86. Chiral Cooperativity: the Effect of Distant Chiral Centers in Ferrocenylamine Ligands upon Enantioselectivity in the Gold(I)-Catalyzed Aldol Reaction

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Long-range chiral cooperativity in enantiomerically pure ferrocenylamine ligands containing both planar and multiple centers of chirality (multiple stereogenic C-atoms) was demonstrated in the Au^I-catalyzed reaction of aldehydes and isocyanoesters. Synthetic methodology was developed for the synthesis of ferrocenylamine ligands with two and three chiral centers of known absolute configuration in the C-side chain in addition to the planar chirality of the molecule. The diastereo- and enantioselectivity of the Au^I-catalyzed formation of the *trans*- and *cis*-dihydrooxazoles **5** and **6**, respectively, from benzaldehyde (**1**) and methyl isocyanoacetate (**2**) depend upon the sequence of chirality (absolute configuration of the chiral centers) in the side chain of the ferrocenylamine ligands. Particularly significant effects were observed upon the enantioselectivity for the minor *cis*-dihydrooxazole **6**, for which, in certain cases, resulted in a change in the enantiomeric dihydrooxazole **6** produced in excess with a change in the absolute configuration of a distant chiral center. Significant effects upon diastereo- and enantioselectivity were observed when chiral ferrocenylamine ligands containing free OH groups were utilized. Using ligands containing a free OH group gave **6** with an absolute configuration opposite to that produced by the corresponding ester and carbamate derivatives. The possible mechanisms for the transmission of chiral information in the proposed stereoselective transition state (TS) was discussed, including both the formation of a stereogenic N-atom and steric effects based upon *Newman*'s rule of six.

Introduction. – The development of synthetic methodology that preferentially leads to the formation of a single enantiomer of a targeted chiral compound is today a topic of fundamental importance. It is widely recognized that the manufacture of agricultural and pharmaceutical compounds containing only the correct biologically active enantiomer is desirable not only because the other enantiomer is usually biologically less effective or inactive, but it may be antagonistic or, at worse, toxic [1]. Of particular importance are C–C bond-forming reactions whose diastereo- and enantioselectivity are derived through the use of catalytic quantities of chiral transition-metal ligands [2–6].

In 1986, *Hayashi* and coworkers reported an elegant synthesis of dihydrooxazoles utilizing a Au^I-catalyzed aldol reaction in the presence of chiral ferrocenylamine ligands that possess both planar and central chirality [7] [8]. *E.g.*, the reaction of **1** with **2** catalyzed by bis(cyclohexyl isocyanide)gold(I) tetrafluoroborate (**3**) [9] in the presence of the chiral ferrocenylamine ligand (*R,S*)-**4** gave a mixture of the *trans*- and *cis*-dihydro-

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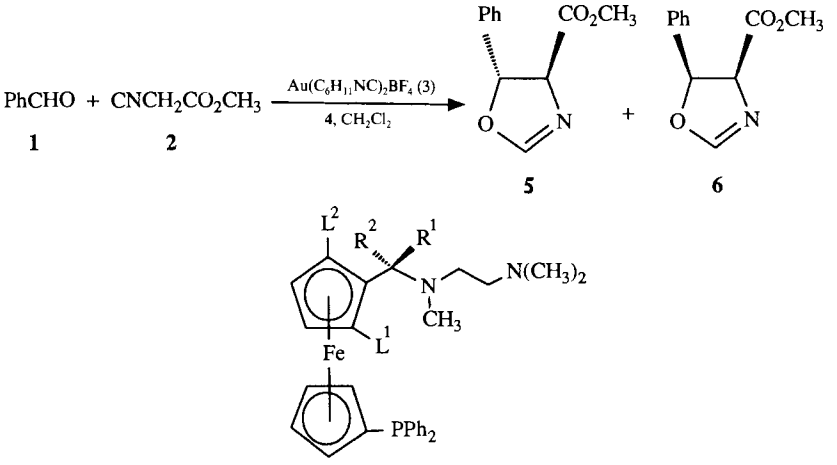
Scheme 1[4])



(*R,S*)-**4** R^1 = Me, R^2 = H, L^1 = PPh_2, L^2 = H
(*S,R*)-**4** R^1 = H, R^2 = Me, L^1 = H, L^2 = PPh_2
(*R,R*)-**4** R^1 = Me, R^2 = H, L^1 = H, L^2 = PPh_2
(*S,S*)-**4** R^1 = H, R^2 = Me, L^1 = PPh_2, L^2 = H

oxazoles **5** and **6**, respectively (*Scheme 1*)[2–4]). The *trans*-isomer **5** illustrated was the dominant isomer formed in 91% enantiomeric excess (ee)[5]) [10].

Kumada and coworkers investigated the effect of the central chirality of the stereogenic C-atom of **4** on the diastereo- and enantioselectivity of transition-metal-catalyzed *Grignard* cross-coupling reactions [11]; they came to the reasonable conclusion from the experimental data obtained that the planar chirality of **4** plays the dominant role in determining product configuration [12]. Based upon this work, subsequent studies on the Au^I-catalyzed aldol reaction and other transition-metal-catalyzed reactions have implicitly presumed that the planar chirality of **4** plays the major role in determining product configuration [13–28].

Quite recently, we reported that this contention was not correct and that the results based upon the *Grignard* cross-coupling reactions could not be generalized [29] [30]. We demonstrated that the central and planar chirality of the chiral ferrocenylamine ligand can act in either a cooperative or noncooperative manner in the control of diastereo- and enantioselectivity. Internal cooperativity of chirality is conceptually analogous to the strategy of double stereodifferentiation (external cooperativity of chirality) advocated by

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[2]) 'Dihydrooxazole' is used throughout this paper for '4,5-dihydrooxazole' (formerly 2-oxazoline).

[3]) Only one enantiomer of **5** and **6** is illustrated.

[4]) The *R,S* nomenclature of *Cahn-Ingold-Prelog* is used in all cases to specify the absolute configuration. In key numbers, the absolute configurations of the stereogenic C-atoms are specified first and starting from the strereogenic C-atom in the ferrocenylamine side-chain closest to the cyclopentadienyl ring and proceding outwards; last stereochemical descriptor refers always to the planar chirality of the ferrocenylamine ligand. In all cases reported in this paper, stereogenic C-atoms are also chirotopic.

[5]) The original ee of 94% was revised in a subsequent paper by *Ito et al.* to 91%, which is in agreement with our results [10].

Masamune et al. [31]. The design of new chiral ferrocenylamine ligands for transition-metal-catalyzed aldol reactions requires a careful consideration of both the central and the planar chirality of the ligand.

The notion of cooperativity of chirality can clearly be discerned in nature and has important biological consequences. In a recent example provided by *Minsky* and coworkers, the formation of nucleic-acid/polypeptide complexes with extremely large asymmetry was found to be dependent upon both the DNA long-range order and the handedness of the polypeptide [32]. The long-range cooperativity effects observed in nature, which in many cases is due in part to a specific ordering of chiral centers, suggests that similar cooperative effects should be obtainable in transition-metal ligands by the proper incorporation of multiple chiral centers.

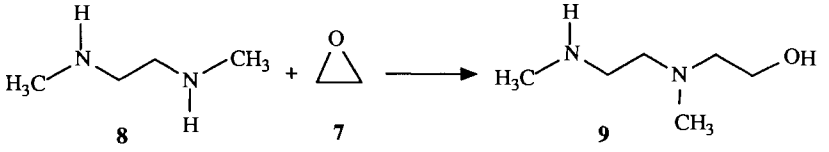
The recent advances in the study of the stereochemistry of complex organic molecules has led to both the reevaluation of and new definitions for terms relevant for describing molecular structure and chirality. *Mislow* and *Siegel* emphasized that chirality is a geometrical attribute of the molecule as a whole [33], and it is strictly incorrect to describe a molecule as having multiple chiral centers, although this usage, which we will continue to use herein, is common in this journal and elsewhere. It should be understood that when we refer herein to the introduction of an additional chiral center, we refer to the addition of an additional atom that is both *stereogenic and chirotopic* with known absolute configuration. *Chiral cooperativity* (internal cooperativity of chirality) *thus refers to individual chirotopic segments of the ligand molecule that act in a cooperative manner to promote a particular diastereo- and enantioselectivity in product formation.*

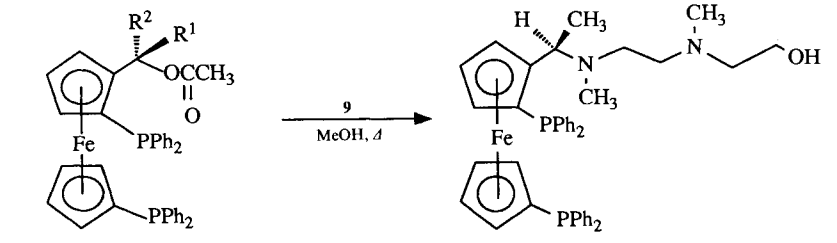
We report herein our efforts towards achieving this goal by the introduction of different sequences of chiral centers (central chirality) into a ferrocenylamine ligand that also possesses planar chirality and studying the resultant effect upon stereoselectivity in the Au^{I}-catalyzed aldol reaction. The results of this study clearly reveal the effect of chiral cooperativity upon product stereoselection and provides a powerful new strategy for the control of stereoselectivity in transition-metal-catalyzed reactions.

Results and Discussion. – *Functionalization of the Ferrocenylamine Side Chain.* The modification of the terminal Me_2N group in the side chain of the chiral ferrocenylamine **4** has been shown by *Hayashi* and coworkers to have a significant effect upon stereoselectivity in product formation [10]. In several cases, the observed improvement in enantioselectivity with a modification of the terminal-amine structure appears to be steric in origin. In the other cases, however, electronic effects are operative at least in part [10] [30]. In a particularly interesting example, a terminal N-atom incorporated in either a morpholino or piperidino ring both gave an increased ee of the same enantiomer in the *trans*-dihydrooxazole product, but both a *different* ee and absolute configuration of the *cis*-dihydrooxazoline product [10]. Our mechanistic investigations revealed that these changes in stereoselectivity are likely due to a different preferred conformation of the ferrocenylamine side chain in the stereoselective transition state (TS) as a result of the dipole moment of the introduced heteroatom [30]. Except for minor changes in the terminal amine structure of **4**, the effect of additional side-chain functionality upon stereoselectivity and the development of synthetic strategies for the introduction of functionality into the ferrocenylamine side chain has received scant attention [30f].

