A Novel Chiral Ferrocene-Based Amidine/Amidinato Ligand and Its Rhodium Complexes

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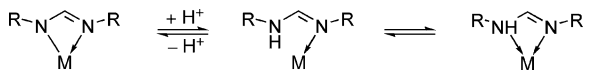
The *N*,*N*′-bisferrocenyl-substituted chiral formamidine **1** (*N*,*N*′-bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)-ethyl}ferrocen-1-yl]formamidine) was prepared from commercially available {(1*R*)-1-(dimethylamino)-ethyl}ferrocene by a multistep procedure in an overall yield of 29%. Deprotonation of **1** followed by addition of $[Rh_2Cl_2(COD)_2]$ yielded the (formamidinato)rhodium(I) complex **2** [(*N*,*N*′-bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)ethyl}ferrocen-1-yl]formamidinato)rhodium(I)]. Direct reaction of formamidine **1** with $[Rh_2Cl_2(COD)_2]$ led to complex **10** [(*κ*-*N*,*P*-bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)ethyl}ferrocen-1-yl]formamidine)(chloro)(η^4-1,5-cyclooctadiene)rhodium(I)], which was converted to **2** upon addition of base. Oxidative addition of methyl chloride or methyl iodide to **2** yielded the *trans* adducts **11** [(*N*,*N*′-bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)ethyl}ferrocen-1-yl]formamidinato)(chloro)(methyl)rhodium(III)] and **12** [(*N*,*N*′-bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)ethyl}ferrocen-1-yl]formamidinato)(iodo)(methyl)-rhodium(III)], the configurations of which were determined by means of NMR and, in the case of the Rh(III) methyl chloride adduct **11**, by X-ray analysis.

Introduction

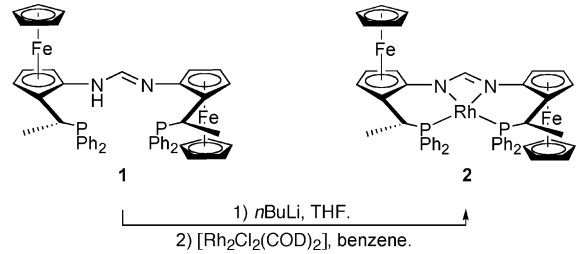
Mononuclear rhodium complexes bearing amidinato ligands are very rare,[1−4] even though in the recent past an increasing number of amidinato transition-metal complexes have been reported.[5] Surprisingly, neither molecules with both a phosphane and an amidinato functionality nor chiral amidinates acting as N,N-donors have ever been used as ligands in mononuclear rhodium complexes of known composition. Consequently, the ability of the latter to act as catalysts in asymmetric catalytic transformations remains fully unexplored.[6] We believe that chiral amidinato ligands with pendant phosphane side chains of appropriate size capable of forming chiral mononuclear rhodium complexes might give access to a new class of chiral catalyst systems worth exploring. Most importantly, the amphoteric nature of the amidine functionality in close proximity to the metal may fulfill the function of taking up or releasing one proton, thereby taking advantage of its different possible coordination modes (Scheme 1).[5]

Scheme 1. Possible Coordination Modes of Amidine/Amidinato Ligands



Ferrocene-based phosphane ligands, on the other hand, are well established in coordination chemistry and have proven to be very successful in asymmetric catalysis.[7] Nevertheless, no attempts have been made to incorporate the amidinato structural motif into a ferrocenyl phosphane.[8] To the best of our knowledge, the only published examples of directly ferrocenyl-substituted amidines are the achiral *C*-ferrocenyl-containing amidines reported by Arnold[4,9] and by Walton[10] and the chiral and achiral *N*,*N*′-bisferrocenyl-substituted amidines reported from our laboratory.[11,12]

Scheme 2



We disclose here the synthesis of the chiral *N*,*N*′-bisferrocenyl-substituted chelating phosphane-amidinato ligand **1** and its Rh(I) complex **2** (Scheme 2). The unique pH-dependent coordination modes of **1** to form Rh(I) complexes are described (the latter were analyzed in solution by NMR). The constitutions and configurations of Rh(III) complexes accessible by oxidative addition of methyl chloride or methyl iodide have been determined in solution. Furthermore, X-ray diffraction studies were performed on the isolated and fully characterized methyl chloride adduct.

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(1) Piraino, P.; Tresoldi, G.; Faraone, F. *J. Organomet. Chem.* **1982**, *224*, 305−312.

(2) Piraino, P.; Bruno, G.; Tresoldi, G.; Faraone, G.; Bombieri, G. *J. Chem. Soc., Dalton Trans.* **1983**, 2391−2395.

(3) Lahoz, F. J.; Tiripicchio, A.; Tiripicchio-Camellini, M.; Oro, L. A.; Pinillos M. T. *J. Chem. Soc., Dalton. Trans.* **1985**, 1487−1493.

(4) Hagadorn, J. R.; Arnold, J. *J. Organomet. Chem.* **2001**, *637*−*639*, 521−530.

(5) For reviews, see: (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219−300. (b) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403−481. For recent examples, see: (c) Munslow, I. J.; Wade, A. R.; Deeth, R. J.; Scott, P. *Chem. Commun.* **2004**, 2596−2597. (d) Li, J.-F.; Huang, S.-P.; Weng, L.-H.; Liu, D.-S. *Eur. J. Inorg. Chem.* **2003**, 810−813. (e) Zhang, Y.; Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2003**, *125*, 8746−8747.

(6) The catalytic hydrogenation of unsymmetrical olefins using systems consisting of $[Rh_2Cl_2(C_8H_{14})_4]$ and different chiral amidinates was reported by Brunner et al. Since no complexes were isolated or described, the possible coordination mode (mono- or multinuclear, monocoordinating or chelating) of the amidinate and thereby the nature of the catalytic species remain unclear. The reported ee's of 1.5−2.0% are low. See: Brunner, H.; Agrifoglio, G. *Monatsh. Chem.* **1980**, *111*, 275−287.

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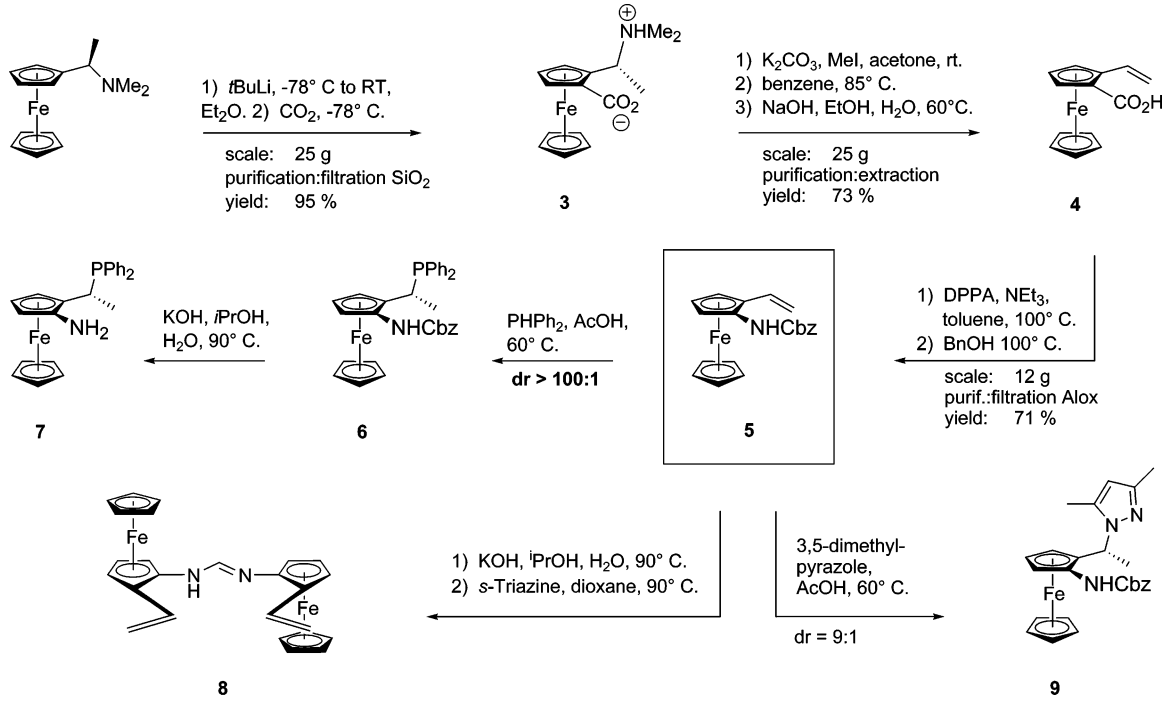
Publication on Web 12/20/2005

Scheme 3



Results and Discussion

Direct Access to Planar-Chiral Aminoferrocenes. The Cbz-protected aminoferrocene **5** was synthesized from the commercially available Ugi amine[13] in a protocol comprising three synthetic operations (Scheme 3). Although most synthetic operations involve more than one chemical transformation, only one purification step is required. Thus, each of the three synthetic operations can be accomplished without the isolation of intermediate species within 1 day at most. The planar-chiral 2-vinyl-substituted Cbz-protected aminoferrocene **5** is easily recognized as a central intermediate in the synthesis of **1** (Schemes 3 and 4).

We took care to optimize the synthetic steps leading from the Ugi amine to the carbamate **5** such that they can be carried out on a large scale. In particular, all three purification steps were carried out with relatively large amounts of material, and no column chromatography is required. This highlights the potential of the pathway presented here to give ready access to enantiopure planar-chiral aminoferrocenes, a synthetic problem that has attracted considerable interest in the past due to the significance of aminoferrocenes as intermediates in the syntheses of ligands and optically active materials.[14−17] Furthermore, the vinylic double bond in the Cbz-protected aminoferrocene **5** represents a highly reactive functionality allowing for a wealth of transformations, optionally leading to either planar-chiral or both central and planar-chiral products. Apart from the highly diastereoselective ionic additions to the vinylic double bond of **5** presented below, vinylferrocenes have been shown to participate in pericyclic reactions such as 1,3-dipolar cycloadditions[18] or Diels−Alder[19] reactions.

Ligand Synthesis. To synthesize the amino acid **3** from Ugi's amine, the latter was lithiated and reacted in situ with gaseous carbon dioxide following a modified procedure based on a protocol of Cullen et al. (Scheme 3).[20] As a direct elimination of the amino function in **3** to yield the (*S*)-1-carboxyl-2-vinylferrocene **4** could not be accomplished, we developed a synthetic sequence consisting of three chemical transformations serving this specific purpose. The methylation of both the amine and acid functionalities of the amino acid **3** yielded an intermediate tetraalkylammonium methyl carboxylate which

(7) Togni, A., Hayashi, T., Eds. *Ferrocenes*; Wiley-VCH: Weinheim, 2002.

(8) *N,N,N′*-Trisubstituted chiral amidine ligands, not able to act as amidinato donors, were reported by Hu, X.; Chen, H.; Dai, H.; Hu, X.; Zheng, Z. *Tetrahedron: Asymmetry* **2003**, *14*, 2073−2080.

