 (td, 2H, H_m, $^3J_{HH} = 7.8$ Hz, $^4J_{HP} = 2.1$ Hz), 6.72 (ddd, 2H, H_o, $^3J_{HP} = 9.0$ Hz, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 1.2$ Hz), 5.73 (d, 6H, η^6-C_6H_6, $^3J_{HP} = 0.9$ Hz), 4.27 (dq, 1H, C*H*CH_3, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 6.6$ Hz), 3.94 (br d, 1H, NH_s, $^2J_{HH} = 12$ Hz), 3.04 (br, 1H, NH_a), 1.97 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP} = 9.3$ Hz), 1.44 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP} = 9.9$ Hz), 1.26 (d, 3H, $CHCH_3$, $^3J_{HH} = 6.6$ Hz); minor isomer (15%), selected data, δ 5.65 (d, 6H, η^6-C_6H_6, $^3J_{HP} = 0.6$ Hz), 4.56 (m, 1H, C*H*CH_3), 2.04 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP} = 9.3$ Hz), 1.71 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP} = 9.9$ Hz), 0.90 (d, 3H, $CHCH_3$, $^3J_{HH} = 6.6$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 300 K): major isomer, δ 158.4 (s, C1), 146.5 (s, C2), 139.3 (d, C6, $^3J_{CP} = 4$ Hz), 131.8 (d, C_i, $^1J_{CP} = 45$ Hz), 131.4 (s, C4), 130.8 (s, C_p), 130.0 (d, C_o, $^2J_{CP} = 8$ Hz), 129.2 (d, C_m, $^3J_{CP} = 9$ Hz), 129.0 (s, C3), 128.8 (s, C10), 126.3 (s, C8), 125.7 (s, C5), 123.8 (s, C9), 123.2 (s, C7), 90.4 (d, η^6-C_6H_6, $^2J_{CP} = 3$ Hz), 58.9 (s, *C*HCH_3), 22.0 (s, CH_3), 18.3 (d, $P(CH_3)_2Ph$, $^1J_{CP} = 32$ Hz), 15.8 (d, $P(CH_3)_2Ph$, $^1J_{CP} = 35$ Hz); minor isomer, selected data, δ 91.0 (d, η^6-C_6H_6, $^2J_{CP} = 3$ Hz), 24.5 (s, CH_3).

[(η^6-C_6H_6)Ru($C_{10}H_{10}$-7-(*R*)-NH_2)(NCCH$_3$)](PF$_6$) (13). The procedure was the same as for **7**. $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (0.2 g, 0.4 mmol), NaOH (0.03 g, 0.8 mmol), KPF_6 (0.29 g, 1.6 mmol), CH_3CN (6 mL), and the chiral amine **6** (0.058 g, 0.4 mmol) gave after 3 days **13** (0.15 g, 70% yield). Anal. Calcd for $C_{18}H_{21}F_6PN_2Ru\cdot 1/2CH_3CN$: C, 42.90; H, 4.26; N, 6.58. Found: C, 42.85; H, 4.25; N, 6.55. ^1H NMR (400 MHz, $CDCl_3$, 300 K): major isomer (83%), δ 7.50 (dd, 1H, H6, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 0.7$ Hz), 7.01 (td, 1H, H5, $^3J_{HH} = 7.4$ Hz, $^5J_{HH} = 0.7$ Hz), 6.78 (dd, 1H, H4, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.0$ Hz), 5.60 (s, 6H, η^6-C_6H_6), 5.24 (br, 1H, NH_a), 3.61 (m, 1H, H7), 2.67 (m, 1H, NH_s), 2.80−2.60 (m, 2H, H10), 2.41 (m, 1H, H8), 2.24 (s, 3H, $NCCH_3$), 1.97 (m, 1H, H9), 1.80−1.40 (m, 2H, H8 + H9); minor isomer (17%), δ 7.85 (dd, 1H, H6, $^3J_{HH} = 7.3$ Hz, $^4J_{HH} = 0.8$ Hz), 7.02 (td, 1H, H5, $^3J_{HH} = 7.5$ Hz, $^5J_{HH} = 0.8$ Hz), 6.79 (dd, 1H, H4, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.0$ Hz), 5.58 (s, 6H, η^6-C_6H_6), 4.67 (br, 1H, NH_a), 4.02 (br t, 1H, NH_s, $^2J_{HH} = {}^3J_{HH} = 10$ Hz), 3.56 (m, 1H, H7), 2.80−2.60 (m, 2H, H10), 2.50−2.30 (m, 1H, H8), 2.30 (s, 3H, $NCCH_3$), 2.10−1.90 (m, 1H, H9), 1.80−1.40 (m, 2H, H8 + H9). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 300 K): major isomer, δ 167.0 (C1), 145.5 (C2), 136.2 (C6), 135.2 (C3), 127.3 (C5), 124.3 (C4), 124.1 (CH_3CN), 87.0 (η^6-C_6H_6), 65.6 (C7), 33.0 (C8), 27.6 (C10), 22.6 (C9), 4.0 (*C*H_3CN); minor isomer, δ 161.1 (C1), 146.0 (C2), 136.0 (C6), 135.0 (C3), 127.6 (C5), 124.6 (C4), 124.1 (CH_3CN), 87.0 (η^6-C_6H_6), 66.0 (C7), 32.6 (C8), 28.0 (C10), 22.6 (C9), 4.0 (*C*H_3CN).