As an initial entry into studying the effect of modified ferrocenylamine side chains, the introduction of a reactive functional substituent without chirality was desirable that

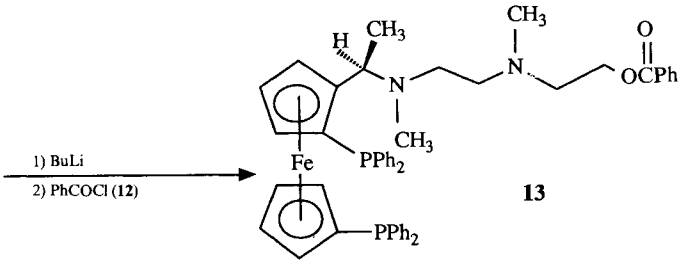
Scheme 2[4])





(*R,S*)-**10** R^1 = Me, R^2 = H
(*S,S*)-**10** R^1 = H, R^2 = Me

(*R,S*)-**11**



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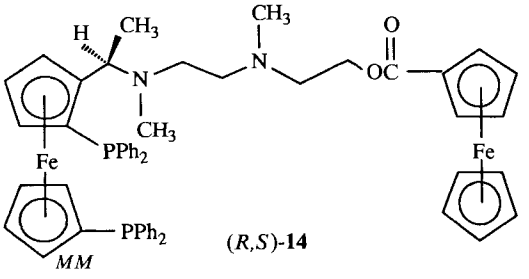
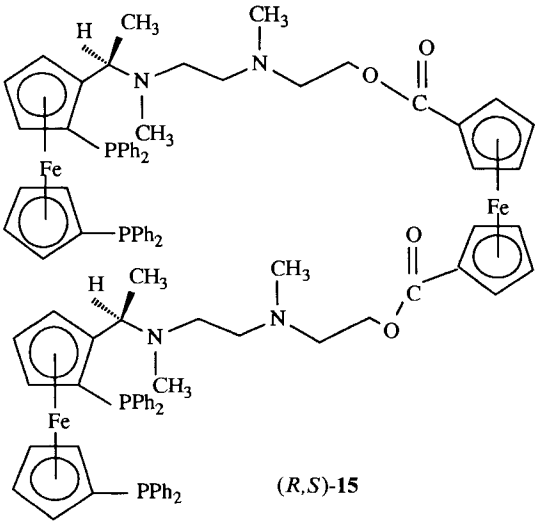


(*R,S*)-**14**



(*R,S*)-**15**

still retained the N-atoms in the same relative positions as in **4**. *Hayashi* and coworkers clearly demonstrated that the location of the terminal basic N-atom is important for achieving high enantioselectivity in the Au^I-catalyzed aldol reaction [7]. Initial mechanistic proposals by these authors and subsequent detailed mechanistic work by ourselves delineated the importance of secondary electrostatic interactions between the enolate and protonated amine in the stereoselective TS [7] [27] [30].

An OH substituent was anticipated to allow the preparation of a wide arsenal of derived ferrocenylamide ligands. The reaction of 1 equiv. of ethylene oxide (**7**) with 3.3 equiv. of *N,N'*-dimethylethylenediamine (**8**) gave aminoalcohol **9** (68%, distilled; *Scheme 2*) [34]. The OH-functionalized ferrocenylamine (*R,S*)-**11** was prepared by the reaction of **9** with ferrocenylethyl acetate (*R,S*)-**10** [35] [36] (79%, column-chromatographed). The OH-substituted ferrocenylamine (*R,S*)-**11** was evaluated as a ligand in the Au^I-catalyzed aldol reaction of **1** with **2** because the absolute configuration of the iosomeric dihydrooxazoles **5** and **6** formed have previously been determined [7]. The isomeric dihydrooxazoles could easily be separated by GLC using a *Chirasil*-L-*Val*® column. The GLC-peak assignments were further verified by using the morpholino-modified ferrocenylamine reported by *Hayashi* and coworkers, for which the ee of the

Table 1. *Stereoselectivity in the Gold(I)-Catalyzed Reaction of* **1** *and* **2** *Using Ligands Derived from* (R,S)-**11**

Entry	Ligand[4])	Yield [%]	**5** (*trans*)			**6** (*cis*)		
			%	ee [%]	configuration	%	ee [%]	configuration
1	(*R,S*)-**4**	99	89	91	(4*S*,5*R*)	11	7	(4*S*,5*S*)
2	(*R,S*)-**11**	70	88	86	(4*S*,5*R*)	12	5	(4*R*,5*R*)
3	(*R,S*)-**13**	82	91	95	(4*S*,5*R*)	9	12	(4*S*,5*S*)
4	(*R,S*)-**14**	90	91	96	(4*S*,5*R*)	9	17	(4*S*,5*S*)
5	(*R,S*)-**15**	87	90	93	(4*S*,5*R*)	10	9	(4*S*,5*S*)
6	(*R,S*)-**17a**	91	90	94	(4*S*,5*R*)	10	15	(4*R*,5*R*)
7	(*R,S*)-**17b**	82	90	94	(4*S*,5*R*)	10	9	(4*R*,5*R*)
8	(*R,S*)-**17c**	92	90	94	(4*S*,5*R*)	10	9	(4*R*,5*R*)
9	(*R,S*)-**17d**	90	91	94	(4*S*,5*R*)	9	6	(4*R*,5*R*)
10	(*R,S*)-**17e**	84	91	95	(4*S*,5*R*)	9	8	(4*S*,5*S*)
11	(*R,R,S*)-**18**	93	91	95	(4*S*,5*R*)	9	23	(4*S*,5*S*)
12	(*R,S,S*)-**18**	93	91	94	(4*S*,5*R*)	9	22	(4*S*,5*S*)
13	(*R,S*)-**23**	34	87	82	(4*S*,5*R*)	13	8	(4*S*,5*S*)

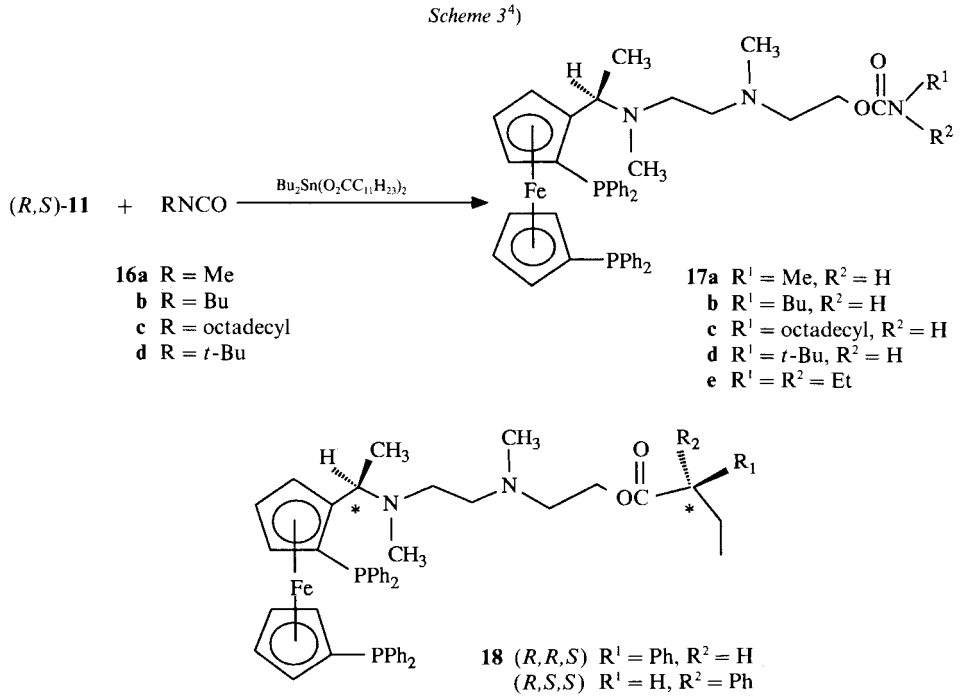
cis-product was higher [10]. The OH-substituted ligand (*R,S*)-**11** gave a somewhat poorer enantioselectivity than the unmodified (*R,S*)-**4** (see *Table 1*). The previously shown dependence of stereoselectivity upon both steric and electronic factors (*vide supra*) provides a ready explanation of these results [30]. In particular, both the internal and external H-bonding interactions possible with ligand (*R,S*)-**11** due to the presence of an OH group would be expected to alter the stereoselectivity. This would be the case either because of changes in the conformational preferences or partial disruption of the enolate-protonated ammonium ion interaction in the stereoselective TS due to H-bonding interactions. Similar stereoselectivity decreases were observed for the other OH-functionalized ferrocenylamines prepared in this study (*vide infra*).

Supportive of this explanation are the results obtained using the benzoates of (*R,S*)-**11**, in which H-bonding of the OH group is eliminated (see *Table 3, Entry 3*). The benzoate (*R,S*)-**13** was prepared by the reaction of the lithium alkoxide, prepared *in situ* from (*R,S*)-**11** and BuLi, with benzoyl chloride (**12**) in Et_2O (97%, column-chromatographed, *Scheme 2*). The diastereo- and enantioselectivity obtained using (*R,S*)-**13** as a ligand was superior to that obtained with (*R,S*)-**4**. Interestingly, the absolute configuration of the minor *cis*-isomer **6** obtained with (*R,S*)-**13** as a ligand was the same as that obtained with (*R,S*)-**4** and opposite to that obtained with (*R,S*)-**11**.

In a similar manner, the mono- and diesters (*R,S*)-**14** and (*R,S*)-**15** (see *Scheme 2*) were prepared by the reaction of (*R,S*)-**11** with the corresponding acyl chlorides of ferrocenecarboxylic acid and ferrocene-1,1′-dicarboxylic acid, respectively, which were prepared *in situ* from the acids and oxalyl chloride. These compounds should prove interesting for studies involving the effect of one-electron oxidation (a mixed ferrocenyl-ferricenyl, *i.e.* Fe^{II}-Fe^{III}, system) upon catalytic activity. This could prove particularly interesting because a modification of bonding paramaters, *e.g.* Fe–Cp bond length (Cp = cyclopentadienyl), would be expected for the oxidized ligand [37]. In the Au^{I}-catalyzed aldol reaction utilizing these (non-oxidized) ligands, a high degree of enantioselectivity was observed in the *trans*-dihydrooxazole isomer (*Table 1*).