(9) (a) Hagadorn, J. R.; Arnold, *Inorg. Chem.* **1997**, *36*, 132−133. A more recent paper describes the in-situ generation of boron complexes bearing the ligand described by Hagadorn and Arnold. See: (b) Hill, N. J.; Findlater, M.; Cowley, A. H. *J. Chem. Soc., Dalton Trans.* **2005**, 3229−3234.

(10) Reddy, N. D.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **2001**, *319*, 224−228.

(11) Bertogg, A.; Camponovo, F.; Togni, A. *Eur. J. Inorg. Chem.* **2005**, 347−356.

(12) Knox et al. observed *N*-ferrocenyl-*N′*,*N′*-diisopropyl formamidine as a trace byproduct in the decyanation of isocyanoferrocene. See: Know, G. R.; Pauson, P. L.; Willison, D. *Organometallics* **1990**, *9*, 301−306.

(13) {(1*R*)-1-(Dimethylamino)ethyl}ferrocene.

(14) Herberhold, M. Ferrocene Compounds Containing Heteroelements. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; Wiley-VCH: Weinheim, 2002.

(15) Aminoferrocene was first synthesized by Nesmeyanov (ref 16), who treated lithiated ferrocene with the *O*-benzyl ether of hydroxylamine and isolated the product in 25% yield. In the same year Arimoto and Haven synthesized aminoferrocene (ref 17) from ferrocenyl carboxylic acid by using the Curtius synthetic strategy, but the overall yield was lower than 20%. The planar-chiral (*R*)-1-amino-2-vinylferrocene presented here has not been described previously.

(16) Nesmeyanov, A. N.; Perevalova, E. G.; Golovnya, R. V.; Shilovtseva, L. S. *Dokl. Akad. Nauk. SSSR* **1955**, *102*, 535; *Chem. Abstr.* **1956**, *50*, 4925g.

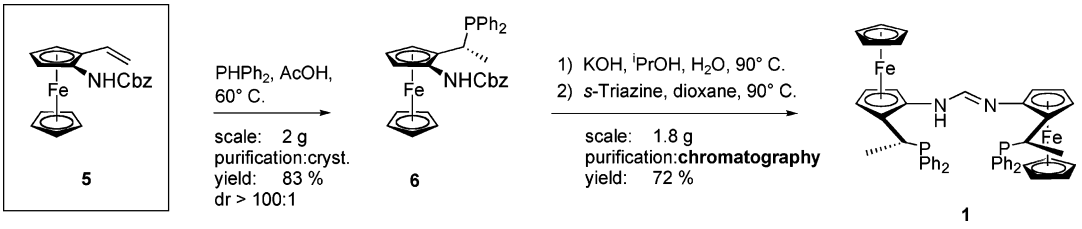
(17) Arimoto, F. S.; Haven, A. C. *J. Am. Chem. Soc.* **1955**, *77*, 6295−6297.

(18) (a) Shvekhgeimer, G. A.; Litim, M. *Izv. Akad. Nauk, Ser. Khim.* **1994**, *1*, 139. (b) Argyropoulos, N.; Coutouli-Argyropoulos, E. *J. Organomet. Chem.* **2002**, *654*, 117−122. (c) Nemeroff, N.; McDonnell, M. E.; Axten, J. M.; Buckley, L. J. *Synth. Commun.* **1992**, *22*, 3271−3275.

(19) (a) Prokesova, M.; Solcaniova, E.; Toma, S.; Muir, K. W.; Torabi, A. A.; Knox, G. R. *J. Org. Chem.* **1996**, *61*, 3392−3397. (b) Klimova, E. I.; Garcia, M. M.; Klimova, T.; Toledano, C. A.; Toscano, R. A.; Ramirez, L. R. *J. Organomet. Chem.* **2000**, *598*, 254−261. (c) Klimova, T.; Klimova, E. I.; Martinez Garcia, M.; Alvarez Toledano, C.; Toscano, R. A. *J. Organomet. Chem.* **2003**, *665*, 23−28.

(20) (a) Cullen, W. R.; Wickenheiser E. B. *Can. J. Chem.* **1990**, *68*, 705−707. (b) Beyer, L.; Richter, R.; Seidelmann, O. *J. Organomet. Chem.* **1998**, *561*, 199−201.

Scheme 4



allowed for a thermal elimination of trimethylamine, thereby avoiding the risk of lactonization thanks to the methyl protection of the carboxylic acid function. Saponification of this intermediate methyl ester then led to the targeted ferrocene carboxylate **4**. Several methods to access the ferrocene−nitrogen bond such as present in **5** have been described in the literature, including protocols starting from bromoferrocene[21] or ferroceneboronic acid.[22] As in our previous syntheses of aminoferrocenes,[11] we chose a different strategy based on a Curtius degradation sequence that surpasses the aforementioned protocols in terms of synthetic feasibility and that allows for a high-yielding large-scale synthesis of the protected aminoferrocene **5**. Using DPPA[23] (diphenylphosphoryl azide) as both an activating reagent and azide donor toward **4**, we converted the carboxylic acid function to the corresponding carbonyl azide, which rearranged in situ to an isocyanate, which was further reacted with benzylic alcohol to yield carbamate **5**.

Tracing the chiral information present in **6** and **9** back to Ugi's amine reveals a chirality transfer from an element of central chirality present in the starting material to the planar chirality of the ferrocenyl core. In turn, we used this planar chirality in going from **5** to either **6** or **9** to generate a new stereocenter. Even though the one present in Ugi's amine was lost in the subsequent elimination sequence, its stereochemical information was preserved in the planar-chiral ferrocene derivative and was finally recovered by performing diastereoselective additions to the olefinic double bond of the vinylferrocene **5**. Reacting the latter with 3,5-dimethylpyrazole in acetic acid yielded the internally hydrogen-bridged[24] heterocyclic adduct **9**[25] with a dr = 9:1, whereas adding diphenylphosphane under analogous conditions led to the phosphane **6** with complete diastereoselectivity. We think that this difference in selectivity is best explained by steric differences between the two reagents.[26]

Hydrolysis of the carbamate function in **6** leads to the air-sensitive, though thermally stable amine **7**, which could be considered an interesting potential ligand in its own right. Conformational analysis of the aminoferrocene **7** based on NMR studies (full assignment and NOESY experiments) revealed hindered rotation around the Ph_2P-C bond such that the phosphorus lone-pair vector bisects the $Cp-CH-CH_3$ angle, thus minimizing steric strain (for a drawing and NMR data, see Experimental Section). Hydrolysis of the Cbz-protected amine **5** and subsequent reaction of the resulting primary amine with *s*-triazine, which acts as a CH group donor,[11,27] allows for the isolation of the amidine **8**. In its monoprotonated form, the potential ligand precursor **8** crystallizes as a hydrogen-bonded dimer. A representation of the solid-state structure is shown in Figure 1, and selected bond lengths and angles are given in Table 1. The observed C−N/C═N bond lengths have to be seen as a result of the hydrogen-bridged structure, leading to bond orders between one and two. The dihedral angles between the ferrocenyl Cp plane and the amidine N═C(H)NH plane appear to be mainly determined by crystal-packing effects.[28]

As can be seen in Scheme 4, we chose not to isolate the aminoferrocene **7** for reasons of synthetic convenience, when completing the preparation of the amidine **1** by reacting the crude amine **7** with *s*-triazine. The access to ligand **1** therewith consists of five synthetic operations mostly comprising several chemical transformations and one purification step. Note again that the first three operations have been performed on a relatively large scale whereby only the final product requires a chromatographic purification.

Synthesis of Rh(I) and Rh(III) Complexes. Much of our interest in ligand **1** arises from its amphoteric nature, allowing for either protonation or deprotonation at the nitrogen atoms, thus leading to an amidinium cation, a neutral amidine, or an

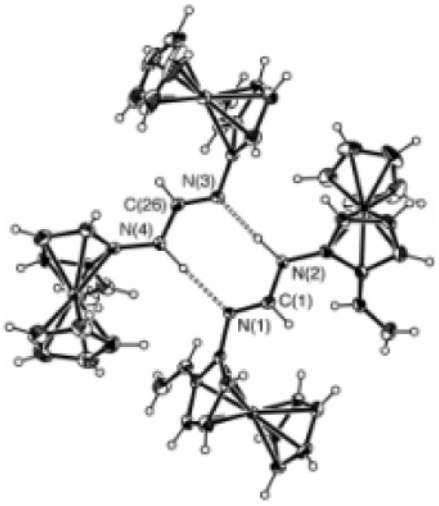


Figure 1. ORTEP view of the hydrogen-bridged dimer of **8** (30% thermal ellipsoids). The hydrogens on N(2) and N(4) were located and refined.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 8

C(1)−N(1)	1.262(6)	N(2)−H(N2)	1.06(2)
C(1)−N(2)	1.347(6)	N(4)−H(N4)	1.08(2)
C(26)−N(3)	1.268(6)	N(3)−H(N2)	1.81(2)
C(26)−N(4)	1.347(6)	N(1)−H(N4)	2.04(4)
N(1)−C(1)−N(2)	124.4(4)	N(2)−H(N2)−N(3)	177(5)
N(3)−C(26)−N(4)	124.2(4)	N(4)−H(N4)−N(1)	161(9)

(21) (a) Nesmejanow, A. N.; Ssasonowa, W. A.; Drosd, V. N. *Chem. Ber.* **1960**, *93*, 2717−2729. (b) Sato, M.; Ebine, S.; Akabori, S. *Synthesis* **1981**, 472−473. (c) Herberhold, M.; Ellinger, M.; Kremnitz, W. *J. Organomet. Chem.* **1983**, *241*, 227−240.

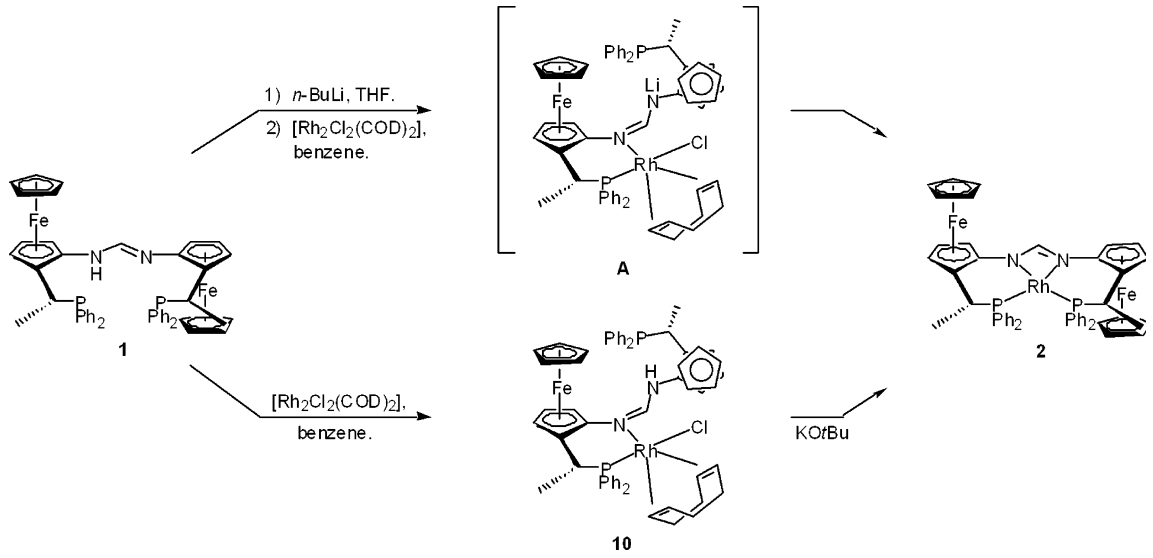
(22) Montserrat, N.; Parkins, A. W.; Tomkins, A. R. *J. Chem. Res.-Synop.* **1995**, 8, 336−337.