[(η^6-C_6H_6)Ru($C_{10}H_{10}$-7-(*R*)-NH_2)(P(CH$_3$)$_2$Ph)](PF$_6$) (14). The procedure was the same as for **10**. **13** (0.05 g, 0.1 mmol) and $P(CH_3)_2Ph$ (0.057 mL, 0.4 mmol) gave after 15 h **14** (0.048 g, 80% yield). Anal. Calcd for $C_{24}H_{29}F_6NP_2Ru$: C, 47.37; H, 4.80; N, 2.30. Found: C, 47.72; H, 4.80; N, 2.35. ES-MS: *m*/*z* (%) 464.1116 (100) $[M]^+$. $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2, 300 K): major isomer, δ 16.97 (s, $P(CH_3)_2Ph$), −143.16 (sept, $^1J_{PF} = 710$ Hz); minor isomer, δ 12.43 (s, $P(CH_3)_2Ph$), −143.10 (sept, $^1J_{PF} = 710$ Hz). ^1H NMR (300 MHz, CD_2Cl_2, 300 K): major isomer (78%), δ 7.43−7.32 (m, 1H, H_p), 7.30−7.14 (m, 3H, H6 + H_m), 6.96 (t, 1H, H5, $^3J_{HH} = 7.5$ Hz), 6.72 (d, 1H, H4, $^3J_{HH} = 7.5$ Hz), 6.55 (ddd, 2H, H_o, $^3J_{HP} = {}^3J_{HH} = 9.0$ Hz, $^4J_{HH} = 0.6$ Hz), 5.68 (d, 6H, η^6-C_6H_6, $^3J_{HP} = 0.6$ Hz), 4.59 (br, 1H, NH), 3.45 (m, 1H, H7), 2.50 (m, 1H, H10), 2.30 (m, 1H, H10), 2.06 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP} = 9.3$ Hz), 1.90 (m, 1H, H8), 1.70 (m, 1H, H9), 1.61 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HH} = 9.9$ Hz), 1.58−1.38 (m, 2H, NH + H9), 0.10 (m, 1H, H8); minor isomer (22%), selected data, δ 7.43−7.32 (m, 4H, H6 + H_m + H_p), 7.30−7.14 (m, 2H, H_o), 6.95 (t, 1H, H5, $^3J_{HH} = 7.5$ Hz), 6.72 (d, 1H, H4, $^3J_{HH} = 7.5$ Hz), 5.58 (6H, η^6-C_6H_6, $^3J_{HP} = 0.6$ Hz), 3.88 (br, 1H, NH), 3.56 (br, 1H, NH), 1.84 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP} = 9.3$ Hz), 1.51 (d, 3H, $P(CH_3)_2Ph$, $^2J_{HP} = 9.6$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 300 K): major isomer, δ 161.7 (s, C1), 145.0 (s, C2), 137.9 (d, C6, $^3J_{CP} = 5$ Hz), 135.9 (s, C3), 130.9 (d, C_i, $^1J_{CP} = 35$ Hz), 130.8 (s, C_p), 130.5 (d, C_o, $^2J_{CP} = 11$ Hz), 129.2 (d, C_m, $^3J_{CP} = 9$ Hz), 126.8 (s, C5), 123.9 (s, C4), 89.9 (s, η^6-C_6H_6), 65.6 (s, C7), 33.2 (s, C8), 27.9 (s, C10), 22.7 (s, C9), 19.3 (d, $P(CH_3)_2Ph$, $^1J_{CP} = 31$ Hz), 16.3 (d, $P(CH_3)_2Ph$, $^1J_{CP} = 36$ Hz); minor isomer, selected data, δ 91.1 (s, η^6-C_6H_6), 59.8 (C7).