The homologous series of carbamates (*R,S*)-**17a–d** were prepared by the reaction of (*R,S*)-**11** with the appropriate isocyanate using dibutyltin dilaurate as a catalyst (*Scheme 3*) [38]. Additionally, *N,N*-diethylcarbamate (*R,S*)-**17e** was prepared by the reaction of the lithium alkoxide of (*R,S*)-**11** with *N,N*-diethylcarbamoyl chloride in tetrahydrofuran

Scheme 3[4])



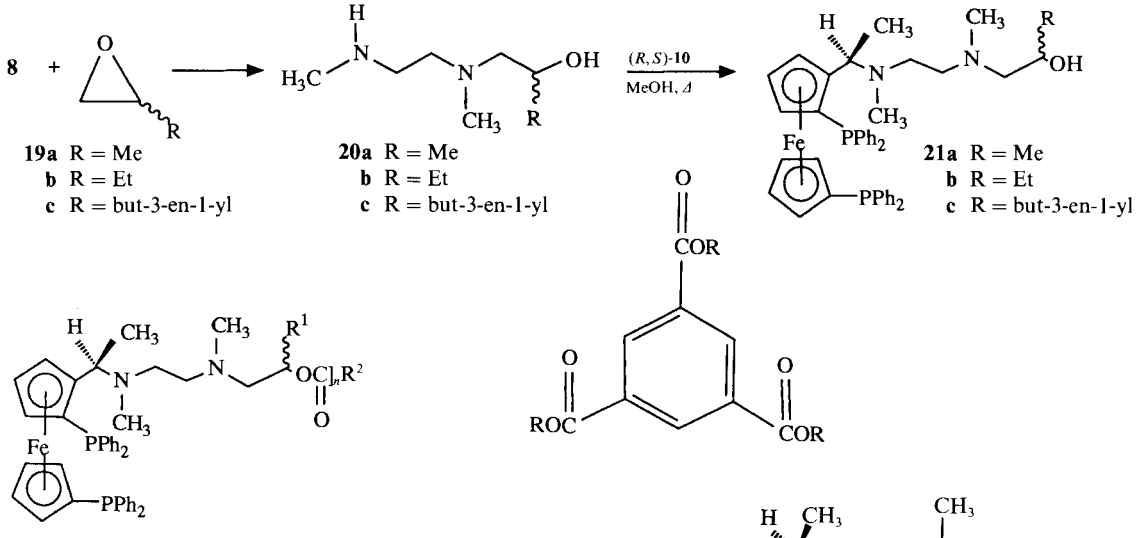
(THF) at reflux temperature (62%, column-chromatographed). Although no significant effect was observed in either the diastereoselectivity of the Au^I-catalyzed aldol reaction or the ee of the major *trans*-dihydrooxazole **5**, a remarkable effect was observed upon the ee of the minor *cis*-dihydrooxazole **6** (*Table 1, Entries 6–10*). As the steric bulk or branching of the alkyl groups attached to the N-atom of the carbamate moiety increased, a reduction of the ee of (4*R*,5*R*)-*cis*-dihydrooxazole **6** was observed. Furthermore, in the case of *N*,*N*-diethylcarbamate (*R*,*S*)-**17e**, (4*S*,5*S*)-*cis*-dihydrooxazole **6** was produced in 8% ee. Both, the absolute configuration and the degree of ee in *cis*-isomer **6** are strongly dependent upon steric effects imposed by the ligand in the stereoselective TS. We have previously reported a similar dependence of the degree of enantioselectivity for *cis*-isomer **6** upon the steric requirements of the substrates themselves [39]. An electronic effect, which has been proposed in certain cases [30] [39], does not appear to be operative because the ligands **17a–e** involve changes in the branching and chain lengths of the alkyl substituents. In any case, the steric requirements are clearly different for achieving maximum ee in the *cis*- and *trans*-dehydrooxazoles. The *cis*-dihydrooxazole **6**, in particular, is quite sensitive to minor changes in the side chain of the ferrocenylamine ligand (*vide infra*).

The availability of (*R*,*S*)-**11** offered a unique opportunity to investigate the effect of an additional stereogenic C-atom (chiral center) in the ferrocenylamine ligand upon the observed stereoselectivity in the Au^I-catalyzed aldol reaction. The diastereoisomers (*R*,*R*,*S*)- and (*R*,*S*,*S*)-**18**[4]) were prepared by the reaction of the lithium alkoxide of (*R*,*S*)-**11** with the corresponding (*R*)- and (*S*)-2-phenylbutanoyl chlorides at −20° in Et_2O (82 and 86%, resp., column-chromatographed; *Scheme 3*). Although little or no difference within experimental error was observed in the ee of the *trans*-dihydrooxazol **5**, a significant increase was observed in the ee of the *cis*-dihydrooxazole **6** with either (*R*,*R*,*S*)- or (*R*,*S*,*S*)-**18** compared to that obtained with **13–15** or **17a–e** (*Table 1*). Our previous work and that of others strongly suggests that the overall increase in ee of the *cis*-dihydrooxazole is steric in origin, *i.e.* increased steric requirements in the TS leading to the *cis*-product due to the size of the 2-phenylbutanoate moiety and is unrelated to the chirality of the ester [10] [30] [39].

Introduction of a Racemic Center. The results obtained using either (*R*,*R*,*S*)- or (*R*,*S*,*S*)-**18** as a ligand suggested that the additional chiral center has little effect upon the ee of *trans*-dihydrooxazole **5**. This observation raised the question as to whether the introduction of an additional distant stereogenic C-atom in a nonstereospecific manner (generation of a diastereoisomeric pair of ligands) would have a significant effect upon stereoselectivity.

A series of racemic aminoalcohols **20a–c** were prepared by the reaction of **8** (excess) with the appropriate monosubstituted oxiranes **19a–c** (*Scheme 4*). The ferrocenylamines **21a–c** were obtained as diastereoisomeric mixtures by the reaction of (*R*,*S*)-**10** with the corresponding aminoalcohols **20a–c** in MeOH at reflux. The ^{1}H-NMR spectra of **21a–c** were clearly that of diastereoisomeric mixtures (*e.g.*, **21a**: 2 *d* at δ 1.07 and 1.09, assigned to $CpCHCH_3$ of each diastereoisomer, integration ratio 1:1). The starting ferrocenylethyl acetate **10** being (*R*,*S*)-configurated, alcohols **21a–c** consisted of (*R*,*R*,*S*)- and (*R*,*S*,*S*)-diastereoisomers. The ester and carbamate ligands **22a–k** were prepared by the reaction of a particular alcohol **21a–c** with the corresponding acyl chloride or isocyanate in a conventional manner.

Scheme 4[4])



19a R = Me
b R = Et
c R = but-3-en-1-yl

20a R = Me
b R = Et
c R = but-3-en-1-yl

21a R = Me
b R = Et
c R = but-3-en-1-yl

22a R^1 = Me, R^2 = Ph, n = 1
b R^1 = Me, R^2 = Pr, n = 1
c R^1 = Me, R^2 = $(CH_2)_4$, n = 2
d R^1 = Me, R^2 = $(CH_2)_8$, n = 2
e R^1 = Me, R^2 = PhNH, n = 1
f R^1 = Me, R^2 = BuNH, n = 1
g R^1 = Me, R^2 = octadecylamino, n = 1
h R^1 = Me, R^2 = $NH(CH_2)_6NH$, n = 2
i R^1 = Et, R^2 = MeNH, n = 1
j R^1 = Et, R^2 = octadecylamino, n = 1
k R^1 = Et, R^2 = $NH(CH_2)_6NH$, n = 2
l R^1 = but-3-en-1-yl, R^2 = MeNH, n = 1
m R^1 = but-3-en-1-yl, R^2 = octadecylamino, n = 1

23 R =

Although the ligands were diastereoisomeric mixtures, several interesting trends could be seen when they were utilized in the Au^I-catalyzed aldol reaction. The free ferrocenylaminoalcohols **21a–c** all gave a lower ee in the major *trans*-dihydrooxazole **5** than either (*R,S*)-**4** or any of the derivatives **22a–m** prepared from them (*Table 2, Entries 1–3*). Quite interesting is the observation that the absolute configuration of *cis*-dihydrooxazole **6** produced in ee from **21a–c** was *opposite* in all cases to that produced in ee from **22a–m** which do not have a free OH group. This supports the previous contention that H-bonding has a significant effect upon the conformations or enolate-ammonium-ion bonding leading to products in the stereoselective TS.

A high ee was observed in the major *trans*-isomer **5** when either the esters or carbamates **22a–k** were used as ligands. In all cases, the enantioselectivity observed was equivalent to or somewhat higher than that obtained using (*R,S*)-**4** (*Table 2, Entries 4–17*). Perhaps significantly, the lowest ee's observed (*Table 2, Entries 6, 7, 14,* and *17*) were those obtained using either a diester or dicarbamate derivative. This fact suggests

Table 2. *Stereoselectivity in the Gold(I)-Catalyzed Reaction of* **1** *and* **2** *Using the (*R,R,S*)- and (*R,S,S*)-Diastereoisomeric Ferrocenylamine Ligands* **22a–m**

Entry	Ligand	Yield [%][a])	**5** (*trans*)			**6** (*cis*)		
			%	ee [%]	Configuration	%	ee [%]	Configuration
1	**21a**	97	88	89	(4*S*,5*R*)	12	7	(4*S*,5*S*)
2	**b**	87	88	88	(4*S*,5*R*)	12	10	(4*S*,5*S*)
3	**c**	90	89	88	(4*S*,5*R*)	11	10	(4*S*,5*S*)
4	**22a**	93	91	97	(4*S*,5*R*)	9	9	(4*R*,5*R*)
5	**b**	95	91	97	(4*S*,5*R*)	9	8	(4*R*,5*R*)
6	**c**	79	89	92	(4*S*,5*R*)	11	8	(4*R*,5*R*)
7	**d**	89	90	93	(4*S*,5*R*)	10	13	(4*R*,5*R*)
8	**e**	96	89	95	(4*S*,5*R*)	11	19	(4*R*,5*R*)
9	**f**	96	90	97	(4*S*,5*R*)	10	27	(4*R*,5*R*)
10	**g**	97	91	95	(4*S*,5*R*)	9	31	(4*R*,5*R*)
11	**g**	94[b])	93	94	(4*S*,5*R*)	7	36	(4*R*,5*R*)
12	**g**	97[c])	93	94	(4*S*,5*R*)	7	28	(4*R*,5*R*)
13	**g**	89[d])	91	95	(4*S*,5*R*)	9	8	(4*R*,5*R*)
14	**h**	90	90	93	(4*S*,5*R*)	10	29	(4*R*,5*R*)
15	**i**	91	91	95	(4*S*,5*R*)	9	35	(4*R*,5*R*)
16	**j**	95	91	96	(4*S*,5*R*)	9	24	(4*R*,5*R*)
17	**k**	89	91	92	(4*S*,5*R*)	9	28	(4*R*,5*R*)
18	**l**	95	90	96	(4*S*,5*R*)	10	26	(4*R*,5*R*)
19	**m**	95	91	96	(4*S*,5*R*)	9	24	(4*R*,5*R*)

[a]) Solvent: CH_2Cl_2 unless otherwise indicated. [b]) Solvent: glyme. [c]) Solvent: diglyme. [d]) Solvent: 1,2-dichloroethane.

that the reduced conformational freedom of the ferrocenyl ligand side chain in the bisadduct adversely affects the geometry of the TS leading to the (4*S*,5*R*)-*trans*-dihydrooxazole. This effect could manifest itself in either the $\Delta H^{\neq}$ (steric interactions) or $\Delta S^{\neq}$ (reduction in conformational freedom) terms contributing to $\Delta G^{\neq}$, or both. This was apparently not the case for the ee in the minor *cis*-dihydrooxazole. An observable decrease in the ee of *trans*-isomer **5** was not apparent using diester (*R,S*)-**15** (*Table 1, Entry 5*). This might be the case because the lack of branching in the hydroxyethyl group may attenuate the reduction in side-chain conformational freedom. The more sterically crowded derivative (*R,S*)-**23** (*Scheme 4*) was prepared to test this contention. Triester (*R,S*)-**23** was prepared by reaction of the lithium alkoxide of (*R,S*)-**11** with benzene-1,3,5-tricarbonyl chloride. The lower diastereo- and enantioselectivity obtained support the proposed conformational argument (*Table 1, Entry 13*).