(23) Ninoma, K.; Shioiri, T.; Yamada, S. *Tetrahedron* **1974**, *30*, 2151−2157.

(24) ^{1}H NMR and NOESY NMR data allowed for the identification of a hydrogen bridge between the carbamate N*H* and the pyrazole 2-*N*, leading to the formation of a seven-membered ring.

(25) The Cbz-protected aminoferrocene **9** can be regarded as a nitrogen analogue of the well-known pyrazole-containing ferrocenyl phosphanes. See: (a) Schnyder, A.; Hintermann, L.; Togni, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 931−933. (b) Burckhardt, U.; Hintermann, L.; Schnyder, A.; Togni, A. *Organometallics* **1995**, *14*, 5415−5425. Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031−1037.

Scheme 5



amidinato anion. By assuming that the phosphorus atoms are not protonated, the maximal theoretical hapticity of the ligand can be set to either two, three, or four, depending on the presence of weak acid or base. Thereby, ligand **1** can be used to form different complexes with a given transition metal.

Reacting a lithium salt obtained after deprotonation of amidine **1** by *n*-butyllithium with $[Rh_2Cl_2(COD)_2]$ for several hours at room temperature yields the fully saturated square planar Rh(I) complex **2** (Scheme 5).

However, shorter reaction times disclose the intermediate formation of a Rh(I) species **A** of uncertain structural assignment that reacts cleanly to the target compound **2** over several hours. Even though a complete NMR characterization of this intermediate species proved impossible due to its reactivity, the ^{31}P NMR data strongly suggests the bidentate coordination mode of the amidinato phosphane ligand. Evidence comes from the inequivalence of the two phosphorus resonances out of which one displays a $^{103}Rh/^{31}P$ coupling constant of 138 Hz at a chemical shift of 54.0 ppm, thus demonstrating phosphorus coordination, while the other one appears at higher field as a singlet. Chloride and 1,5-cyclooctadiene complete the coordination sphere of the 18-e Rh(I) center.

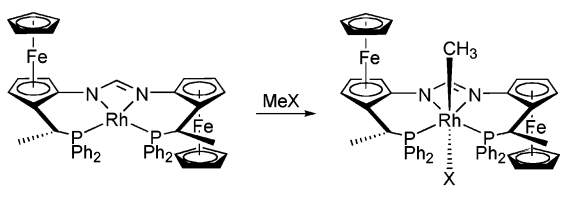
To gain further evidence for the intermediate species and due to our interest in the different coordination modes of amidines and amidinates, we reacted amidine **1** with $[Rh_2Cl_2(COD)_2]$ without prior deprotonation. The five-coordinate Rh(I) complex **10** was identified as the reaction product by performing extensive NMR studies on the product solution. In addition to the spectral data discussed above, $^{103}Rh/^{1}H$ coupling between the Rh center and the formamidinate C*H* proton proves the bidentate PN coordination mode in complex **10**. Further NMR data supporting the structure of Rh(I) complex **10** can be found in the Experimental Section. As expected, addition of base to compound **10** led to the square-planar Rh(I) complex **2**. The observation that complex **2** can be accessed either by reacting the lithium formamidinate with $[Rh_2Cl_2(COD)_2]$ or by simply mixing **1** with $[Rh_2Cl_2(COD)_2]$, followed by the addition of base, is crucial with regard to the use of **2** as catalyst under basic reaction conditions.

Attempts to oxidatively add either methyl chloride or methyl iodide to complex **2** proved successful and yielded both the Rh(III) complexes **11** and **12**, respectively (Scheme 6). Most probably, the anionic nature of the chelating formamidinato unit and its ability to act as σ donor allow the oxidative addition of methyl chloride to occur quickly at room temperature. We look at this addition reaction as an initial experiment in the context of the application of **2** as a catalyst in asymmetic transformations involving oxidative addition and reductive elimination steps of substrate molecules. That both **11** and **12** are formed as single configurational isomers deserves mention. Obviously, this complete selectivity in activating both methyl chloride and methyl iodide, molecules that are generally thought to react via different transition states, defines a promising starting point for asymmetric catalysis studies.

Structure Elucidation of Rh(III) Complexes in Solution and in the Solid State. While the structure elucidation proved simple for the C_2-symmetric Rh(I) complex **2**, the configurations of the methyl halide adducts **11** and **12** are less easily assigned as a result of the considerable number of possible stereoisomers.[29] We discuss here the structure elucidation of **11**; anologous data for **12** can be found in the Experimental Section.

The ^{31}P NMR spectral data proved crucial in view of establishing the oxidation state of the Rh center by means of

Scheme 6



(26) Substitution reactions at planar-chiral derivatives of Ugi's amine occurring with replacement of the dimethylamino group by an incoming nucleophile often proceed with high levels of diastereoselectivity. Since such substitution reactions are known to follow a S_N1 pathway in acetic acid as a solvent, the intermediate carbocation is easily recognized as a common intermediate in both the S_N1 reactions and the addition reactions presented here. Therefore, one must assume that the levels of diastereoselectivity for substitution reactions and addition reactions are based in either case on the steric requirement of both the attacking reagent and the substituent in ortho position. The nature of the leaving group and the way in which the carbocation is generated, on the other hand, do not influence the diastereoselectivity of the reaction.

(27) Grundmann, C.; Kreutzberger, A. *J. Am. Chem. Soc.* **1955**, *77*, 6559−6562.

(28) For a conformational analysis of *N*-ferrocenyl-substituted N-heterocyclic carbenes see ref 11.

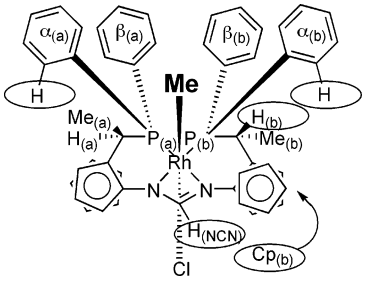


Figure 2. NOESY contacts between the metal-bound methyl group and hydrogen atoms (encircled) of the chelating ligand.

the $^{31}P/^{103}Rh$ coupling constants—$J(^{31}P_{(a)}/^{103}Rh) = 134$ Hz; $J(^{31}P_{(b)}/^{103}Rh) = 131$ Hz[30]—while the $^{31}P/^{31}P$ coupling constants—$J(^{31}P_{(a)}/^{31}P_{(b)}) = 18$ Hz—provided evidence for the mutual *cis* arrangement of the two phosphorus atoms in the Rh(III) complex. The $^{31}P/^{1}H$ couplings—$J(^{31}P_{(a)}/^{1}H_{(Me)}) = 2.2$ Hz; $J(^{31}P_{(b)}/^{1}H_{(Me)}) = 2.2$ Hz—measured by means of ^{1}H NMR and $^{31}P/^{1}H$ correlation spectroscopy, provide direct evidence for the methyl−rhodium bond. Furthermore, the couplings from either phosphorus nuclei to their adjacent methyne and methyl groups, as well as to the formamidinato proton, are indicative of the tetradentate coordination mode of the formamidinato ligand. The $^{103}Rh/^{1}H$ correlation data gave additional evidence for this coordination mode and provided the coupling constants between the Rh(III) center and the hydrogen nuclei in its vicinity. Conformational analysis of the two six-membered chelate rings in the Rh(NP) structural motif based on those coupling constants between the ^{103}Rh nucleus and the two methyne hydrogen atoms— $^{1,4}J(^{103}Rh/^{1}H_{(methyne\ a)}) = 0.6$ Hz; $^{1,4}J(^{103}Rh/^{1}H_{(methyne\ b)}) = 0.5$ Hz—as compared to the couplings between ^{103}Rh and the formamidinato hydrogen atom—$^{1,4}J(^{103}Rh/^{1}H_{(formamidinato)}) = 3.0$ Hz—is not possible, as coefficients for an appropriate Karplus equation are not available. Nevertheless, the apparent pseudosymmetry of the formamidinato ligand with very similar $^{103}Rh/^{1}H$ couplings to either methyne hydrogen atom strongly supports an equatorial arrangement of the tetradentate ligand. The final proof for this *trans* chelation mode, thus ruling out all other possible stereoisomers, is based on NOESY spectral data that display contacts of the metal-bound methyl group to parts of the formamidinato ligand, as expected for an equatorial ligand arrangement (Figure 2). Most importantly, the observed NOESY contacts between the metal-bound methyl group and the ortho hydrogen atoms of both α-phenyl groups at phosphorus $P_{(a)}$ and phosphorus $P_{(b)}$ are only consistent with an equatorial arrangement of the tetradentate ligand. Furthermore, the contacts to the methyne$_{(b)}$ hydrogen atom, to $Cp_{(b)}$, and to the formamidinato hydrogen atom clearly prove the *trans* Rh(III) complex to be the only isomer of **11** present in solution.