[(η^6-C_6H_6)Ru((*R*)-1-$C_{10}H_7$-1-CH(CH$_3$)NH$_2$)Cl$_2$] (15). A suspension of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ (200 mg, 0.4 mmol) and (*R*)-1-naphthyl-1-ethylamine (137 mg, 0.8 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 1 h. After concentration to ca. 10 mL *in vacuo*, an orange solid precipitated upon addition of pentane. The product was collected on a frit and washed with pentane (235 mg, 70% yield). Anal. Calcd for $C_{18}H_{19}Cl_2NRu\cdot 1/3CH_2Cl_2$: C, 48.97; H, 4.41; N, 3.12. Found: C, 49.01; H, 4.42; N, 2.86. ES-MS: *m*/*z* (%) 386.0246 (100) $[M - Cl]^+$, 350.0467 (30) $[M - H - 2Cl]^+$. ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.17 (d, 1H, H7, $^3J_{HH} = 8.5$ Hz), 7.98 (dt, 1H, H10, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 0.5$ Hz), 7.94 (d, 1H, H5, $^3J_{HH} = 8.0$ Hz), 7.70−7.67 (m, 2H, H8 + H1), 7.63 (dd, 1H, H6, $^3J_{HH} = 8.0$ Hz, $^3J_{HH} = 7.5$ Hz), 7.60 (ddd, 1H, H9, $^3J_{HH} = 8.5$ Hz, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 1.5$ Hz), 5.35 (m, 1H, CH), 5.16 (s, 6H, η^6-C_6H_6), 3.79 (br, 1H, NH), 3.31 (br, 1H, NH), 1.70 (d, 3H, CH_3, $^3J_{HH} = 6.5$ Hz). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 298 K): δ 139.1 (C2), 134.3 (C4), 130.5 (C3), 129.6 (C10), 129.0 (C5), 127.5 (C8), 126.6 (C9), 125.9 (C6), 122.9 (C1), 122.6 (C7), 82.7 (η^6-C_6H_6), 52.9 (*C*HCH_3), 26.7 (CH_3).

[(η^6-C_6H_6)Ru((*R*)-1-$C_{10}H_7$-1-CH(CH$_3$)NH$_2$)Cl(NCCH$_3$)](PF$_6$) (15′). To a solution of **15** (10 mg, 2.3×10^{-5} mol) in CD_3CN (0.6 mL) was added KPF_6 (10 mg, 5.4×10^{-5} mol). The reaction was monitored by ^1H NMR after 2 h stirring. NaOH (1 mg, 2.5 10^{-5} mol) was then added to the reaction mixture, and typical NMR signals of **11** arose after 3 days. ^1H NMR (300 MHz, CD_3CN, 298 K): δ 8.10 (d, 1H, H_{ar}, $^3J_{HH} = 7.5$ Hz), 7.98 (d, 1H, H_{ar}, $^3J_{HH} = 7.4$ Hz), 7.92 (d, 1H, H_{ar}, $^3J_{HH} = 7.8$ Hz), 7.70 (d, 1H, H_{ar}, $^3J_{HH} = 6.7$ Hz), 7.66−7.55 (m, 3H, H_{ar}), 5.69 and 5.68 (s, 6H, η^6-C_6H_6 of both diastereoisomers), 4.96 (m, 1H, CH), 4.41 (br, 1H, NH), 3.81 (br, 1H, NH), 1.70 and 1.65 (d, 3H, CH_3 of both diastereoisomers, $^3J_{HH} = 6.5$ and 6.8 Hz).