In the case of ligand **22g**, little change was observed in the ee of *trans*-isomer **5** upon change of the solvent from CH_2Cl_2 to either ethyleneglycol dimethyl ether (glyme), diethyleneglycol dimethyl ether (diglyme), or 1,2-dichloroethane (*Table 2, Entries 10–13*). A slightly higher diastereoselectivity for *trans*-isomer **5** was observed in the glyme solvents. A significant variation on the ee of *cis*-isomer **6** was observable upon changing solvents. We have previously observed, in certain cases, a significant solvent effect upon enantioselectivity [30a]. The suggestion was made that the dielectric constant of the reaction medium can markedly affect the preferred conformation or enolate-ammonium-ion bonding in the stereoselective TS [30] [39–41]. A similar explanation in the present case is advanced.

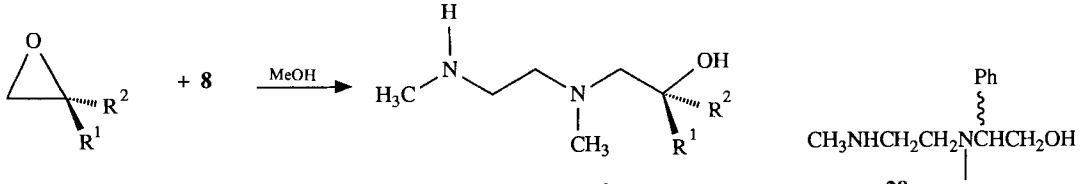
An examination of the results obtained using the esters **22a,b** or the carbamates **22e,f** reveals that the ee of *cis*-product **6** was significantly higher for the carbamates. Although **22a,b** and **22e,f** differ by an additional N-atom in the case of the carbamates, it is apparent that in the esters either the Ph or Bu group is one atom closer to the reaction center. Although the observed differences in ee of *cis*-isomer **6** may be due to the closer proximity of the ester than that of the carbamate moiety, other conformational factors cannot be ruled out.

Somewhat disconcerting is the fact that a high ee of *trans*-isomer **5** was obtained using ferrocenylamine ligands *that were diastereoisomeric mixtures*. That the racemic center was not in close-enough proximity to the reaction center to affect stereochemistry is *not* a reasonable explanation because significant changes in the enantioselectivity for the *cis*-isomer **6** were observed. As a reasonable argument may be advanced that the observed invariant enantioselectivity for the *trans*-isomer **5** is an artifact and that a single diastereoisomer provides a low-energy pathway to the (4*R*,5*S*)-*trans*-dihydrooxazole observed. Preferential reactivity through a single diastereoisomer of the ligand used could mask or attenuate the normal stereoselectivity of the other diastereoisomeric ligand present. This explanation can, in fact, also be advanced for the observed changes in enantioselectivity for *cis*-isomer **6**.

Introduction of One Additional Chiral Center. A clear understanding of the results obtained required the introduction of an additional chiral center with known absolute configuration. The reaction of optically active propylene oxide with nucleophiles to give optically active products with retention of configuration is well described in the literature [42]. A specific example of the reaction of (*R*)-styrene oxide with an amine to give (*R*)-aminoalcohol was reported by *Brown* and *Pai* [43].

The (*R*)- and (*S*)-aminopropanols **26** were prepared by the reaction of an excess of **8** with the corresponding (*R*)- or (*S*)-propylene oxides **24** (*Scheme 5*). Similarly, the chiral phenethyl derivatives **27** were prepared from either (*R*)- or (*S*)-styrene oxide **25**, and **8**, respectively. In the case of the reaction of **8** with styrene oxide, a small quantity of regioisomer **28** was detected in the ^{1}H-NMR spectrum of the product. Although **28** was not readily removed at this stage, the product of this regioisomer with **10** was removed by column chromatography. The separate reaction of the enantiomers of **26** or **27** with (*R,S*)-**10** gave the desired OH-functionalized ligands **29** and **30**. In the case of the aminopropanols **26**, the diastereoisomeric products formed by the reaction with (*S,S*)-**10** were also prepared. The *N*-methyl- and *N*-octadecylcarbamate **31a,b** and **32a,b** were

Scheme 5[4])



(*R*)-**24** R^1 = H, R^2 = Me
(*S*)-**24** R^1 = Me, R^2 = H
(*R*)-**25** R^1 = H, R^2 = Ph
(*S*)-**25** R^1 = Ph, R^2 = H

(*R*)-**26** R^1 = H, R^2 = Me
(*S*)-**26** R^1 = Me, R^2 = H
(*R*)-**27** R^1 = H, R^2 = Ph
(*S*)-**27** R^1 = Ph, R^2 = H

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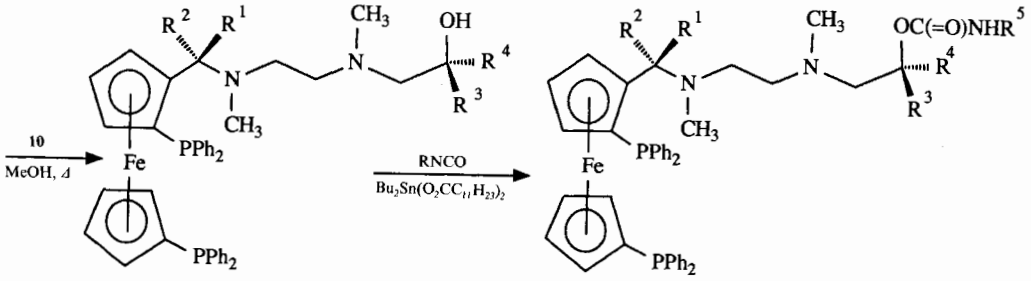
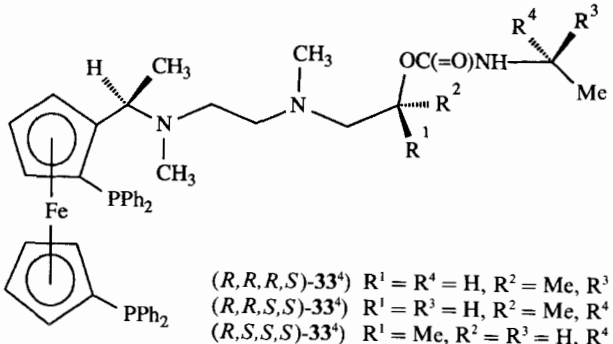
Scheme 5 (cont.)

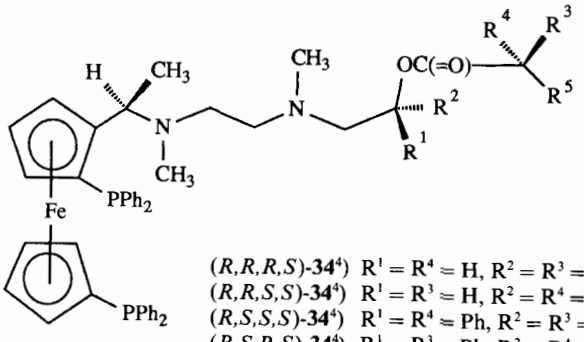


(*R,R,S*)-**29** $R^1 = R^4 = Me$, $R^2 = R^3 = H$
(*R,S,S*)-**29** $R^1 = R^3 = Me$, $R^2 = R^4 = H$
(*S,R,S*)-**29** $R^1 = R^3 = H$, $R^2 = R^4 = Me$
(*S,S,S*)-**29** $R^1 = R^4 = H$, $R^2 = R^3 = Me$
(*R,R,S*)-**30** $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = Ph$
(*R,S,S*)-**30** $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = Ph$

(*R,R,S*)-**31a** $R^1 = R^4 = Me$, $R^2 = R^3 = H$, R^5 = octadecyl
(*R,S,S*)-**31a** $R^1 = R^3 = Me$, $R^2 = R^4 = H$, R^5 = octadecyl
(*S,R,S*)-**31a** $R^1 = R^3 = H$, $R^2 = R^4 = Me$, R^5 = octadecyl
(*S,S,S*)-**31a** $R^1 = R^4 = H$, $R^2 = R^3 = Me$, R^5 = octadecyl
(*R,R,S*)-**31b** $R^1 = R^4 = R^5 = Me$, $R^2 = R^3 = H$
(*R,S,S*)-**31b** $R^1 = R^3 = R^5 = Me$, $R^2 = R^4 = H$
(*R,R,S*)-**32a** $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = Ph$, R^5 = octadecyl
(*R,S,S*)-**32a** $R^1 = Me$, $R^2 = R^4 = H$, $R^3 = Ph$, R^5 = octadecyl
(*R,R,S*)-**32b** $R^1 = R^5 = Me$, $R^2 = R^3 = H$, $R^4 = Ph$
(*R,S,S*)-**32b** $R^1 = R^5 = Me$, $R^2 = R^4 = H$, $R^3 = Ph$



(*R,R,R,S*)-**33**[4]) $R^1 = R^4 = H$, $R^2 = Me$, R^3 = naphth-1-yl
(*R,R,S,S*)-**33**[4]) $R^1 = R^3 = H$, $R^2 = Me$, R^4 = naphth-1-yl
(*R,S,S,S*)-**33**[4]) $R^1 = Me$, $R^2 = R^3 = H$, R^4 = naphth-1-yl
(*R,S,R,S*)-**33**[4]) $R^1 = Me$, $R^2 = R^4 = H$, R^3 = naphth-1-yl



(*R,R,R,S*)-**34**[4]) $R^1 = R^4 = H$, $R^2 = R^3 = Ph$, $R^5 = Et$
(*R,R,S,S*)-**34**[4]) $R^1 = R^3 = H$, $R^2 = R^4 = Ph$, $R^5 = Et$
(*R,S,S,S*)-**34**[4]) $R^1 = R^4 = Ph$, $R^2 = R^3 = H$, $R^5 = Et$
(*R,S,R,S*)-**34**[4]) $R^1 = R^3 = Ph$, $R^2 = R^4 = H$, $R^5 = Et$
(*R,R,S*)-**35**[4]) $R^1 = R^3 = R^4 = H$, $R^2 = R^5 = Ph$
(*R,S,S*)-**35**[4]) $R^1 = R^5 = Ph$, $R^2 = R^3 = R^4 = Ph$

obtained from the corresponding OH-functionalized ligands **29** or **30** with either methyl or octadecyl isocyanate.