Single-crystal X-ray analysis of the Rh(III) complex **11** revealed a structure that is in complete agreement with the observed configuration in solution. The solid-state structure is represented in Figure 3, whereas selected bond lengths and angles can be found in Table 2. The organometallic species **11**

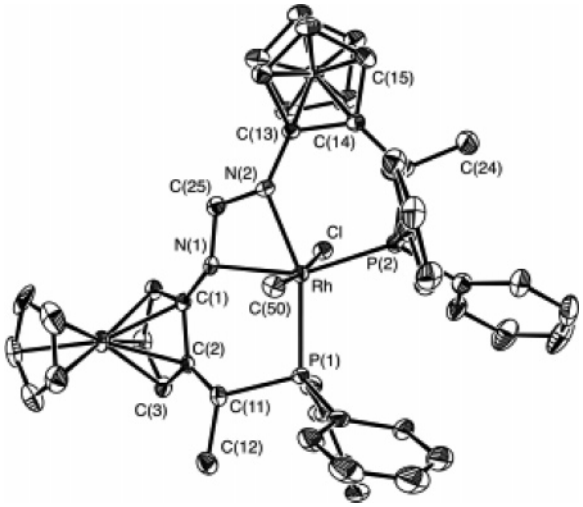


Figure 3. ORTEP view of the Rh(III) complex **11** (30% thermal ellipsoids).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 11

N(1)−Rh	2.075(6)	N(1)−Rh−N(2)	63.4(3)
N(2)−Rh	2.055(6)	N(1)−Rh−P(1)	94.23(18)
C(50)−Rh	2.071(6)	N(2)−Rh−P(2)	93.73(19)
P(1)−Rh	2.2824(19)	P(1) −Rh−P(2)	108.63(7)
P(2)−Rh	2.2623(19)	N(1)−C(25)−N(2)	109.9(7)
Cl−Rh	2.4998(19)	C(50)−Rh−Cl	173.3(2)
C(25)−N(1)	1.340(10)	C(25)−N(2)	1.311(10)

is best described as an octahedral complex with a strongly distorted arrangement of the donor atoms in a regular equatorial plane occupied by the tetradentate formamidinato ligand. On the other hand, the axial methyl and chloride ligands lie almost in line—angle $C_{(50)}$−Rh−Cl 173.3(4)°—and show the expected bond lengths to the metal—$C_{(50)}$−Rh 2.071(6) Å; Cl−Rh 2.4997(19) Å. Conformational freedom in the two six-membered chelate rings appears to be rather restricted, partly due to the necessity for phosphorus and nitrogen atoms to lie in the equatorial coordination plane and partly due to the well-known tendency of derivatives of Ugi's amine to give rise to small dihedral angles between the ferrocene Cp planes and their neighboring methyl groups (dihedral angles $C_{(24)}-C_{(23)}-C_{(14)}-C_{(15)}$ 6.3(12)°; $C_{(12)}-C_{(11)}-C_{(2)}-C_{(3)}$ −13.4(11)°). The bite angle $N_{(1)}$−Rh−$N_{(2)}$ of 63.4(3)° as well as the bond lengths of the formamidinato unit are in a surprisingly exact agreement with the sparse structural data available for Rh amidinato complexes.[3,4] In fact, two X-ray structures of mononuclear Rh complexes containing amidinato ligands are known in the literature. However, in contrast to the Rh(III) complex discussed here, these are Rh(I) compounds. Although both of those complexes lack further chelating atoms, they nevertheless exhibit bonding parameters very similar to the ones measured for **11**. Therefore, one may assume that in **11** the position of the Rh(III) core is mainly determined by the formamidinato unit, whereas the two phosphorus donor atoms further stabilize the structure by creating a cavity that fits the radius of the Rh(III) center. The two P/N bite angles of 93.73(19)° and 94.22(18)° and the normal Rh−P bond lengths $P_{(1)}$−Rh of 2.2824(19) Å and $P_{(2)}$−Rh of 2.2623(19) Å account for this view, whereas the slight bending of the formamidinato unit out of the N/Rh/N plane—dihedral angle Rh−$N_{(1)}$−$C_{(25)}$−$N_{(2)}$ 10.0(4)°—is probably best explained by crystal-packing effects.

Conclusions

The *N*,*N*′-bisferrocenyl-substituted chiral formamidine **1** was prepared in 29% overall yield from the commercially available

(29) Ordering those possible isomers according to the arrangement of the tetradentate ligand in the complex discloses one *trans*, two α-*cis*, and four *β*-*cis* configurations. Only in the *trans* configuration does the ligand not adopt a helical conformation. In the α-*cis* arrangement and in the *β*-*cis* arrangement on the other hand, the helicity mentioned above gives rise to Δ and Λ isomers. Furthermore, the *β*-*cis* arrangement allows for two additional isomers by exchanging the two nonequivalent monodentate ligands. As a result of the chirality of the formamidinato ligand, all seven possible isomers are diasteroisomeric with respect to each other.

(30) For a collection of ^{31}P and ^{13}C NMR data on transition-metal complexes see: Pregosin, P.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer: Berlin, 1979.

Ugi amine[13] by applying a synthetic strategy exploiting a Curtius degradation as the key step. As a direct product of the latter, the planar-chiral, *N*-protected 2-vinyl aminoferrocene **5** not only serves as a precursor to **1** but also allows for accessing planar-chiral aminoferrocenes on a large synthetic scale in a short and reliable synthetic route.

Deprotonation of the formamidine **1** followed by addition of $[Rh_2Cl_2(COD)_2]$ yielded the (formamidinato)rhodium(I) complex **2**, whereas in the absence of base the (chloro)(1,5-cyclooctadiene)(formamidine)rhodium(I) complex **10** was formed. Notably, formamidine **1** acts as a P,N-bidentate ligand in **10**, while its anionic counterpart acts as a tetradentate donor in derivative **2**. The latter was also accessible by adding base to a solution of **10**. These pH-dependent coordination modes of the amidinato/amidine ligand system account for its ability to act as a proton scavenger, which is of considerable interest with regard to catalytic transformations. Currently, efforts are being undertaken to use both **2** and **10** as catalysts, thereby taking advantage of the amphoteric nature of ligand **1**.

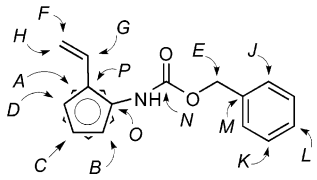
To study the activity of **2** toward the oxidative addition of alkyl halides, we reacted it with both methyl chloride and methyl iodide to give the corresponding Rh(III) complexes **11** and **12**. The configuration of the three complexes **2**, **11**, and **12** is such that the four donor atoms share the main equatorial plane in the coordination sphere of the metal. We think that this indicates a significant conformational rigidity of the ligand in its tetradentate form, which may be important in view of asymmetric catalytic applications.

Experimental Section

General Considerations. All experiments were conducted under an atmosphere of argon or dinitrogen using standard Schlenk-type glassware or a glovebox. All solvents were stored over activated 4 Å molecular sieves unless otherwise indicated. In the case of freshly distilled solvents, the following drying agents were used: Na/benzophenone for THF and Et_2O; Na for toluene, benzene, C_6D_6, and d_8-THF. Chromatography was carried out with Merck silica gel 60. The NMR spectra were recorded on Bruker Avance 250 (250.1 MHz, ^{1}H; 62.5 MHz, ^{13}C; 101 MHz, ^{31}P), 300 (300.1 MHz, ^{1}H; 75.0 MHz, ^{13}C; 122 MHz, ^{31}P), 500 (500.2 MHz, ^{1}H; 125 MHz, ^{13}C; 203 MHz, ^{31}P; 15.9 MHz, ^{103}Rh), and 700 (700.1 MHz, ^{1}H; 175 MHz, ^{13}C; 284 MHz, ^{31}P; 22.2 MHz, ^{103}Rh) spectrometers. ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, and ^{103}Rh NMR chemical shifts (δ) were referenced internally by the residual solvent signal. All spectra were recorded at room temperature. Optical rotations were measured in 1 dm cells on a Perkin-Elmer model 341 polarimeter at 22 °C. High-resolution MALDI mass spectra were measured by the analytical service of the Laboratorium für Organische Chemie of the ETH Zürich on a IonSpec ultima FT MALDI mass spectrometer. Elemental analyses were obtained on a Leco CHN-900 analyzer. All commercially available chemicals were used without further purification. We were generously supplied with {(1*R*)-1-(dimethylamino)ethyl}ferrocene (ee ≈ 96%) by Solvias AG (Basel, Switzerland). Prior to use, the latter was recrystallized as tartrate salt according to the procedure reported by Gokel et al.[31] in order to completely separate it from its antipode.

(1*S*)-1-Carboxyl-2-{(1*R*)-1-(dimethylamino)ethyl}ferrocene (3). In a flame-dried 1 L Schlenk vessel, optically pure [(1*R*)-1-(dimethylamino)ethyl]ferrocene (24.81 g, 96.50 mmol, 1 equiv) was dissolved in 200 mL of freshly distilled Et_2O, cooled to −78 °C, and treated with *t*BuLi (59.6 mL, 101.3 mL, 1.05 equiv). After stirring for 1 h, the clear red solution was warmed to rt and further stirred for 3 h, which resulted in the formation of a yellow precipitate. The addition of CO_2(g) during 1 h at −78 °C caused the immediate formation of a yellow solid. To make sure that the lithiated intermediate had reacted completely, ca. 30 g of CO_2(*S*) was added to the reaction mixture followed by its slow warming to rt. Then, the solvent was evaporated and a solution of the crude product in MeOH was quickly filtered on silica gel (400 g, column ϕ ca. 9 cm). After evaporation of the solvent, the crude product was taken up in CH_2Cl_2, and the solution was dried over $MgSO_4$, filtered, and evaporated under reduced pressure, affording the isolation of the title compound as a red amorphous solid. Yield: 27.6 g (95%). ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 1.42 (d, J = 6.6 Hz, 3 H, CHC*H*$_3$), 2.05 (bs, 3 H, NC*H*$_3$CH$_3$), 2.56 (bs, 3 H, NCH$_3$C*H*$_3$), 4.20 (s, 5 H, Cp$_{unsubst}$), 4.27−4.32 (m, 2 H, CH$_{Cp\ subst}$), 4.54 (q, J = 6.8 Hz, 1 H,C*H*CH$_3$), 5.02 (dd, J_1 = 2.4 Hz, J_2 = 1.5 Hz, 1 H, CH$_{Cp\ subst}$). CAS 211574-86-6 (other enantiomer), CAS 128713-34-8 (racemate).

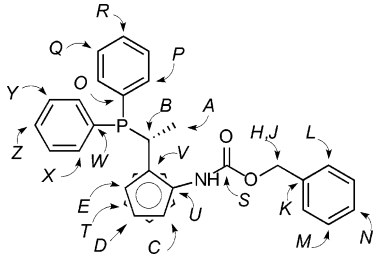
(*S*)-1-Carboxyl-2-vinylferrocene (4). Treating a mixture of compound **3** (25.43 g, 85.30 mmol, 1 equiv), K_2CO_3 (94.58 g, 684 mmol, 8 equiv), and acetone (510 mL) with MeI (43.67 mL, 684 mmol, 8 equiv) led to a clear, deep red solution with an underlying precipitate (K_2CO_3) that was stirred at rt for 3.5 h. Filtration and evaporation of the volatiles resulted in the formation of a red foam, which was taken up in benzene (760 mL) and heated at 85 °C for 45 min. The red oil, which was isolated after filtration and evaporation of the volatiles, was mixed with EtOH (450 mL), H_2O (450 mL), and NaOH (10.28 g, 256 mmol, 3 equiv) and stirred at 60 °C for 13 h. Addition of MTBE at rt, acidification, separation of the resulting organic phase, drying over $MgSO_4$, and evaporation of the solvents afforded **4** as a yellow amorphous solid. Yield: 15.99 g (73%). ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 4.23 (s, 5 H, Cp$_{unsubst}$), 4.53 (t, J = 2.6 Hz, 1 H, CH$_{Cp\ subst}$), 4.85 (t, J = 1.8 Hz, 1 H, CH$_{Cp\ subst}$), 4.95 (dd, J_1 = 2.4 Hz, J_2 = 1.5 Hz, 1 H, CH$_{Cp\ subst}$), 4.95 (dd, J_1 = 2.4 Hz, J_2 = 1.5 Hz, 1 H, CH$_{Cp\ subst}$), 5.22 (dd, J_1 = 10.8 Hz, J_2 = 1.5 Hz, 1 H, CHC*H*$_2$), 5.53 (dd, J_1 = 17.7 Hz, J_2 = 1.5 Hz, 1 H, CHC*H*$_{2t}$), 7.27 (dd, J_1 = 17.7 Hz, J_2 = 10.8 Hz, 1 H, C*H*CH$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 69.1 (Cp$_{subst}$), 70.8 (Cp$_{subst,quat}$), 71.2 (Cp$_{subst}$), 71.4 (Cp$_{unsubst}$), 72.3 (Cp$_{subst}$), 86.1 (Cp$_{subst,quat}$), 113.5 (C$_{olefin}$), 133.2 (C$_{olefin}$), 178.7 (CO_2H). MS (HR MALDI): *m*/*z* 256.0187 (calcd for $C_{13}H_{12}FeO_2$); found 256.0181 [M$^+$]. $C_{13}H_{12}FeO_2$ (256.08): calcd C 60.97, H 4.72, O 12.5, Fe 21.81; found C 60.77, H 4.85. Mp = 115.5 °C. $[\alpha]_{22}$ = +820 (*c* 1, $CHCl_3$).