[(η^6-C_6H_6)Ru(PhCH$_2$NH$_2$)Cl$_2$] (16). The procedure was the same as for **15**. $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (0.05 g, 0.1 mmol) and the benzylamine **2** (0.021 g, 0.2 mmol) gave after 1 h **16** (0.05 g, 71% yield). ES-HRMS: *m*/*z* calcd for $C_{13}H_{15}{}^{35}ClN^{102}Ru$ 321.9936; found 321.9925. ^1H NMR (300 MHz, CD_2Cl_2, 300 K): δ 7.45−7.31 (m, 5H, $H_{aromatic}$), 5.60 (s, 6H, η^6-C_6H_6), 4.24 (m, 2H, CH_2), 3.25 (br, 2H, NH_2).

[(η^5-C_5(CH$_3$)$_5$)Rh(C_6H_4-2-CH$_2$N(CH$_3$)$_2$)(NCCH$_3$)](PF$_6$) (17). To a suspension of $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ (0.368 g, 0.6 mmol), NaOH (0.048 g, 1.2 mmol), and KPF_6 (0.44 g, 2.4 mmol) in CH_3CN (8 mL) was added *N*,*N*-dimethylbenzylamine (180 μL, 1.2 mmol), and the reaction mixture was stirred at 45 °C safe from light during 50 h. The resulting dark orange suspension was vigorously stirred with 20 mL of hexane during 2 h, in order to extract the residual free amine. The CH_3CN layer was concentrated *in vacuo* and filtered over standardized Al_2O_3 (8 × 3 cm) using CH_3CN as eluent. An orange fraction was collected and evaporated *in vacuo*. The resulting residue was redissolved in CH_3CN (2 mL), and diethyl ether (10 mL) was added to this solution to give an orange solid, which was dried *in vacuo* after standing for 18 h at −15 °C (455 mg, 68%). Anal. Calcd for $C_{21}H_{30}F_6N_2PRh$: C, 45.17; H, 5.42; N, 5.02. Found: C, 44.36; H, 5.45; N, 5.34. ^1H NMR (300 MHz, CD_3CN, 300 K): δ 7.50 (d, 1H, H6, $^3J_{HH} = 7.5$ Hz), 7.13−7.07 (td, 1H, H5, $^3J_{HH} = 7.2$ Hz, $^4J_{HH} = 2.1$ Hz), 7.06−6.96 (m, 2H, H3 + H4), 3.67 (s, 2H, CH_2), 2.64 (s, 6H, NMe_2), 1.96 (s, 3H, CH_3CN), 1.59 (s, 15H, η^5-$C_5(CH_3)_5$). ^1H NMR (400 MHz, CD_3CN, 233 K): δ

Table 2. Crystallographic Data for 10, 12, and 14−16

	10	12	14	15	16
formula	$C_{22}H_{27}F_6NP_2Ru$	$C_{26}H_{29}F_6NP_2Ru$	$C_{24}H_{29}F_6NP_2Ru$	$C_{18}H_{19}Cl_2NRu$	$C_{13}H_{15}Cl_2NRu$
fw	582.46	632.51	608.49	421.31	357.23
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$Pbcn$
a, Å	8.1270(2)	10.9010(6)	8.7890(2)	10.3240(2)	13.0190(2)
b, Å	16.4400(3)	21.6160(3)	12.4280(3)	10.6040(3)	11.0470(2)
c, Å	9.1430(2)	22.4140(4)	11.6700(3)	15.3620(4)	18.3470(3)
α, deg	90	90	90	90.00	90.00
β, deg	101.7260(13)	90	91.3240(8)	90.00	90.00
γ, deg	90	90	90	90.00	90.00
V, Å^3	1196.08(5)	5281.6(3)	1274.37(5)	1681.77(7)	2638.68(8)
Z	2	8	2	4	8
ρ_{calcd}, g/cm^3	1.617	1.591	1.586	1.664	1.798
μ, mm^{-1}	0.846	0.773	0.798	1.245	1.569
F(000)	588	2560	616	848	1424
cryst size, mm^3	0.12 × 0.12 × 0.10	0.10 × 0.10 × 0.08	0.12 × 0.10 × 0.09	0.12 × 0.12 × 0.10	0.12 × 0.12 × 0.10
θ range, deg	2.56 to 30.00	2.62 to 30.04	2.84 to 30.03	2.75 to 30.08	2.66 to 30.03
index ranges	$-11 \le h \le 11$	$-15 \le h \le 15$	$-12 \le h \le 12$	$-14 \le h \le 14$	$-18 \le h \le 18$
	$-23 \le k \le 22$	$-30 \le k \le 30$	$-17 \le k \le 15$	$-14 \le k \le 14$	$-15 \le k \le 15$
	$-12 \le l \le 12$	$-31 \le l \le 31$	$-16 \le l \le 16$	$-21 \le l \le 21$	$-25 \le l \le 25$
no. of reflns collcd	6774	15 304	6853	4786	3850
no. of indep collcd/R_{int}	6774/0.0470	15 304/0.0320	6853/0.045	4357/0.04	3139/0.0208
completeness to θ_{max}, %	99.8	99.7	99.7	99.5	99.9
no. of refined params	271	589	249	199	154
GOF (F^2)	1.039	1.020	1.038	0.937	0.896
R1(F) ($I > 2\sigma(I)$)	0.0435	0.0817	0.0642	0.0305	0.030
wR2(F^2) ($I > 2\sigma(I)$)	0.1088	0.1437	0.1653	0.0651	0.0778
absolute struct param	−0.06(4)	−0.02(4)	0.03(8)	−0.01(3)	
largest diff peak/hole, e·Å^{-3}	1.474/−0.959	1.738/−0.966	1.009/−0.981	0.796/−0.900	1.087/−0.996