The four possible enantiomerically pure diastereoisomers **31a** were evaluated as ligands in the Au^{I}-catalyzed reaction of **1** with **2** (*Table 3, Entries 1–4*). The examination of the results obtained with the diastereoisomers **31a** substantiate our previous communication on the importance of central chirality upon stereoselectivity in product formation. The previously observed lower diastereo- and enantioselectivity in the formation of the major *trans*-isomer **5** when (*S,S*)-**4** is used in place of (*R,S*)-**4** is also observed for **31a** (*Table 3*, compare *Entries 1* and *2* with *3* and *4*) [29] [30a].

Table 3. *Stereoselectivity in the Gold(I)-Catalyzed Reaction of* **1** *and* **2** *Using Ferrocenylamine Ligands with Two Stereogenic C-Atoms*

Entry	Ligand	Yield [%][a][b]	**5** (*trans*)			**6** (*cis*)		
			%	ee [%]	Configuration	%	ee [%]	Configuration
1	(*R,R,S*)-**31a**	84	90	96	(4*S*,5*R*)	10	40	(4*R*,5*R*)
2	(*R,S,S*)-**31a**	88	90	93	(4*S*,5*R*)	10	9	(4*R*,5*R*)
3	(*S,R,S*)-**31a**	90	80	42	(4*R*,5*S*)	20	19	(4*S*,5*S*)
4	(*S,S,S*)-**31a**	90	79	44	(4*R*,5*S*)	21	33	(4*S*,5*S*)
5	(*R,R,S*)-**31b**	95	89	96	(4*S*,5*R*)	11	45	(4*R*,5*R*)
6	(*R,S,S*)-**31b**	90	90	94	(4*S*,5*R*)	10	13	(4*R*,5*R*)
7	(*R,R,S*)-**32a**	92	90	96	(4*S*,5*R*)	10	35	(4*R*,5*R*)
8	(*R,S,S*)-**32a**	95	90	94	(4*S*,5*R*)	10	4	(4*S*,5*S*)
9	(*R,R,S*)-**32b**	83	89	96	(4*S*,5*R*)	11	40	(4*R*,5*R*)
10	(*R,S,S*)-**32b**	87	91	94	(4*S*,5*R*)	9	2	(4*R*,5*R*)

[a]) Solvent: CH_2Cl_2. [b]) Yield after distillation.

Furthermore, the additional stereogenic C-atom has a significant effect upon the observed enantioselectivity, especially for *cis*-isomer **6** (*Table 3*, compare, *e.g., Entries 1* and *2*). Moreover, the results strongly support the contention that the planar and central chirality can act in either a cooperative (*internal cooperativity of chirality*) or noncooperative manner in the control of diastereo- and enantioselectivity. The examination of the present results clearly indicate that an additional chiral center can act in either a cooperative or noncooperative manner with the other elements of chirality in the formation of a particular enantiomer of either the *cis*- or *trans*-dihydrooxazole.

When the absolute configuration of both stereogenic C-atoms (chiral centers) is opposite to that of the planar chirality[4]) [44] [45] the highest ee of (4*R*,5*R*)-**6** is obtained. The use of (*R,S,S*)-**31a** instead of (*R,R,S*)-**31a** leads to a slight reduction of *trans*-enantioselectivity and a significant reduction of *cis*-enantioselectivity. That the small reduction in ee of the (4*S*,5*R*)-*trans*-isomer **5** is *not* an artifact due to experimental error is demonstrated by an almost identical drop in enantioselectivity observed for the other (*R,S,S*)-ligands studied (*Table 3*, compare *Entries 1* and *2*, *5* and *6*, *7* and *8*, and *9* and *10*). In an analogous manner, when the absolute configuration of the central and planar chirality are the same, *i.e.* (*S,S,S*)-**31a**, the maximum ee of the (4*S*,5*S*)-*cis*- and (4*R*,5*S*)-*trans*-dihydrooxazole is observed. The gradual change from a maximum ee of (4*R*,5*R*)-**6** with the (*R,R,S*)-ligand **31a** to a maximum ee of (4*S*,5*S*)-**6** with the (*S,S,S*)-ligand **31a** is evident. Similar observations were made for the enantioselectivity for the *trans*-dihydrooxazole.

The results obtained do not mean, in the case of ligand **31a**, that the highest enantioselectivity for the (4*R*,5*S*)-*trans*- and (4*S*,5*S*)-*cis*-isomer can be obtained using (*S,S,S*)-**31a**. In fact, the highest ee for these enantiomers would be obtained using (*S,S,R*)-**31a**, which is the enantiomer of (*R,R,S*)-**31a**. This must clearly be the case because (*S,S,R*)-**31a** would give the products that are the mirror image to that obtained with the enantiomeric (*R,R,S*)-**31a**. For the ligands presently studied, the *maximum degree of internal cooperativity of chirality is obtained when the axial and central chirality have opposite absolute configurations* (*vide infra*). With this conclusion, the caveat must be attached that the absolute configuration of a particular stereogenic C-atom (chiral center) required for maximum ee must be dependent upon the TS structure of the stereoselective step of the reaction. The particular sequence of chirality required could change simply because the *Cahn-Ingold-Prelog* nomenclature is, of course, based upon a specific sequencing of atoms that is independent of their geometric requirements.

Surprisingly, no difference was observed in the ee of the (4*S*,5*R*)-**5** obtained upon changing from a Me to a Ph group on the stereogenic C-atom of the ferrocenylamine side chain (*Table 3, Entries 7–10*). Similarly, no change in ee was observed between the *N*-methyl- and *N*-octadecylcarbamates in the *trans*-product **5**. Small changes were observed in the ee of the *cis*-isomer **6**. What is striking, however, is that the *sequence of chirality appears to have the dominant effect upon stereoselectivity. E.g.*, in all cases, a change from a (*R,R,S*)- to a (*R,S,S*)-ligand results in a reduction in ee of the (4*R*,5*R*)-*cis*-isomer **6**.

The question naturally arised as to what degree the changes in stereoselectivity observed are due to a simple increase in the size of the ferrocenyl side chain. An attempt to separate steric effects from those due to cooperativity can be made by comparison of the various diastereoisomers of **31a** with those of **4** (*Table 4*). If the assumption is made that the differences in stereoselectivity obtained with (*R,S*)-**4** and (*R,S,S*)-**31a** are due to an increase in size of the ferrocenylamine side chain, then further differences observed between (*R,S,S*)-**31a** and (*R,R,S*)-**31a** are due to the effect of chiral cooperativity (*Table 4, Entries 1–3*)[6]. A similar argument can be made for the comparison of (*S,S*)-**4** with (*S,R,S*)-**31a** and (*S,S,S*)-**31a** (*Table 4, Entries 4–6*). This analysis clearly shows that the sequence of chirality affects the stereoselectivity obtained over that of a simple steric effect.

With the enantiomerically pure diastereoisomers **31a** in hand, the stereoselectivity obtained with (*R,R,S*)-**31a** and (*R,S,S*)-**31a** can be compared with that produced by **22g**, which is a 1:1 mixture of these diastereoisomers (*vide supra*). Quite interestingly, the results obtained with **22g** (*Table 2, Entry 10*) approach the average of the stereoselectivity obtained with (*R,R,S*)-**31a** and (*R,S,S*)-**31a** (*Table 3, Entries 1* and *2*). That the stereoselectivity obtained appears to slightly favor the selectivity of the (*R,R,S*)-diastereoisomer is reasonable based upon the fact that, since it displays the highest cooperativity, a lower free energy of activation (ΔG^*) for product formation from that diastereoisomer is

[6]) Of course, the argument can be reversed by first comparing (*R,S*)-**4** with (*R,R,S*)-**31a**, and then differences obtained for (*R,S,S*)-**31a** are due to cooperativity. Although the end result is comparable, the comparisons made in the text, *e.g.*, (*R,S*)-**4** with (*R,S,S*)-**31a**, give the least change in enantioselectivity, and this change in ee is considered due to steric effects. Effects over this assigned steric effect are then assigned to cooperativity. This approach is more appealing, and the results obtained are conceptually easier to analyse, than the approach that considers cooperativity (or the lack thereof) as a negative attribute on a larger steric effect.

Table 4. *Separation of Steric Effects and Cooperativity*

Entry	Ligand	Chirality		**5** (*trans*)			**6** (*cis*)		
		central	planar	%	ee [%]	Configuration	%	ee [%]	Configuration
1	**31a**	(*R*,*R*)	(*S*)	90	96	(4*S*,5*R*)	10	40	(4*R*,5*R*)
2	**31a**	(*R*,*S*)	(*S*)	90	93	(4*S*,5*R*)	10	9	(4*R*,5*R*)
3	**4**	(*R*)	(*S*)	90	91	(4*S*,5*R*)	10	7	(4*S*,5*S*)
4	**4**	(*S*)	(*S*)	84	41	(4*R*,5*S*)	17	20	(4*S*,5*S*)
5	**31a**	(*S*,*R*)	(*S*)	80	42	(4*R*,5*S*)	20	19	(4*S*,5*S*)
6	**31a**	(*S*,*S*)	(*S*)	79	44	(4*R*,5*S*)	21	33	(4*S*,5*S*)
7	**33**	(*R*,*R*,*R*)	(*S*)	90	95	(4*S*,5*R*)	10	34	(4*R*,5*R*)
8	**33**	(*R*,*R*,*S*)	(*S*)	89	95	(4*S*,5*R*)	11	35	(4*R*,5*R*)
9	**31a**	(*R*,*R*)	(*S*)	90	96	(4*S*,5*R*)	10	40	(4*R*,5*R*)
10	**31a**	(*R*,*S*)	(*S*)	90	93	(4*S*,5*R*)	10	9	(4*R*,5*R*)
11	**33**	(*R*,*S*,*S*)	(*S*)	89	93	(4*S*,5*R*)	11	2	(4*S*,5*S*)
12	**33**	(*R*,*S*,*R*)	(*S*)	89	90	(4*S*,5*R*)	11	10	(4*S*,5*S*)
13	**34**	(*R*,*R*,*R*)	(*S*)	89	92	(4*S*,5*R*)	11	23	(4*S*,5*S*)
14	**34**	(*R*,*R*,*S*)	(*S*)	89	92	(4*S*,5*R*)	11	17	(4*S*,5*S*)
15	**35**	(*R*,*R*)	(*S*)	88	90	(4*S*,5*R*)	12	7	(4*S*,5*S*)
16	**35**	(*R*,*S*)	(*S*)	89	90	(4*S*,5*R*)	11	5	(4*S*,5*S*)
17	**34**	(*R*,*S*,*R*)	(*S*)	89	90	(4*S*,5*R*)	11	6	(4*S*,5*S*)
18	**34**	(*R*,*S*,*S*)	(*S*)	89	90	(4*S*,5*R*)	11	21	(4*S*,5*S*)

expected. This result is consistent with the proposed kinetic analysis of the Au^I-catalyzed aldol reaction [30a].