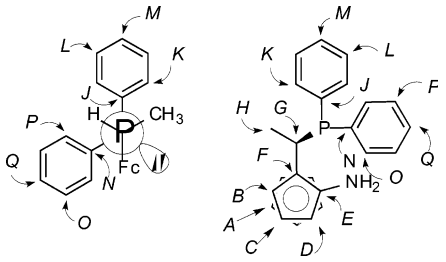
Benzyl *N*-{(*S*)-2-Vinylferrocenyl}carbamate (5). Dry NEt_3 (9.82 mL, 70.3 mmol, 1.5 equiv) and diphenylphosphoryl azide (11.3 mL, 51.5 mmol, 1.1 equiv) were added in this order to a solution of **4** (11.97 g, 46.80 mmol, 1 equiv) in freshly distilled toluene (68 mL) at rt. The clear, deep red solution was stirred for 20 min and then quickly heated to 95 °C. After 10 min the formation of a gas (N_2) was observed. Thirty minutes later benzylic alcohol (9.70 mL, 93.6 mmol, 2.0 equiv) was added, and after another 5 min of stirring at 95 °C, the reaction mixture was cooled to rt. Extraction with MTBE/H_2O, drying of the organic phases with $MgSO_4$, and evaporation of the solvents gave a crude product that was purified by filtration on passivated aluminum oxide (basic, activity II) to give **5** as an amorphous red solid. Yield: 12.00 g (71%). ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 4.10 (s, 5 H, Cp A), 4.11 (dd, J_1 = 2.7 Hz, J_2 = 2.7 Hz, 1 H, Cp D), 4.31 (t, J = 2.7 Hz, 1 H, Cp C), 4.81 (bs, Cp B), 5.18 (dd, J_1 = 11.1 Hz, J_2 = 1.5 Hz, 1 H, vinyl F), 5.18 (s, 2 H, methylene E), 5.42 (dd, J_1 = 17.7 Hz, J_2 = 1.5 Hz, 1 H, vinyl H), 6.02 (bs, 1H, NH), 6.50 (dd, J_1 = 17.5 Hz, J_2 = 10.8 Hz, 1 H, vinyl G), 7.32−7.45 (m, 5 H, phenyl J,K,L). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 62.5 (D), 63.9 (B), 64.9

(31) Gokel, G. W.; Ugi, I. K. *J. Chem. Educ.* **1972**, *49*, 294−296.

(C), 67.2 (E), 70.4 (A), 76.1 (P), 92.9 (O), 113.2 (F,H), 127.9 (K,L), 128.6 (J), 131.4 (G), 136.2 (M), 154.2 (N). MS (HR MALDI): *m*/*z* 361.0765 (calcd for $C_{20}H_{19}FeNO_2$); found 361.0760 [M^+]. $C_{20}H_{19}FeNO_2$ (361.22): calcd C 66.50, H 5.30, N 3.88, O 8.86, Fe 15.46; found C 66.31, H 5.32, N 3.87. $[\alpha]_{22} = +167$ (*c* 1, $CHCl_3$).



Benzyl *N*-[(*S*)-2-{(1*R*)-1-(Diphenylphosphino)ethyl}ferrocenyl]-carbamate (6). Diphenylphosphane (3.86 mL, 22.2 mmol, 4 equiv) was added to a solution of **5** (2.00 g, 5.54 mmol, 1 equiv) in dry acetic acid (9.0 mL) at rt. Stirring for 16 h at 65 °C, evaporation of the solvent and of excess diphenylphosphane under reduced pressure using a distillation apparatus, and washing with pentane yielded a crude product that was recrystallized from *i*PrOH to give **6** as a red crystalline solid. Yield: 2.51 g (83%). Since no signal of a diastereomeric species could be detected in either the ^{1}H or ^{31}P NMR spectra, we assume a dr > 100:1. ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 1.55 (q, $J = 7.0$ Hz, 3 H, A), 3.25 (dq, $J_q = 6.8$ Hz, $J_d = 4.3$ Hz, 1 H, B), 3.87−3.89 (m, 1H, E), 3.99 (dd, $J_1 = 2.6$ Hz, $J_2 = 2.6$ Hz, 1 H, D), 4.12 (s, 5 H, T), 4.59 (bs, 1 H, C), 4.81 (bs, 1 H, NH), 4.98−5.11 (m, 2 H, H,J), 6.99−7.18 (m, 5 H, P,Q,R), 7.31−7.45 (m, 8 H, L−N,X−Z), 7.49−7.58 (m, 2 H, L−N,X−Z). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.9 MHz): δ 18.2 (d, $J = 18.2$ Hz, A), 30.0 (d, $J = 15.0$ Hz, B), 59.9 (s, C), 63.2 (s, E), 63.4 (s, D), 66.7 (s, H,J), 69.5 (s, T), 83.1 (d, $J = 14.7$ Hz, V), 93.9 (s, U), 128.0−129.3 (m, L−N,Q−R,Y−Z), 133.0 (d, $J = 17.6$ Hz, P), 134.0 (d, $J = 19.6$ Hz, X), 135.9 (d, $J = 16.0$ Hz, O or W), 136.3 (d, $J = 16.7$ Hz, O or W), 153.3 (s, S). ^{31}P NMR ($CDCl_3$ 101.3 MHz): δ 3.4. MS (HR MALDI): *m*/*z* 548.1442 (calcd for $C_{32}H_{31}FeNO_2P$); found 548.1436 [MH^+]. $C_{32}H_{30}FeNO_2P$ (547.40): calcd C 70.21, H 5.52, N 2.56, O 5.85, P 5.66, Fe 10.20; found C 69.99, H 5.63, N 2.53, P 5.76. Mp = 153.5 °C. $[\alpha]_{22} = -375$ (*c* 1, $CHCl_3$).



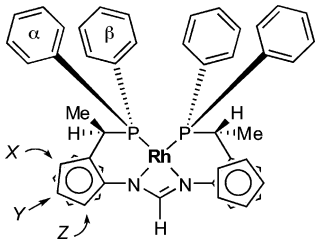
(*S*)-2-{(1*R*)-1-(Diphenylphosphino)ethyl}aminoferrocene (7; the picture shows its conformation in solution). A suspension of **6** (2.39 g, 4.36 mmol) in *i*PrOH (30 mL) and H_2O (30 mL) was degassed with Ar using an ultrasonic bath and then treated with KOH (16.5 g, results in a 9.8 M aqueous solution). Stirring at 90 °C for 17 h led to a clear, red organic phase and a colorless aqueous phase. Drying of the organic phase with $MgSO_4$, filtration, and evaporation of the solvents gave **7** as a red solid. Yield: 1.66 g (92%). For the yield of the direct conversion of **6** to **1** see the next paragraph. ^{1}H NMR (C_6D_6 500.2 MHz): δ 1.53 (bs, 2 H, NH_2), 1.67 (dd, $J_1 = 7.0$ Hz, $J_2 = 6.5$ Hz, 3 H, H), 3.59 (dq, $J_q = 3.0$ Hz, $J_d = 6.0$ Hz, 1 H, G), 3.79 (t, $J = 2.0$ Hz, 1 H, D), 3.83 (t, $J = 2.5$ Hz, 1 H, C), 3.89−3.90 (m, 1 H, B), 4.12 (m, 5 H, A), 7.05−7.11 (m, 3 H, P,Q), 7.23−7.29 (m, 3 H, L,M), 7.33−7.38 (m, 2 H, O), 7.67−7.72 (m, 2 H, K). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ 18.6 (d, $J_P = 17.9$ Hz, H), 29.9 (d, $J_P = 15.2$ Hz, G), 59.9 (s, D), 61.9 (s, C), 63.4 (d, $J_P = 4.7$ Hz, B), 69.8 (s, A), 84.2 (d, $J_P = 16.1$ Hz, F), 104.0 (s, E), 128.2 (P), 128.5 (Q), 128.8 (d, $J_P = 6.8$ Hz, L), 129.4 (M), 133.7 (d, $J_P = 17.4$ Hz, O), 134.9 (d, $J_P = 19.9$ Hz, K), 136.9 (d, $J_P = 18.6$ Hz, J), 138.7 (d, $J_P = 18.7$ Hz, N). ^{31}P NMR (C_6D_6 121.5 MHz): δ 3.9. MS (HR MALDI): *m*/*z* 413.0996 (calcd for $C_{24}H_{24}FeNP$); found 413.0950 [MH^+]. $C_{24}H_{24}FeNP$ (413.27): calcd C 69.75, H 5.85, N 3.39 P 7.49, Fe 13.51; found C 69.46, H 6.10, N 3.32. The optical rotation and the melting point of **7** were not determined due to its air sensitivity.