7.47 (d, 1H, H6, $^3J_{HH}$ = 7.4 Hz), 7.07 (td, 1H, H5, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.6 Hz), 7.02−6.92 (m, 2H, H3 + H4), 3.75 (d, 1H, CH_2, $^2J_{HH}$ = 13.6 Hz), 3.53 (d, 1H, CH_2, $^2J_{HH}$ = 13.4 Hz), 2.85 (s, 3H, NMe), 2.36 (s, 3H, NMe), 1.56 (s, 15H, η^5-$C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN, 300 K): δ 167.1 (d, C_1, $^1J_{CRh}$ = 30 Hz), 147.1 (s, C_2), 136.3 (s, C_6), 128.2 (s, C_5), 124.8 (s, C_4), 123.5 (s, C_3), 98.7 (d, η^5-$C_5(CH_3)_5$, $^1J_{CRh}$ = 6.6 Hz), 74.1 (s, CH_2), 54.4 (s, $N(CH_3)_2$), 9.6 (s, η^5-$C_5(CH_3)_5$).

[(η^5-$C_5(CH_3)_5$)Rh(C_6H_4-2-(R)-$CH(CH_3)NH_2$)($NCCH_3$)](PF_6) (18). To a suspension of [Rh(η^5-C_5Me_5)Cl_2]$_2$ (0.247 g, 0.4 mmol), NaOH (0.03 g, 0.75 mmol), and KPF_6 (0.29 g, 1.57 mmol) in CH_3CN (6 mL) was added (*R*)-1-phenylethylamine (51 μL, 0.4 mmol), and the reaction mixture was stirred at 20 °C safe from light during 72 h. The resulting dark orange suspension was vigorously stirred with 20 mL of hexane during 2 h, in order to extract the residual free amine. The CH_3CN layer was concentrated *in vacuo* and filtered over standardized Al_2O_3 (8 × 3 cm) using CH_3CN as eluent. An orange fraction was collected and evaporated *in vacuo*. The resulting residue was redissolved in a mixture of CH_3CN (0.5 mL) and CH_2Cl_2 (0.5 mL), and diethyl ether (10 mL) was added to this solution to give an orange solid, which was dried *in vacuo*, after standing for 18 h at −15 °C (152 mg, 68%). Anal. Calcd for $C_{20}H_{28}F_6N_2PRh$: C, 44.13; H, 5.18; N, 5.15. Found: C, 44.21; H, 5.10; N, 5.10. ^{1}H NMR (300 MHz, CD_3CN, 300 K): δ 7.47 (dd, 1H, H6, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.3 Hz), 7.07 (t, 1H, H5, $^3J_{HH}$ = 7.5 Hz), 6.99 (td, 1H, H4, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 0.9 Hz), 6.85 (d, 1H, H3, $^3J_{HH}$ = 7.5 Hz), 4.28 (br, 1H, NH), 3.96 (br, 1H, C*H*CH_3), 3.28 (br, 1H, NH), 1.67 (s, 15H, η^5-$C_5(CH_3)_5$), 1.48 (br, 3H, CHCH_3). ^{1}H NMR (400 MHz, CD_3CN, 233 K): major isomer (92%), δ 7.41 (dd, 1H, H6, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.6 Hz), 7.05 (t, 1H, H5, $^3J_{HH}$ = 7.2 Hz), 6.97 (td, 1H, H4, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz), 6.81 (d, 1H, H3, $^3J_{HH}$ = 7.6 Hz), 4.40 (br, 1H, NH), 3.83 (dqd, 1H, C*H*CH_3, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz), 3.40 (t, 1H, NH, $^3J_{HH}$ = 11 Hz), 1.62 (s, 15H, η^5-$C_5(CH_3)_5$), 1.46 (d, 3H, CHCH_3, $^3J_{HH}$ = 6.4 Hz); minor isomer (8%), δ 7.45 (dd, 1H, H6, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.4 Hz), 7.00 (td, 1H, H5, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.9 Hz), 6.92 (td, 1H, H4, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz), 6.88 (dd, 1H, H3, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.9 Hz), 4.28 (br, 1H, NH), 4.16 (m, 1H, C*H*CH_3), 3.70 (d, 1H, NH, $^3J_{HH}$ = 8 Hz), 1.62 (s, 15H, η^5-$C_5(CH_3)_5$), 1.20 (d, 3H, CHCH_3, $^3J_{HH}$ = 6.8 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN, 300 K): selected data, δ 136.8 (s, C_6), 128.4 (s, C_5), 124.8 (s, C_4), 123.3 (s, C_3), 97.7 (d, η^5-$C_5(CH_3)_5$, $^1J_{CRh}$ = 6.5 Hz), 60.4 (s, *C*HCH_3), 22.3 (br, CH_3), 9.5 (s, η^5-$C_5(CH_3)_5$).