Introduction of Two Additional Chiral Centers. The availability of the chiral ferrocenylamine alcohols **29** and **30** offered the opportunity to add a second additional stereogenic C-atom (chiral center) in a defined manner. The carbamate ligands **33** were prepared by the reaction of (*R*,*R*,*S*)- or (*R*,*S*,*S*)-**29** with either (*R*)- or (*S*)-1-(naphth-1-yl)ethyl isocyanate. The carboxylate derivatives **34** were prepared by the reaction of (*R*,*R*,*S*)-**30** with either (*R*)- or (*S*)-2-phenylbutanoyl chloride, which were prepared *in situ* from the corresponding (*R*)- or (*S*)-acid and oxalyl chloride [46].

An examination of the results obtained using **33** and **34** as ligands in the Au^I-catalyzed aldol reaction reveals that the additional chiral centers have little effect upon the ee

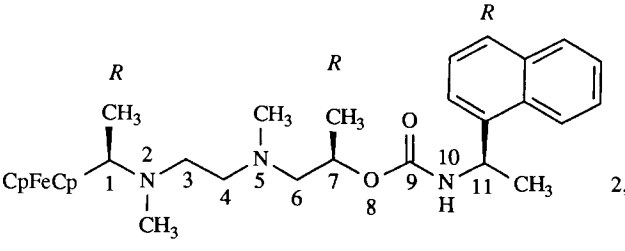
Table 5. *Stereoselectivity in the Gold(I)-Catalyzed Reaction of* **1** *and* **2** *Using Ferrocenylamine Ligands with Three Stereogenic C-Atoms*

Entry	Ligand	Yield [%][a][b]	**5** (*trans*)			**6** (*cis*)		
			%	ee [%]	Configuration	%	ee [%]	Configuration
1	(*R*,*R*,*R*,*S*)-**33**	88	90	95	(4*S*,5*R*)	10	34	(4*R*,5*R*)
2	(*R*,*R*,*S*,*S*)-**33**	96	89	95	(4*S*,5*R*)	11	35	(4*R*,5*R*)
3	(*R*,*S*,*S*,*S*)-**33**	95	89	93	(4*S*,5*R*)	11	2	(4*S*,5*S*)
4	(*R*,*S*,*R*,*S*)-**33**	89	89	90	(4*S*,5*R*)	11	10	(4*S*,5*S*)
5	(*R*,*R*,*R*,*S*)-**34**	91	89	92	(4*S*,5*R*)	11	23	(4*S*,5*S*)
6	(*R*,*R*,*S*,*S*)-**34**	80	89	92	(4*S*,5*R*)	11	17	(4*S*,5*S*)
7	(*R*,*S*,*S*,*S*)-**34**	80	89	90	(4*S*,5*R*)	11	21	(4*S*,5*S*)
8	(*R*,*S*,*R*,*S*)-**34**	89	89	90	(4*S*,5*R*)	11	6	(4*S*,5*S*)
9	(*R*,*R*,*S*)-**35**	68	88	90	(4*S*,5*R*)	12	7	(4*S*,5*S*)
10	(*R*,*S*,*S*)-**35**	73	89	90	(4*S*,5*R*)	11	5	(4*S*,5*S*)

[a]) Solvent: CH_2Cl_2. [b]) Yield after distillation.

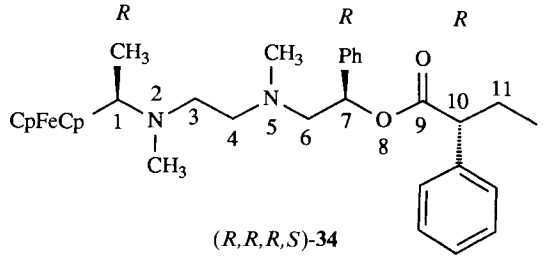
trans-isomer **5**, although the ee of **5** was somewhat lower in the case of carboxylate ligand **34** (*Tables 4* and *5*). In all cases, a slightly higher ee of the (4*S*,5*R*)-*trans*-enantiomer was obtained using either (*R*,*R*,*R* or *S*)-**33** or -**34** than with (*R*,*S*,*R* or *S*,*S*)-**33** or -**34**. In the case of the carbamate ligands **33**, a change from (*R*,*R*,*R* or *S*,*S*)- to a (*R*,*S*,*R* or *S*,*S*)-sequence of chirality results in a change from an ee of the (4*R*,5*R*)-*cis*-enantiomer **6** to that of the (4*S*,5*S*)-enantiomer. A similar observation was made for the (*R*,*R*,*S*)- and (*R*,*S*,*S*)-carbamates **31** or **32** (*vide supra; Table 4*, compare *Entries 7–12*).

In the case of the esters **34**, however, the (4*S*,5*S*)-*cis*-enantiomer **6** was produced in all cases (*Table 5*). A reasonable explanation of these results, which takes into account that the ee of (4*S*,5*R*)-*trans*-enantiomer **5** was lower using the esters **34**, is that the terminal chiral center of **34** is in closer proximity to the reaction center where C–C bond formation is occurring than in the carbamates **33**. The different steric requirements imposed in the stereoselective TS results in a change of stereoselectivity for the *cis*-product, which was similarly observed previously in the case of the diastereoisomeric ligands. That different steric and possibly electronic requirements are expected can be seen by an inspection of the chiral side chain drawn in an extended form (*Fig.*). It would appear unlikely that



2,7-synperiplanar, 7,11-antiperiplanar

(*R*,*R*,*R*,*S*)-**33**



2,7-synperiplanar, 7,10-antiperiplanar

(*R*,*R*,*R*,*S*)-**34**

Figure. *Extented from the ligand side chain of* (R,R,R,S)-**33** *and* (R,R,R,S)-**34**

the observed difference was due to the presence of Ph rather than Me at the stereogenic C-atom, because no significant differences were observed between the stereoselectivity using the simple carbamates of **29** or **30**. A separation of steric and cooperative effects as previously discussed can be found in *Table 4* (*Entries 7–18*). In this case, however, the various derivatives **34** are compared with the phenylacetates (*R*,*R*,*S*)-**35** and (*R*,*S*,*S*)-**35**, because the stereoselectivity of the carbamates and carboxylates are established to be clearly different. The results obtained using the various diastereoisomers of **33** and **34**

clearly suggest that the effect of the third chiral center upon stereoselectivity is attenuated, probably due to an increase in the distance of the additional chiral center from the C–C bond forming process. The subtle differences in ee observed for *cis*-product **6** suggest, nevertheless, that the additional chiral center has an influence in the geometry of the TS of the stereoselective step. Small, but clear trends in enantioselectivity for the *cis*-dihydrooxazole are observed, particularly when **34** is used as a ligand.

The mechanism for transmission of chiral information from the stereogenic C-atoms C(7) and C(10) or C(11) (numbering of the *Fig.*) is not immediately obvious in light of the TS structure proposed [30a]. A significant difference between the previously prepared ferrocenylamine ligands and those of this study is that, upon protonation, the *terminal N-atom becomes both stereogenic and chirotopic, i.e.* a new chiral center is formed. This must be the case, because upon protonation, the lone pair of electrons no longer undergoes rapid pyramidal inversion. In the reaction mechanisms proposed [7] [30a], the terminal N-atom becomes protonated during formation of the enolate from the α-isocyanoacetate and remains both protonated and electrostatically bound to the enolate in the stereoselective step of the reaction. In the case of ligands such as **4**, of course, the terminal N-atom does not become stereogenic because it is bound to two identical ligands.

Prior to protonation, the rapid pyramidal inversion of the lone pair of electrons provides a ready access to either the (*R*)- or (*S*)-configuration at the N-atom. The formation of either the (*R*)- or (*S*)-configuration at the protonated N-atom will be strongly influenced by the proximate stereogenic C(7) atom because the two protonated forms are diastereoisomeric and, by definition, different in energy.

Additionally, the Me group bonded to the stereogenic C(1) atom is positioned six bonds away from the Me group bonded to the forming stereogenic N(5) atom. Steric effects that arise from 1,6-interactions of Me groups on stereogenic atoms are well documented and form the basis of *Newman*'s classic rule of six [47] [48]. In the reaction of β-keto-esters with alkyl-metal derivatives, the effects upon stereoselectivity of a chiral center within the molecule are well studied. Such classic studies led to the well known rules of both *Cram* and *Prelog*. Similar conformational arguments are advanced here to explain the transmission of chiral information. Although information about the preferred conformation of the terminal carbamate and carboxylate derivatives are presently lacking for **33** and **34**, the terminal stereogenic C-atom (chiral center) is, nevertheless, expected to sterically interact to some degree with the stereogenic C(7) atom. That the chiral information of the terminal chiral center in **33** and **34** is transferred by an interaction with the chiral center C(7) is supported by the fact that no differences were observed for the diastereoisomeric esters (*R,R,S*)-**18** and (*R,S,S*)-**18**, which lack a stereogenic C(7) atom. In any case, the absolute configuration of the forming stereogenic N-atom will strongly affect the stereoselectivity because it is electrostatically bonded to the enolate of the α-isocyanoester in the stereoselective TS[7]).

Conclusions. – The results of this study clearly support the previously communicated concept of internal chiral cooperativity. The results obtained reveal that the sequence of the chiral centers (chirotopic and stereogenic C-atoms) in the ferrocenylamine side chain

[7]) If and to what degree the proton on the N(5) atom could also be H-bonded to the N(2) atom is not known, although such bonding would not necessarily affect this argument.

has a strong influence upon the ee of the products obtained in the Au^I-catalyzed aldol reaction. Furthermore, the results substantiate the previous contention that both the central and planar chirality of chiral ferrocenylamine ligands have a significant effect upon stereoselectivity in this reaction. The proposed mechanistic model for the TS of the stereoselective step of the Au^I-catalyzed aldol reaction [30a] provides a steric explanation for the observed chiral cooperativity, although we have demonstrated that electronic influences may also be operative in certain cases [30a] [30b] [39]. The transmission of the chiral information from the stereogenic C-atoms (chiral centers) in the ferrocenylamine ligand remote from the C–C bond-forming process in the stereoselective TS is suggested to be due to the formation of a chiral center at the terminal N(5) atom, which is subject to both proximate and remote 1,6-steric effects (*Newman*'s rule of six).