***N*,*N*′-Bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)ethyl}ferrocen-1-yl]formamidine (1).** A suspension of **6** (2.45 g, 4.48 mmol) in *i*PrOH (30 mL) and H_2O (20 mL) was degassed with Ar using an ultrasonic bath and then treated with KOH (11.0 g). Stirring at 90 °C for 12 h led to a clear, red organic phase and a colorless aqueous phase. Drying of the organic phase with $MgSO_4$, filtration, and evaporation of the solvents gave **7** as a orange to red solid. After the addition of *s*-triazine (2.25 g, 27.8 mmol, 6.2 equiv) and dioxane (6.0 mL), the resulting solution was stirred at 90 °C for 21 h and the solvent was evaporated at reduced pressure using a distillation apparatus. The product **1** was isolated as an orange foam after column chromatography (SiO_2, hexane/AcOEt/NEt_3 = 3:1:0.04). Yield over the two steps from **6** to **1**: 1.42 g (72%). ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 1.54 (q, $J = 6.9$ Hz, 6 H, 2 CH_3), 3.44 (dq, $J_q = 6.5$ Hz, $J_d = 6.0$ Hz, 2 H, 2 $CH_{methyne}$), 3.93−3.99 (m, 4 H, 4 $CH_{Cp\ subst}$), 4.06−4.19 (m, 12 H, 2 $CH_{Cp\ subst}$ and 2 $Cp_{unsubst}$), 6.86 (s, 1 H, $CH_{formamidinato}$), 6.99−7.08 (m, 4 H, $CH_{arom.}$), 7.11−7.19 (m, 4 H, $CH_{arom.}$), 7.19−7.25 (m, 2 H, $CH_{arom.}$), 7.36−7.43 (m, 6 H, $CH_{arom.}$), 7.50−7.58 (m, 4 H, $CH_{arom.}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 62.9 MHz): δ 18.2 (bs, 2 $CH_{3\ methyl}$), 29.1 (bs, 2 $CH_{methyne}$), 63.1 (s, 2 $CH_{Cp\ subst}$), 63.2 (s, 2 $C_{Cp\ subst}$), 64.1 (s, 2 $CH_{Cp\ subst}$), 64.7 (s, 2 $C_{Cp\ subst}$), 69.5 (s, 2 $Cp_{unsubst}$), 69.8 (s, 2 $CH_{Cp\ subst}$), 127.9 (2 $CH_{arom.}$), 128.0 (2 $CH_{arom.}$), 129.0 (2 $CH_{arom.}$), 129.0 (2 $CH_{arom.}$), 133.2 (2 $CH_{arom.}$), 134.7 (2 $CH_{arom.}$), 136.5 (2 $CH_{arom.}$), 138.1 (2 $CH_{arom.}$), 147.9 (bs, $CH_{formamidinate}$). ^{31}P NMR ($CDCl_3$ 101.3 MHz): δ 6.1. IR ($CHCl_3$) $\tilde{\nu}$(cm^{-1}) 1640 {ν(C=N) of amidine}. MS (HR MALDI): *m*/*z* 837.1908 (calcd for $C_{49}H_{47}Fe_2N_2P_2$); found 837.1916 [MH^+]. $C_{49}H_{46}Fe_2N_2P_2$·1/2AcOEt (880.59): calcd C 69.56, H 5.72, N 3.18, O 1.82, P 7.03, Fe 12.68; found C 69.58, H 5.70, N 3.21. $[\alpha]_{22} = -633$ (*c* 1, $CHCl_3$).

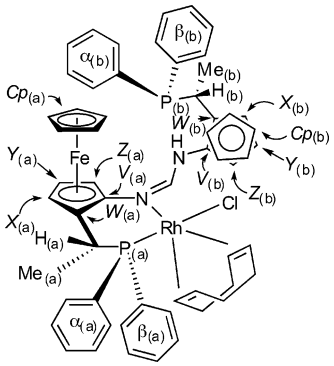
***N*,*N*′-Bis{(*S*)-2-vinylferrocen-1-yl}formamidine (8).** The Cbz-protected aminoferrocene **5** (605 mg, 1.67 mmol, 1.0 equiv) was suspended in *i*PrOH (12 mL) and KOH(aq) (12 mL, 5 M) and quickly heated to 90 °C. After stirring for 4 h and cooling to rt, the organic phase was separated from the aqueous layer, dried with $MgSO_4$, filtered, and concentrated to dryness under reduced pressure. The orange solid was mixed with *s*-triazine (679 mg, 8.37 mmol, 5.0 equiv), dissolved in dioxane (3.0 mL), degassed, and stirred at 100 °C for 28 h. After the addition of another portion of *s*-triazine (679 mg, 8.37 mmol, 5.0 equiv) and further stirring for 26 h and cooling to rt, the reaction mixture was concentrated to dryness under reduced pressure. Excess *s*-triazine was sublimed by heating during 3 h at 80 °C, after which the crude product obtained was subjected to column chromatography (SiO_2, hexane/EtOAc/NEt_3 = 3:1:0.04). Yield: 143 mg (37%) of a red amorphous solid. ^{1}H NMR ($CDCl_3$, 250.1 MHz): δ 4.10−4.14 (m, 12 H, 10 $CH_{Cp\ subst}$ and 2 $CH_{Cp\ unsubst}$), 3.34−3.38 (m, 2 H, 2 $CH_{Cp\ unsubst}$), 3.38−4.40 (m, 2 H, 2 $CH_{Cp\ unsubst}$), 5.20 (dd, $J_1 = 11.0$ Hz, $J_2 = 1.5$ Hz, 1 H, vinyl H), 5.51 (dd, $J_1 = 17.5$ Hz, $J_2 = 1.5$ Hz, 1 H, vinyl H), 6.67 (dd, $J_1 = 17.5$ Hz, $J_2 = 11.0$ Hz, 1 H, vinyl H), 8.00 (s, 1 H, $CH_{formamidinato}$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 61.1 (2 CH, Cp_{subst}), 63.2 (2 CH, Cp_{subst}), 64.8 (2 CH, Cp_{subst}), 70.6 (2 CH, $Cp_{unsubst}$), 76.8 (2 C, Cp_{subst}), 101.8 (2 C, Cp_{subst}), 113.0 (CH_{vinyl}), 132.4 ($CH_{2\ vinyl}$), 151.5 ($CH_{formamidinate}$). MS (HR MALDI): *m*/*z* 465.0717 (calcd for $C_{25}H_{25}Fe_2N_2$); found 465.0703 [MH^+]. $C_{25}H_{24}Fe_2N_2$ (464.17): calcd C 64.69, H 5.21, Fe 24.06, N 6.04; found C 64.52, H 5.38, N 6.07. $[\alpha]_{22} = -66.2$ (*c* 1, $CHCl_3$).

Benzyl *N*-[(*S*)-2-{(1*R*)-1-(3,5-dimethylpyrazol-1-yl)ethyl}-ferrocenyl]carbamate (9). 3,5-Dimethylpyrazole (639 mg, 6.65 mmol, 5 equiv) was added to a solution of **5** (500 mg, 1.38 mmol, 1 equiv) in dry acetic acid (30 mL) at room temperature. Stirring

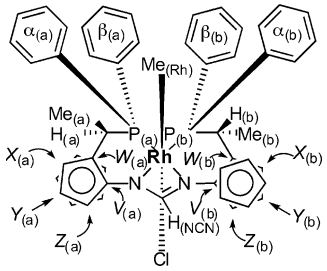
for 105 min at 60 °C and evaporation of the solvent under reduced pressure yielded a mixture of the crude product and residual 3,5-dimethylpyrazole. The product was purified by column chromatography (SiO_2, hexane/EtOAc/NEt_3 = 10:1:0.05). Yield: 450 mg (82%) of a red oil. The dr of 9:1 was determined by integration of relevant peaks in the ^1H NMR spectrum. ^1H NMR ($CDCl_3$, 300.1 MHz): δ 1.67 (d, J = 7.2 Hz, 3 H, $CHCH_3$), 2.25 (s, 3 H, CCH_3), 2.36 (s, 3 H, CCH_3), 3.81 (s, 5 H, $CH_{Cp\ unsubst}$), 3.90−3.92 (m, 2 H, 2 $CH_{Cp\ subst}$), 5.04 (q, J = 7.2 Hz, 1 H, $CHCH_3$), 5.15−5.27 (m, 3 H, CH_2 and $CH_{Cp\ subst}$), 5.84 (s, 1 H, $CH_{triazole}$), 7.31−7.44 (m, 5 H, CH_{phenyl}), 10.06 (bs, 1 H, N*H*).



(*N*,*N*′-Bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)ethyl}ferrocen-1-yl]formamidinato)rhodium(I) (2). The formamidine ligand **1** (116 mg, 138.6 μmol, 1 equiv) was dissolved in freshly distilled THF (4.2 mL), treated with *n*BuLi (112 μL, 180 μmol, 1.3 equiv) at 0 °C, and then slowly warmed to rt. After 2.5 h, $[Rh_2Cl_2(COD)_2]$ (34.2 mg, 69.3 μmol, 0.5 equiv) was added inside the glovebox and stirred overnight. The reaction mixture was filtered, and the volatiles were evaporated under reduced pressure to yield the product as an orange powder. Yield: 111 mg (85%). ^1H NMR (d_8-THF, 700.1 MHz): δ 1.09 (dd, J_P = 7.0 Hz, J_P = 4.2 Hz, 6 H, 2 CH_3), 3.70−3.72 (m, 2 H, 2 $CH_{(X)}$), 3.78 (t, J = 2.5 Hz, 2 H, 2 $CH_{(Y)}$), 3.90 (s, 10 H, 2 Cp), 4.01−4.15 (m, 2 H, 2 $CH_{methyne}$), 4.50−4.52 (m, 2 H, 2 $CH_{(Z)}$), 6.98 (t, J = 7.7 Hz, 4 H, 4 $CH_{phenyl\ meta}$), 7.01 (t, J = 7.7 Hz, 4 H, 4 $CH_{phenyl\ meta}$), 7.14 (dd, J_1 = 9.1 Hz, J_2 = 7.7 Hz, 4 H, 4 $CH_{phenyl\ para}$), 7.40−7.44 (m, 4 H, 4 $CH_{phenyl\ ortho}$), 7.53−7.58 (m, 4 H, 4 $CH_{phenyl\ ortho}$), 9.36 (t, J = 3.2 Hz, 1 H, $CH_{formamidinato}$). $^{13}C\{^1H\}$ NMR (d_8-THF, 75.5 MHz): δ 16.2 (s, 2 CH_3), 30.7 (t, J = 11.2 Hz, 2 $CH_{methyne}$), 54.4 (s, 2 $CH_{(Z)}$), 60.5 (s, 2 $CH_{(Y)}$), 63.9 (s, 2 $CH_{(X)}$), 68.6 (s, 2 $C_{quat.}$) 69.4 (s, 2 Cp), 83.4 (t, J = 4.2 Hz, 2 $C_{quat.}$), 126.7 (t, J = 4.6 Hz, 4 $CH_{phenyl\ meta}$), 127.5 (t, J = 4.3 Hz, 4 $CH_{phenyl\ meta}$), 128.2 (s, 2 $CH_{phenyl\ para}$), 132.4 (t, J = 5.6 Hz, 4 $CH_{phenyl\ ortho}$), 133.0−133.0 (m, 2 $C_{phenyl\ ipso}$), 134.4 (t, J = 6.1 Hz, 2 $CH_{phenyl\ ortho}$), 135.3−136.2 (m, 2 $C_{phenyl\ ipso}$), 160.4 (ddd, J_{Rh} = 2.5 Hz, J_P = 2.3 Hz, J_P = 2.3 Hz, one (2 $C_{phenyl\ ipso}$) not found. ^{31}P NMR (d_8-THF, 121.5 MHz): δ 74.8 (d, J_{Rh} = 201 Hz). ^{103}Rh NMR (d_8-THF, 22.1 MHz): δ −42.5. MS (HR MALDI): m/z 938.0812 (calcd for $C_{49}H_{45}Fe_2N_2P_2Rh$); found 938.0828 [M^+], 938.0864 [MH^+]. Due to the air sensitivity of the product, no correct elemental analysis could be obtained.