[(η^5-$C_5(CH_3)_5$)Rh(C_6H_4-2-(R)-$CH(CH_3)NH_2$)Cl] (19). To a suspension of [Rh(η^5-C_5Me_5)Cl_2]$_2$ (0.368 g, 0.6 mmol), NaOH (0.045 g, 1.12 mmol), and KPF_6 (0.433 g, 2.35 mmol) in CH_3CN (10 mL) was added (*R*)-1-phenylethylamine (77 μL, 0.6 mmol), and the reaction mixture was stirred at 20 °C safe from light during 72 h. Acetonitrile was removed *in vacuo*. The crude cycloruthenated acetonitrile complex **18** was dissolved in freshly distilled dichloromethane and vigorously stirred during 30 min with 10 volumes of a saturated aqueous KCl solution. The organic layer was separated, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was filtered over standardized Al_2O_3 (8 × 3 cm) using CH_2Cl_2/MeOH (95:5) as eluent. An orange fraction was collected and evaporated *in vacuo*. The residue was redissolved in dichloromethane (0.5 mL), and pentane was added to give an orange solid (200 mg, 42%). Anal. Calcd for $C_{18}H_{25}NClRh\cdot 1/4CH_2Cl_2$: C, 52.82; H, 6.19; N, 3.37. Found: C, 53.13; H, 6.51; N, 3.56. ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): major isomer (73%), δ 7.51 (d, 1H, H6, $^3J_{HH}$ = 7.5 Hz), 7.09 (t, 1H, H5, $^3J_{HH}$ = 6.9 Hz), 6.92 (td, 1H, H4, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz), 6.74 (d, 1H, H3, $^3J_{HH}$ = 7.5 Hz), 3.92 (dqd, 1H, C*H*CH_3, $^3J_{HH}$ = 11 Hz, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 6 Hz), 3.24 (m, 2H, NH_2), 1.66 (s, 15H, η^5-$C_5(CH_3)_5$), 1.53 (d, 3H, CHCH_3, $^3J_{HH}$ = 6.6 Hz); minor isomer (27%), δ 7.48 (m, 1H, H6), 7.35 (m, 1H, H4 or H5), 7.03 (m, 1H, H5 or H4), 6.85 (m, 1H, H3), 4.28 (br, 1H, C*H*CH_3), 4.28 (br, 1H, NH), 2.60 (br, 1H, NH), 1.69 (s, 15H, η^5-$C_5(CH_3)_5$), 1.27 (br, 3H, CHCH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 300 K): major isomer (73%), δ 170.8 (d, C_1, $^1J_{CRh}$ = 30 Hz), 148.8 (s, C_2), 136.9 (s, C_6), 127.9 (s, C_5), 122.9 (s, C_4), 121.7 (s, C_3), 94.4 (d, η^5-$C_5(CH_3)_5$, $^1J_{CRh}$ = 6.6 Hz), 59.5 (s, *C*HCH_3), 23.0 (s, CH_3), 9.6 (s, η^5-$C_5(CH_3)_5$); minor isomer (27%), selected data δ 152.8 (s, C_2), 136.7 (s, C_6), 127.9 (s, C_5), 122.9 (s, C_4), 120.9 (s, C_3), 94.7 (d, η^5-$C_5(CH_3)_5$, $^1J_{CRh}$ = 6.7 Hz), 59.6 (s, *C*HCH_3), 25.4 (s, CH_3), 9.8 (s, η^5-$C_5(CH_3)_5$).