It is intriguing to speculate as to whether similar cooperative effects between combinations of central planar, axial, and helical chirality can be found. Based upon our studies, such cooperative effects are indeed expected and should provide a new avenue of exploration in the design of transition-metal catalysts.

Experimental Part

General. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use. Tetrahydrofuran (THF), Et_2O, toluene, and benzene were distilled prior to use from a deep-blue soln. of sodium ketyl under N_2. Reactions were carried out in dried apparatus under a dry inert atmosphere of Ar using standard inert-atmosphere and *Schlenk* techniques. GLC: 50-m *Chirasil*-L-*Val* column on a *Carlo-Erba* GLC, model *HRGC 5300*. Column chromatography (CC): *Woelm* alumina *N* (act. IV), *ICN Biomedicals* alumina *N* (act. I), and *Merck* silica gel *60* (70–230 mesh). M.p.: in open capillary tubes; uncorrected. IR spectra: in cm^{-1}. ^{1}H-NMR (300.133 MHz), ^{19}F-NMR (282.421 MHz), and ^{31}P-NMR (121.496 MHz) spectra: *Bruker-300-FT* NMR spectrometer; ^{31}P-NMR, with full proton decoupling; δ's in ppm rel. to a standard (^{1}H, tetramethylsilane; ^{31}P, 85% H_3PO_4 (external); ^{19}F, CCl_3F ($\delta(CF_3CO_2D) = -78.5$)) where a positive sign is downfield from the standard, coupling constants J in Hz. Elemental analysis were performed by Analytical Research Services, *Ciba-Geigy AG*.

General Procedure: Reaction on an Aldehyde with an α-Isocyanoacetate. To a soln. of 45.65 mg (0.055 mmol) of the ferrocenylamine ligand in 6 ml of CH_2Cl_2 was added 25.70 mg (0.05 mmol) of bis(cyclohexane isocyanide)gold(I) tetrafluoroborate. The mixture was stirred 10 min and then, to the resultant soln., were added sequentially 5 mmol of alkyl isocyanoacetate and 5.5 mmol of aldehyde. The mixture was stirred for 24 h at r.t., the solvent evaporated, and the residue dissolved in 20 ml of Et_2O. Any insolubles were removed by filtration, and the solvent was evaporated. The residue was bulb-to-bulb distilled to give a *cis/trans* mixture of dihydrooxazoles **5**/**6**.

2-{N-Methyl-N-[2-(methylamino)ethyl]amino}ethanol (**9**). To a soln. of 176.3 g (2 mol) of **8** in 400 ml of MeOH at 35° were introduced, below the surface, with a gas dispersing tube, 26.4 g (0.6 mol) of **7** within 3 h. The solvent was evaporated and the residue distilled: 54.0 g (68%) of a colorless liquid. **B.p.** 70°/0.1 Torr. IR (neat): 3288 (OH, NH). ^{1}H-NMR ($CDCl_3$): 2.29 (*s*, CH_3N); 2.40 (*s*, CH_3N); 2.56 (overlapping *t*, NCH_2CH_2N); 2.67 (*t*, NCH_2CH_2O); 3.61 (*t*, NCH_2CH_2O). Anal. calc. for $C_6H_{16}N_2O$: C 54.5, H 12.2, N 21.2; found: C 54.3, H 12.0, N 21.2.

2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethanol ((*R,S*)-**11**). A mixture of 9.66 g (15 mmol) of (*R,S*)-**10**, 52.80 g (400 mmol) of **9**, and 150 ml of MeOH was heated at reflux for 20 h. The solvent was evaporated, the residue dissolved in 200 ml of Et_2O, the Et_2O soln. extracted with H_2O (3 × 100 ml), the org. phase dried ($MgSO_4$) and evaporated, and the residue purified by CC (SiO_2, EtOH): 8.39 g (79%) of yellowish-orange viscous liquid. $[\alpha]_D^{22} = -331.19$ ($c = 0.481$, $CHCl_3$). IR (KBr): 3400 (OH). ^{1}H-NMR ($CDCl_3$): 1.15 (*d*, ^3J(H,H) = 6.5, CpCCH_3); 1.66 (*s*, CpCNCH_3); 1.83 (complex *m*, 2 H); 2.06 (*s*, CH_3N); 2.30 (complex *m*, 3 H); 2.43 (*m*, 1 H); 2.95 (br. *s*, OH); 3.45 (overlapping *m*, 3 H, Cp, CH_2O); 3.63 (*m*, 1 H, Cp); 3.92 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.16 (*dq*, ^3J(H,H) = 6.5, ^4J(H,P) = 2.5, CpC*H*); 4.35 (*m*, 2 H, Cp); 7.01–7.50 (complex *m*, 20 H). Anal. calc. for $C_{42}H_{46}FeN_2OP_2$: C 70.8, H 6.5, N 3.9; found: C 70.4, H 6.2, N 4.0.

2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl Benzoate (**13**). To a soln. of 356 mg (0.5 mmol) of (*R,S*)-**11** in 20 ml of anh. Et_2O at −50° were added dropwise within 10 min 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane. The mixture was warmed to −5° and then was added dropwise 1.0 ml (0.5 mmol) of 0.5M benzoyl chloride in Et_2O. The mixture was stirred for 30 min at r.t. and then cooled. After addition of 5 ml of sat. $NaHCO_3$ soln., the org. phase was extracted with H_2O (3 × 20 ml), dried ($MgSO_4$) and evaporated. The residue was purified by chromatography (SiO_2, AcOEt): 370 mg (97%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -288.26$ (*c* = 0.460, $CHCl_3$). IR (KBr): 1718 (C=O). ^{1}H-NMR ($CDCl_3$): 1.16 (*d*, CpCC*H*$_3$); 1.70 (overlapping *s* and *m*, CH_2, CpCNC*H*$_3$); 2.16 (*s*, CH_3N); 2.30 (*m*, 1 H); 2.46 (*m*, 1 H); 2.58 (*m*, NC*H*$_2$CH$_2$O); 3.47 (*s*, 1 H, Cp); 3.63 (*m*, 1 H, Cp); 3.90 (*m*, 1 H, Cp); 4.05 (*m*, 2 H, Cp); 4.16 (*m*, CpC*H*CH$_3$); 4.28 (*t*, NCH$_2$C*H*$_2$O); 4.34 (*m*, 2 H, Cp); 7.00–8.03 (complex *m*, 25 H). Anal. calc. for $C_{49}H_{50}FeN_2O_2P_2$: C 72.1, H 6.2, N 3.4; found: C 71.9, H 6.3, N 3.7.

2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl Ferrocenecarboxylate ((*R,S*)-**14**). As described for **13**, (*R,S*)-**14** was prepared from 356 mg (0.5 mmol) of (*R,S*)-**11**, 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane, and 124 mg (0.5 mmol) of ferrocenecarbonyl chloride (prepared from ferrocenecarboxylic acid and oxalyl chloride) in 20 ml of Et_2O (30 min at r.t). The residue was purified twice CC (SiO_2, Et_2O): 340 mg (84%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -251.97$ (*c* = 0.456, $CHCl_3$). IR (KBr): 1703 (C=O). ^{1}H-NMR ($CDCl_3$): 1.15 (*d*, CpCC*H*$_3$); 1.69 (*s*, CpCNC*H*$_3$); 1.81 (*m*, CH_2); 2.16 (*s*, CH_3N); 2.28 (*m*, 1 H); 2.50 (*m*, 3 H); 3.48 (*s*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.95 (*m*, 1 H, Cp); 4.05 (*m*, 2 H, Cp); 4.16–4.20 (*m*, 7 H, CpC*H*CH$_3$); 4.33 (*m*, 2 H, Cp); 4.38 (*m*, 2 H, Cp); 4.78 (*t*, NCH$_2$C*H*$_2$O); 7.05–7.46 (complex *m*, 20 H). Anal. calc. for $C_{53}H_{54}Fe_2N_2O_2P_2$: C 68.8, H 5.9, N 3.0; found: C 68.8, H 6.0, N 3.3.

Bis{2-{N-{2-{N-{(1R)-1-[(S)-1',2-bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl} Ferrocene-1,1'-dicarboxylate ((*R,S*)-**15**). As described for **13**, (*R,S*)-**15** was prepared from 712 mg (1 mmol) of (*R,S*)-**11**, 0.626 ml (1 mmol) of 1.6M BuLi in hexane, and 156 mg (0.5 mmol) of ferrocene-1,1'-dicarbonyl dichloride (prepared from ferrocene-1,1'-dicarboxylic acid and oxalyl chloride) in 20 ml of EtO_2 (2 h at r.t.). The residue was purified twice by CC (SiO_2, acetone; SiO_2, AcOEt/acetone 95:5): 400 mg (24%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -272.97$ (*c* = 0.444, $CHCl_3$). IR (KBr): 1705 (C=O). ^{1}H-NMR ($CDCl_3$): 1.08 (*d*, 2 CpCC*H*$_3$); 1.61 (*s*, 2 CpCNC*H*$_3$); 1.76 (*m*, 4 H, CH_2); 2.08 (*s*, 2 CH_3N); 2.21 (*m*, 2 H); 2.43 (*m*, 6 H); 3.40 (*s*, 2 H, Cp); 3.55 (*s*, 2 H, Cp); 3.86 (*m*, 2 H, Cp); 3.98 (*m*, 4 H); 4.10 (*m*, 6 H); 4.26 (*m*, 4 H); 4.32 (*m*, 4 H, Cp); 4.72 (*m*, 4 H); 7.00–7.58 (complex *m*, 40 H). Anal. calc. for $C_{96}H_{98}Fe_3N_4O_4P_4$: C 69.3, H 5.9, N 3.4; found: C 69.4, H 5.9, N 3.3.