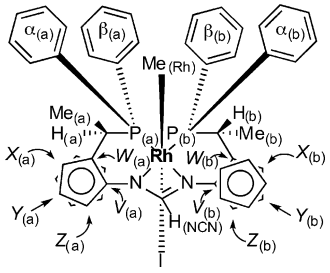


(κ-*N*,*P*-Bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)ethyl}ferrocen-1-yl]formamidine)(chloro)(η^4-1,4-cyclooctadiene)rhodium(I) (10) and Its Conversion to (*N*,*N*′-Bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)ethyl}ferrocen-1-yl]formamidinato)rhodium(I) (2). The formamidine ligand **1** (76.0 mg, 90.8 μmol, 1 equiv) was dissolved in freshly distilled C_6D_6 (2.4 mL) at rt. Addition of $[Rh_2Cl_2(COD)_2]$ (22.4 mg, 45.4 μmol, 0.5 equiv) resulted in the immediate formation of **10**. Upon addition of KO*t*Bu (15.3 mg, 136 μmol, 1.5 equiv), **10** was converted in situ to **2**, as ascertained by ^1H NMR and ^{31}P NMR. ^1H NMR (C_6D_6, 500.2 MHz): δ 1.13 (t, J_P = 8.4 Hz, 3 H, $CH_{3(methyl\ a)}$), 1.60−1.71 (m, 5 H, $CH_{3(methyl\ b)}$ + $CH_{2(COD)}$), 2.10−2.19 (m, $CH_{2(COD)}$), 2.26−2.38 (m, $CH_{2(COD)}$), 3.08−3.12 (m, $CH_{(Xa)}$), 3.12−3.23 (m, $CH_{2(COD)}$), 3.42−3.50 (m, 1 H, $CH_{(methyne\ a)}$), 3.55−3.58 (m, $CH_{(Ya)}$), 3.58−3.61 (m, $CH_{(Xb)}$), 3.86−3.90 (m, $CH_{(Yb)}$), 3.91−3.95 (m, $CH_{(Za)}$), 4.11−4.19 (m, 7 H, $Cp_{(a)}$ + $CH_{(COD)}$), 4.20−4.28 (m, $CH_{(COD)}$), 4.43−4.46 (m, $CH_{(Zb)}$), 4.58 (s, 5 H, $Cp_{(b)}$), 5.35−5.45 (m, 1 H, $CH_{(methyne\ b)}$), 7.20−7.25 (m, 4 CH, $phenyl_{\beta(b)\ para}$ + $phenyl_{\beta(b)\ meta}$ + $phenyl_{\beta(a)\ para}$), 7.25−7.29 (m, 2 H, $phenyl_{\beta(a)\ meta}$), 7.32 (t, J = 7.5 Hz, 1 H, $phenyl_{\alpha(b)\ para}$), 7.36 (t, J = 7.1 Hz, 1 H, $phenyl_{\alpha(a)\ para}$), 7.43 (t, J = 7.1 Hz, 2 H, $phenyl_{\alpha(a)\ meta}$), 7.50 (t, J = 7.5 Hz, 2 H, $phenyl_{\alpha(b)\ meta}$), 7.58 (t, J = 7.1 Hz, 2 H, $phenyl_{\alpha(a)\ ortho}$), 7.69−7.75 (m, 2 H, $phenyl_{\beta(b)\ ortho}$), 7.87 (t, J = 7.3 Hz, 2 H, $phenyl_{\beta(a)\ ortho}$), 8.20 (t, J = 6.4 Hz, 2 H, $phenyl_{\alpha(b)\ ortho}$), 8.49 (d, J = 9.7 Hz, 1 H, $CH_{formamidinato}$), 12.44 (d, J = 9.7 Hz, 1 H, NH). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.0 MHz): δ 11.4−11.6 (m, $CH_{3(methyl\ a)}$), 16.0 ($CH_{3(methyl\ b)}$), 28.6 ($CH_{(methyne\ b)}$), 28.7 ($CH_{2(COD)}$), 29.8 (d, $J_{P(a)}$ = 8.7 Hz, $CH_{(methyne\ a)}$), 35.0 ($CH_{2(COD)}$), 61.2 ($CH_{(Ya)}$), 61.8 ($CH_{(Za)}$), 63.7 ($CH_{(Xa)}$), 64.0 ($CH_{(Yb)}$), 65.2 ($CH_{(Zb)}$), 65.4 ($CH_{(Xb)}$), 69.8 ($Cp_{(a)}$), 70.6 ($Cp_{(b)}$), 73.7 (2 $CH_{(COD)}$), 83.5 (2 $CH_{(COD)}$), 84.6 ($C_{(Va)}$), 87.0 ($C_{(Vb)}$), 94.6 ($C_{(Wb)}$), 111.6 ($C_{(Wa)}$), 127.5 (C_{phenyl}), 128.0 (C_{phenyl}), 128.0 (C_{phenyl}), 128.4 (C_{phenyl}), 128.5 (C_{phenyl}), 129.1 (C_{phenyl}), 129.3 (C_{phenyl}), 130.2 (C_{phenyl}), 131.5 (d, J = 21.4 Hz, $C_{phenyl\ \alpha(a)\ ipso}$), 132.8 (d, J = 7.7 Hz, 2 $CH_{phenyl\ \alpha(a)\ ortho}$), 133.3 (d, J = 14.8 Hz, 2 $CH_{phenyl\ \alpha(b)\ ortho}$), 136.4 (d, J = 20.9 Hz, 2 $CH_{phenyl\ \beta(b)\ ortho}$), 137.1 (d, J = 12.7 Hz, 2 $CH_{phenyl\ \beta(a)\ ortho}$), 139.1 (d, J = 18.9 Hz, $C_{phenyl\ \alpha(b)\ ipso}$), 163.4 ($CH_{formamidinato}$), two (2 $C_{phenyl\ ipso}$) not found. ^{31}P NMR (C_6D_6, 203 MHz): δ 9.8 (s, $P_{(b)}$), 56.0 (dd, J_{Rh} = 137.3 Hz, $P_{(a)}$). ^{103}Rh NMR (C_6D_6, 15.9 MHz): δ 990.



(*N*,*N*′-Bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)ethyl}ferrocen-1-yl](chloro)(methyl)formamidinato)rhodium(III) (11). The formamidine ligand **1** (116 mg, 138.6 μmol, 1 equiv) was dissolved in freshly distilled THF (4.2 mL) and treated with *n*BuLi (113 μL, 180 μmol, 1.3 equiv) at 0 °C. After warming to rt and stirring for 2.5 h, $[Rh_2Cl_2(COD)_2]$ (34.2 mg, 69.3 μmol, 0.5 equiv) was added and the red solution was stirred for 22 h and filtered. As a stream of MeCl was passed over the clear, red solution for 10 min, its color darkened considerably. All volatiles were evaporated under reduced pressure, and the crude product was taken up in benzene (3.5 mL). Pentane was allowed to slowly diffuse overnight into the solution, leading to the formation of red crystals. After decanting the mother liquor, the crystals were dried in vacuo. Complete evaporation of the solvent in order to obtain the pure product suitable for elemental analysis required extensive drying at low pressure. Yield: 101 mg (77%). ^1H NMR (C_6D_6, 500.2 MHz): δ 0.68 (ddd, J_{Rh} = 2.2 Hz, $J_{P(a)}$ = 2.2 Hz, $J_{P(b)}$ = 2.2 Hz, 3 H, $CH_{3(Rh)}$), 1.17 (dd, J_P = 12.5 Hz, J_P = 12.0 Hz, 3 H, $CH_{3(methyl\ b)}$), 1.48 (dd, J_P = 13.0 Hz, J_P = 13.0 Hz, 3 H, $CH_{3(methyl\ a)}$), 3.72 (dd, J_1 = 2.5 Hz, J_2 = 2.5 Hz, 1 H, $CH_{(Xb)}$), 3.85 (dd, J_1 = 6.5 Hz, J_2 = 6.5 Hz,

1 H, $CH_{(methyne\ b)}$), 3.96 (dd, $J_1 = 2.8$ Hz, $J_2 = 2.8$ Hz, 1 H, $CH_{(Yb)}$), 4.01 (dd, $J_1 = 2.5$ Hz, $J_2 = 2.5$ Hz, 1 H, CH(Ya)), 4.13 (s, 5 H, $Cp_{(b)}$), 4.30−4.31 (m, 1 H, $CH_{(Xa)}$), 4.40 (dd, $J_1 = 2.5$ Hz, $J_2 = 2.5$ Hz, 1 H, $CH_{(Za)}$), 4.45 (dd, $J_1 = 2.5$ Hz, $J_2 = 2.5$ Hz, 1 H, $CH_{(Zb)}$), 4.51 (s, 5 H, $Cp_{(a)}$), 5.52 (dd, $J_1 = 6.8$ Hz, $J_2 = 6.8$ Hz, 1 H, $CH_{(methyne\ a)}$), 6.65 (t, $J = 8.5$ Hz, 2 H, 2 $CH_{phenyl\ (\alpha a)\ ortho}$), 6.89 (td, $J_t = 8.0$ Hz, $J_d = 2.0$ Hz, 2 H, 2 $CH_{phenyl\ (\alpha a)\ meta}$), 6.95−7.04 (m, 5 H, 2 $CH_{phenyl\ (\beta a)\ meta}$, $CH_{phenyl\ (\alpha a)\ para}$, 2 $CH_{phenyl\ (\alpha b)\ meta}$), 7.10 (td, $J_t = 7.5$ Hz, $J_d = 1.5$ Hz, 1 H, $CH_{phenyl\ (\beta a)\ para}$), 7.14−7.19 (m, 3 H, 1 $CH_{phenyl\ (\alpha b)\ para}$, 2 $CH_{phenyl\ (\alpha b)\ ortho}$, 7.20−7.26 (m, 3 H, 1 $CH_{phenyl\ (\beta b)\ para}$, 2 $CH_{phenyl\ (\beta b)\ meta}$, 8.36−8.40 (m, 2 H, $CH_{phenyl\ (\beta b)\ ortho}$), 8.50 (bs, 2 H, $CH_{phenyl\ (\beta a)\ ortho}$), 9.22 (ddd, $J_{Rh} = 3.0$ Hz, $J_P = 2.5$ Hz, $J_P = 2.5$ Hz, 1 H, $CH_{formamidinato}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 176.0 MHz): δ 7.9 (ddd, $J_{Rh} = 22.3$ Hz, $J_P = 6.3$ Hz, $J_P = 6.3$ Hz, 3 H, $CH_{3(Rh)}$), 13.3 (d, $J_{P(b)} = 6.2$ Hz, $CH_{3(methyl\ b)}$), 13.5 (d, $J_{P(a)} = 7.4$ Hz, $CH_{3(methyl\ a)}$), 31.5 (d, $J_{P(b)} = 22.2$ Hz, $CH_{3(methyne\ b)}$), 32.6 (d, $J_{P(a)} = 22.4$ Hz, $CH_{3(methyne\ a)}$), 56.5 (d, $J_{P(b)} = 3.7$ Hz, $CH_{(Zb)}$), 57.5 (d, $J_{P(a)} = 5.2$ Hz, $CH_{(Za)}$), 62.5 (s, $CH_{(Ya)}$), 62.9 (s, $CH_{(Yb)}$), 64.5 (d, $J_{P(ab)} = 2.5$ Hz, $CH_{(Xa)}$), 65.3 (s, $CH_{(Xb)}$), 70.3 (s, $Cp_{(b)}$), 71.6 (s, $Cp_{(a)}$), 79.8 (d, $J = 7.0$ Hz, $C_{(Wb)}$), 81.4 (d, $J = 4.0$ Hz, $C_{(Wa)}$), 97.7 (d, $J = 3.4$ Hz, $C_{(Va)}$), 101.9 (d, $J = 3.4$ Hz, $C_{(Vb)}$), 126.6 (d, $J = 35.1$ Hz, $C_{phenyl\ ipso}$), 126.9 (d, $J = 9.3$ Hz, 2 $CH_{phenyl\ (\beta b)\ meta}$), 127.4 (d, $J = 10.0$ Hz, 2 $CH_{phenyl\ (\beta a)\ meta}$), 127.6 (2 $CH_{phenyl\ (\alpha a)\ meta}$), 127.8 (2 $CH_{phenyl\ (\alpha b)\ meta}$), 128.7 (s, $CH_{phenyl\ (\alpha b)\ para}$), 128.8 (d, $J = 2.1$ Hz, $CH_{phenyl\ (\alpha a)\ para}$), 129.4 (d, $J = 40.7$ Hz, $C_{phenyl\ ipso}$), 130.1 (d, $J = 2.3$ Hz, $CH_{phenyl\ (\beta b)\ para}$), 130.6 (d, $J = 2.3$ Hz, $CH_{phenyl\ (\beta a)\ para}$), 131.4 (d, $J = 35.2$ Hz, $C_{phenyl\ ipso}$), 132.1 (d, $J = 36.4$ Hz, $C_{phenyl\ ipso}$), 132.6 (d, $J = 7.0$ Hz, 2 $CH_{phenyl\ (\alpha a)\ ortho}$), 132.7 (d, $J = 7.2$ Hz, 2 $CH_{phenyl\ (\alpha b)\ ortho}$), 135.8 (d, $J = 8.6$ Hz, 2 $CH_{phenyl\ (\beta b)\ ortho}$), 137.1 (d, $J = 9.5$ Hz, 2 $CH_{phenyl\ (\beta a)\ ortho}$), 158.6 (dt, $J_d = 3.3$ Hz, $J_t = 3.3$ Hz, 1 $CH_{formamidinato}$)). ^{31}P NMR (C_6D_6, 121.5 MHz): δ 45.0 (dd, $J_{Rh} = 131.0$ Hz, $J_P = 17.5$ Hz, $P_{(a)}$), 53.5 (dd, $J_{Rh} = 134.1$ Hz, $J_P = 17.5$ Hz, $P_{(b)}$). ^{103}Rh NMR (C_6D_6, 22.2 MHz): δ 1600. MS (HR MALDI): *m*/*z* 953.1047 (calcd for $C_{50}H_{48}Fe_2N_2P_2Rh$); found 953.1041 [M − Cl^+]. $C_{50}H_{48}ClFe_2N_2P_2Rh$ (988.93): calcd C 60.73, H 4.89, Cl 3.59, Fe 11.29, N 2.83, P 6.26, Rh 10.41; found C 60.50, H 4.90, N 2.58.