[(η^5-$C_5(CH_3)_5$)Ir(C_6H_4-2-$CH_2N(CH_3)_2$)($NCCH_3$)](PF_6) (20). To a suspension of [Ir(η^5-$C_5(CH_3)_5$)Cl_2]$_2$ (0.120 g, 0.15 mmol), NaOH (0.012 g, 0.3 mmol), and KPF_6 (0.11 g, 0.6 mmol) in CH_3CN (4 mL) was added *N*,*N*-dimethylbenzylamine (45 μL, 0.3 mmol), and

the reaction mixture was stirred at 45 °C safe from light during 50 h. The workup and crystallization conditions were the same as for **17**. Yield: 113 mg, 58%. Anal. Calcd for $C_{21}H_{30}F_6N_2PIr$: C, 38.94; H, 4.67; N, 4.33. Found: C, 38.94; H, 4.90; N, 3.79. ^{1}H NMR (300 MHz, CD_3CN, 300 K): δ 7.52 (dd, 1H, H6, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 1.5 Hz), 7.14 (d, 1H, H3, $^3J_{HH}$ = 7.2 Hz), 6.95−7.05 (m, 2H, H4 + H5), 3.82 (s, 2H, CH_2), 2.87 (s, 6H, $N(CH_3)_2$), 1.65 (s, 15H, η^5-$C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN, 300 K): δ 150.1 (s, C_1), 148.5 (s, C_2), 135.8 (s, C_6), 127.9 (s, C_5), 124.5 (s, C_4), 123.1 (s, C_3), 91.7 (s, η^5-$C_5(CH_3)_5$), 76.4 (s, CH_2), 55.7 (s, $N(CH_3)_2$), 9.3 (s, η^5-$C_5(CH_3)_5$).

X-ray Crystallography. Single crystals suitable for X-ray diffraction analysis were obtained by cooling a saturated solution of CH_2Cl_2 to −20 °C (**16**), by slow evaporation of a saturated solution of CH_3CN (**15**), or by slow diffusion of *n*-pentane into a saturated solution in CH_2Cl_2 (**9**, **12**, **14**). The X-ray data were collected on a KappaCCD diffractometer with Mo Kα graphite-monochromated radiation (λ = 0.71073 Å) at 173 K. Details of data collection parameters and refinements results are listed in Table 2. The structures were solved using direct methods. Hydrogen atoms were introduced as fixed contributors at calculated positions (C−H = 0.95 Å, B(H) = 1.3 B_{eqv}). Final difference maps revealed no significant maxima. All calculations were done using the SHELXL-97 package.[74]

Acknowledgment. The authors are grateful to Christina Sizun and Roland Graff for NMR experiments (selective inversions). We thank DSM (N.L.) and the Ministère de l'Education Nationale (F) for fellowships (to N.P. and J.-B.S., respectively) and the CNRS for partial support of this work.

Supporting Information Available: Structural data of complexes **8**, **10**, **12**, **14**, section of ROESY spectrum and NMR inversion−recovery experiments on complex **8**, and an ORTEP view of complex **10** in PDF format. Crystallographic data in CIF format for **10**, **12**, and **14**−**16** (for compound **8** see ref 28). These materials are available free of charge via the Internet at http://pubs.acs.org.

OM060973T

(74) Sheldrick, M. *SHELXL-97, Program for crystal structure refinement*; University of Göttingen: Germany, 1997.