(*N*,*N*′-Bis[(*S*)-2-{(1*R*)-1-(diphenylphosphino)ethyl}ferrocen-1-yl]formamidinato)(iodo)(methyl)rhodium(III) (12). The formamidine ligand **1** (116 mg, 138.6 μmol, 1 equiv) was dissolved in freshly distilled THF (4.2 mL) and treated with *n*BuLi (113 μL, 180 μmol, 1.3 equiv) at 0 °C. After warming to rt and stirring for 2.5 h, $[Rh_2Cl_2(COD)_2]$ (34.2 mg, 69.3 μmol, 0.5 equiv) was added and the red solution was stirred for 22 h and filtered. The addition of dry MeI (26 μL, 59 mg, 416 μmol, 3.0 equiv) caused a slight darkening of the clear, red solution, which was evaporated to dryness after 3 h of stirring. The resulting red powder was taken up in C_6D_6. Yield: 132 mg (88%). ^1H NMR (C_6D_6, 700.1 MHz): δ 0.81−0.85 (m, 3 H, $CH_{3(Rh)}$), 1.04 (dd, $J_P = 12.6$ Hz $J_P = 7.0$ Hz, 3 H, $CH_{3(methyl\ b)}$), 1.46 (dd, $J_P = 12.6$ Hz, $J_P = 7.0$ Hz, 3 H, $CH_{3(methyl\ a)}$), 3.81−3.83 (m, 1 H, $CH_{(Xb)}$), 3.89 (dd, $J_1 = 7.0$ Hz, $J_2 = 6.3$ Hz, 1 H, $CH_{(methyne\ b)}$), 3.99 (dd, $J_1 = 2.8$ Hz, $J_2 = 2.8$ Hz, 1 H, $CH_{(Yb)}$), 4.03 (dd, $J_1 = 2.5$ Hz, $J_2 = 2.5$ Hz, 1 H, $CH_{(Ya)}$), 4.10 (s, 5 H, $Cp_{(b)}$), 4.27−4.29 (m, 1 H, $CH_{(Xa)}$), 4.45 (dd, $J_1 = 2.1$ Hz, $J_2 = 1.4$ Hz, 1 H, $CH_{(Za)}$), 4.50 (dd, $J_1 = 2.1$ Hz, $J_2 = 1.4$ Hz, 1 H, $CH_{(Zb)}$), 4.52 (s, 5 H, $Cp_{(a)}$), 5.56 (dd, $J_1 = 7.0$ Hz, $J_2 = 3.5$ Hz, 1 H, $CH_{(methyne\ a)}$), 6.50−55 (m, 2 H, 2 $CH_{phenyl\ (\alpha a)\ ortho}$), 6.86 (t, $J = 7.0$ Hz, 2 H, 2 $CH_{phenyl\ (\beta b)\ meta}$), 6.95−7.00 (m, 4 H, 2 $CH_{phenyl\ (\beta a)\ meta}$), 2 $CH_{phenyl\ (\alpha b)\ meta}$), 7.02 (t, $J = 7.0$ Hz, 1 H, $CH_{phenyl\ (\alpha a)\ para}$), 7.13 (t, $J = 7.4$ Hz, 1 H, $CH_{phenyl\ (\beta a)\ para}$), 7.16 (t, $J = 7.4$ Hz, 1 H, $CH_{phenyl\ (\alpha b)\ para}$), 7.18−7.25 (m, 3 H, 3 $CH_{phenyl\ (\alpha a)\ meta}$ and phenyl (βb) para), 7.27−7.30 (m, 2 H, $CH_{phenyl\ (\alpha b)\ ortho}$), 8.15 (t, $J = 8.4$ Hz, 2 H, $CH_{phenyl\ (\beta b)\ ortho}$), 8.39 (t, $J = 9.1$ Hz, 2 H, $CH_{phenyl\ (\beta a)\ ortho}$), 8.97 (ddd, $J_{Rh} = 3.5$ Hz, $J_P = 4.9$ Hz, $J_P = 4.9$ Hz, 1 H, $CH_{formamidinato}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 62.9 MHz): δ 13.7 (d, $J_{P(b)} = 6.3$ Hz, $CH_{3(methyl\ b)}$), 14.2 (d, $J_{P(a)} = 7.1$ Hz, $CH_{3(methyl\ a)}$), 16.2 (dd, $J_{Rh} = 22.3$ Hz, $J_2 = 6.7$ Hz, 3 H, $CH_{3(Rh)}$), 31.0 (d, $J_{P(b)} = 23.5$ Hz, $CH_{3(methyne\ b)}$), 35.9 (d, $J_{P(a)} = 22.5$ Hz, $CH_{3(methyne\ a)}$), 56.8 (d, $J_{P(b)} = 4.5$ Hz, $CH_{(Zb)}$), 57.0 (d, $J_{P(a)} = 4.3$ Hz, $CH_{(Za)}$), 62.6 (s, $CH_{(Ya)}$), 63.1 (s, $CH_{(Yb)}$), 64.2 (s, $CH_{(Xa)}$), 65.8 (s, $CH_{(Xb)}$), 70.5 (s, $Cp_{(b)}$), 71.4 (s, $Cp_{(a)}$), 79.3 (d, $J = 6.9$ Hz, $C_{(Wb)}$), 81.5 (d, $J = 3.6$ Hz, $C_{(Wa)}$), 99.0 (t, $J = 3.5$ Hz, $C_{(Va)}$), 100.7 (t, $J = 3.9$ Hz, $C_{(Vb)}$), 126.6 (2 $CH_{phenyl\ (\alpha a)\ meta}$), 127.0 (2 $CH_{phenyl\ (\beta a)\ meta}$ or 2 $CH_{phenyl\ (\alpha b)\ meta}$), 127.3 (2 $CH_{phenyl\ (\beta b)\ meta}$), 127.8 (2 $CH_{phenyl\ (\beta a)\ meta}$ or 2 $CH_{phenyl\ (\alpha b)\ meta}$), 128.8 ($CH_{phenyl\ (\alpha a)\ para}$), 128.8 ($CH_{phenyl\ (\beta a)\ para}$), 130.0 (d, $J = 40.7$ Hz, $C_{phenyl\ ipso}$), 130.4 (s, $CH_{phenyl\ (\beta b)\ para}$), 130.7 (d, $J = 35.4$ Hz, $C_{phenyl\ ipso}$), 130.9 (s, $CH_{phenyl\ (\alpha b)\ para}$), 132.8 (d, $J = 6.7$ Hz, 1 $CH_{phenyl\ (\alpha a)\ ortho}$), 133.0 (d, $J = 3.6$ Hz, 1 $CH_{phenyl\ (\alpha b)\ ortho}$), 135.6 (d, $J = 8.5$ Hz, 1 $CH_{phenyl\ (\beta b)\ ortho}$), 139.0 (d, $J = 11.0$ Hz, 1 $CH_{phenyl\ (\beta a)\ ortho}$), 156.6 (d, $J = 3.5$ Hz, 1 $CH_{formamidinato}$), two (2 $C_{phenyl\ ipso}$) not found. ^{31}P NMR (C_6D_6, 121.5 MHz): δ 44.2 (dd, $J_{Rh} = 131.1$ Hz, $J_P = 16.2$ Hz, $P_{(b)}$), 53.5 (dd, $J_{Rh} = 129.0$ Hz, $J_P = 16.3$ Hz, $P_{(a)}$). ^{103}Rh NMR (C_6D_6, 22.2 MHz): δ 1471. MS (HR MALDI): *m*/*z* 953.1047 (calcd for $C_{50}H_{48}Fe_2N_2P_2Rh$); found 953.1036 [M − I^+].

Acknowledgment. Support from the Swiss National Science Foundation is gratefully acknowledged. We thank Dr. Heinz Rüegger for NMR assistance and Dr. Isabelle Haller for performing the X-ray crystallographic studies of compounds **8** and **11**.

Supporting Information Available: Crystallographic data as CIF files. These data are available free of charge via the Internet at http://pubs.acs.org.

OM050845P