2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl N-Methylcarbamate (**17a**). To a soln. of 356 mg (0.5 mmol) of (*R,S*)-**11** in 20 ml of anh. THF was added 57 mg (0.7 mmol) of methyl isocyanate. To the mixture were added 5 mg of dibutyltin dilaurate, and the mixture was stirred at r.t. for 2 days. Any resultant insoluble precipitate was removed by filtration, the solvent evaporated, and the residue purified twice by CC (SiO_2, Et_2O followed by acetone): 360 mg (95%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -292.76$ (*c* = 0.428, $CHCl_3$). IR ($CHCl_3$): 3450 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 1.16 (*d*, CpCC*H*$_3$); 1.70 (*s*, CpCNC*H*$_3$); 1.85 (*m*, 2 H); 2.11 (*s*, CH_3N); 2.28 (*m*, 1 H); 2.45 (*m*, 3H); 2.76 (*d*, C(O)NHC*H*$_3$); 3.48 (*m*, 1 H, Cp); 3.65 (*m*, 1 H, Cp); 3.91 (*m*, 1H, Cp); 4.02 (*t*, CH_2O); 4.06 (*m*, 2 H, Cp); 4.16 (*dq*, CpC*H*CH$_3$); 4.35 (*m*, 2 H, Cp); 4.83 (br. *s*, NH); 7.05–7.45 (complex *m*, 20 H). Anal. calc. for $C_{44}H_{49}FeN_3O_2P_2$: C 68.7, H 6.4, N 5.5; found: C 68.9, H 6.7, N 5.6.

2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl N-Butylcarbamate (**17b**). As described for **17a**, **17b** was prepared from 356 mg (0.5 mmol) of (*R,S*)-**11**, 100 mg (1.0 mmol) of butyl isocyanate, and 5 mg of dibutyltin dilaurate in 10 ml of THF (2 days at r.t.). The residue was purified twice by CC (SiO_2, Et_2O followed by acetone): 340 mg (84%) of viscous yellowish-orange liquid. R_f (acetone) 0.65. $[\alpha]_D^{22} = -266.88$ (*c* = 0.459, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1708 (C=O). ^{1}H-NMR ($CDCl_3$): 0.84 (*m*, CH_3); 1.15 (*d*, CpCC*H*$_3$); 1.28 (*m*, 2 H); 1.40 (*m*, 2 H); 1.68 (overlapping *m*, 5 H, CpCNC*H*$_3$, CH_2); 2.08 (*s*, CH_3N); 2.28 (*m*, 1 H); 2.41 (*m*, 3 H); 3.08 (*dt*, ^3J(H,H) = ^3J(H,NH) = 7.5, C(O)NHC*H*$_2$); 3.41 (*m*, 1 H, Cp); 3.63 (*m*, 1 H, Cp); 3.81 (*m*, 1 H, Cp); 3.95 (*t*, CH_2O); 4.00 (*m*, 2 H, Cp); 4.13 (*m*, CpC*H*CH$_3$), 4.28 (*m*, 2 H, Cp); 4.61 (*m*, NH); 7.03–7.50 (complex *m*, 20 H). Anal. calc. for $C_{47}H_{55}FeN_3O_2P_2$: C 69.5, H 6.8, N 5.2; found: C 69.5, H 6.9, N 5.3.

2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl N-Octadecylcarbamate (**17c**). As described for **17a**, **17c** was prepared from 356 mg (0.5 mmol) of (*R,S*)-**11**, 295 mg (1.0 mmol) of octadecyl isocyanate, and 5 mg of dibutyltin dilaurate in 10 ml of THF (4 days at r.t.). The residue was purified by CC (SiO_2, Et_2O followed by acetone): 330 mg (66%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -216.71$ (*c* = 0.413, $CHCl_3$). IR ($CHCl_3$): 3420 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 0.80 (*m*, CH_3); 1.18 (complex overlapping *m*, 33 H, CpCC*H*$_3$, CH_2); 1.40 (*m*, 2 H); 1.65 (overlapping *m*, 5 H, CpCNC*H*$_3$, CH_2); 2.06 (*s*, CH_3N); 2.25 (*m*, 1 H); 2.40 (*m*, 3 H); 3.06 (*dt*, C(O)NHC*H*$_2$); 3.41 (*m*, 1 H, Cp); 3.60 (*m*, 1 H, Cp);

3.85 (*m*, 1 H, Cp); 3.95 (*t*, CH_2O); 4.00 (*m*, 2 H, Cp); 4.11 (*m*, CpC*H*CH_3); 4.28 (*m*, 2 H, Cp); 4.61 (*m*, NH); 7.08–7.71 (complex *m*, 20 H). Anal. calc. for $C_{61}H_{83}FeN_3O_2P_2$: C 72.7, H 8.3, N 4.2; found: C 72.3, H 8.4, N 4.3.

2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl N-(tert-Butyl)carbamate (**17d**). As described for **17a**, **17d** was prepared from 356 mg (0.5 mmol) of (*R,S*)-**11**, 99 mg (1.0 mmol) of *tert*-butyl isocyanate [49], and 5 mg of dibutyltin dilaurate in 10 ml of THF (20 h at r.t.). The residue was purified twice by CC (SiO_2, Et_2O followed by acetone): 370 mg (91%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -284.05$ ($c = 0.439$, $CHCl_3$). IR ($CHCl_3$): 3430 (NH), 1720 (C=O). ^{1}H-NMR ($CDCl_3$): 1.15 (unresolved *d*, CpCC*H*$_3$); 1.25 (*s*, *t*-Bu); 1.65 (overlapping *m*, 5 H, CpCNC*H*$_3$, CH_2); 2.08 (*s*, CH_3N); 2.21–2.61 (complex *m*, 4 H); 3.41 (*m*, 1 H, Cp); 3.66 (*m*, 1 H, Cp); 3.78 (*m*, 1 H, Cp); 3.90 (*t*, CH_2O); 4.00 (*m*, 2 H, Cp); 4.13 (*m*, CpC*H*CH_3); 4.30 (*m*, 2 H, Cp); 4.63 (br. *s*, NH); 7.00–7.66 (complex *m*, 20 H). Anal. calc. for $C_{47}H_{55}FeN_3O_2P_2$: C 69.5, H 6.8, N 5.2; found: C 69.5, H 7.0, N 5.4.

2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl N,N-Diethylcarbamate (**17e**). Following the procedure [49] used to prepare **13**, **17e** was obtained from 356 mg (0.5 mmol) of (*R,S*)-**11**, 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane, and 1.0 ml (0.5 mmol) of 0.5M *N,N*-diethylcarbamoyl chloride in THF in 20 ml of THF (4 h at reflux temp.). The residue was purified twice by CC (SiO_2, Et_2O; SiO_2, AcOEt): 250 mg (62%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -291.77$ ($c = 0.401$, $CHCl_3$). IR (KBr): 1683 (C=O). ^{1}H-NMR ($CDCl_3$): 1.10 (*t*, 6 H); 1.17 (*d*, CpCC*H*$_3$); 1.70 (s, CpCNC*H*$_3$); 1.80 (*m*, 2 H, CH_2); 2.13 (*s*, CH_3N); 2.30 (*m*, 1 H); 2.46 (*m*, 3 H); 3.25 (*m*, 2 NC*H*$_2$CH$_3$); 3.48 (*s*, 1 H, Cp); 3.65 (*m*, 1 H, Cp); 3.84 (*m*, 1 H, Cp); 4.05 (*m*, 4 H, Cp, OCH_2); 4.16 (*m*, CpC*H*CH_3); 4.35 (*m*, 2 H, Cp); 7.00–7.50 (complex *m*, 20 H). Anal. calc. for $C_{47}H_{55}FeN_3O_2P_2$: C 69.5, H 6.8; found: C 69.4, H 7.0[8]).

2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl (R)-2-Phenylbutanoate ((*R,R,S*)-**18**). As described for **13**, (*R,R,S*)-**18** was prepared from 356 mg (0.5 mmol) of (*R,S*)-**11**, 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane, and 91 mg (0.5 mmol) of (−)-(*R*)-2-phenylbutanoyl chloride (prepared from (−)-(*R*)-2-phenylbutanoic acid and oxalyl chloride) in 20 ml of Et_2O (acyl chloride added at −20°, then 1 h at r.t.). The residue was purified twice by CC (SiO_2, Et_2O): 350 mg (82%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -278.89$ ($c = 0.488$, $CHCl_3$). IR (KBr): 1722 (C=O). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, 3 H); 1.13 (*d*, CpCC*H*$_3$); 1.65 (*s*, CpCNC*H*$_3$); 1.78 (*m*, 2 H, CH_2); 2.02 (*s*, CH_3N); 2.08 (*m*, 2 H); 2.19 (*m*, 1 H); 2.35 (*m*, 3 H); 3.45 (*t*, ^3J(H,H) = 7.5, C(O)PhC*H*); 3.48 (*s*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.93 (*m*, 1 H, Cp); 4.03 (*m*, 4 H, Cp, OCH_2); 4.13 (*dq*, ^3J(H,H) = 7.5, ^4J(H,P) = 2.0, CpC*H*CH_3); 4.34 (*m*, 2 H, Cp); 7.00–7.50 (complex *m*, 20 H). Anal. calc. for $C_{52}H_{56}FeN_2O_2P_2$: C 72.7, H 6.6, N 3.3; found: C 73.0, H 6.6, N 3.5.

2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl (S)-2-Phenylbutanoate ((*R,S,S*)-**18**). As described for **13**, (*R,S,S*)-**18** was prepared from 356 mg (0.5 mmol) of (*R,S*)-**11**, 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane, and 91 mg (0.5 mmol) of (−)-(*S*)-2-phenylbutanoyl chloride (prepared from (−)-(*S*)-2-phenylbutanoic acid and oxalyl chloride) in 20 ml of Et_2O (acyl chloride added at −20°, then 30 min at r.t.). The residue was purified twice by CC (SiO_2, Et_2O): 370 mg (86%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -259.09$ ($c = 0.418$, $CHCl_3$). IR (KBr): 1722 (C=O). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, 3 H); 1.13 (*d*, CpCC*H*$_3$); 1.65 (*s*, CpCNC*H*$_3$); 1.78 (*m*, 2 H, CH_2); 2.02 (*s*, CH_3N); 2.08 (*m*, 2 H); 2.19 (*m*, 1 H); 2.35 (*m*, 3 H); 3.45 (*t*, ^3J(H,H) = 7.5, C(O)C*H*Ph); 3.48 (*s*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.93 (*m*, 1 H, Cp); 4.03 (*m*, 4 H, Cp, CH_2O); 4.13 (*dq*, ^3J(H,H) = 7.5, ^4J(H,P) = 2.0, CpC*H*CH_3); 4.34 (*m*, 2 H, Cp); 7.00–7.50 (complex *m*, 20 H). Anal. calc. for $C_{52}H_{56}FeN_2O_2P_2$: C 72.7, H 6.6, N 3.3; found: C 72.5, H 6.8, N 3.2.

(2RS)-1-{N-Methyl-N-[2-(methylamino)ethyl]amino}propan-2-ol (**20a**). To a soln. of 176.3 g (2 mol) of **8** in 400 ml of MeOH at 35° were added dropwise within 3 h 11.6 g (0.2 mol) of **19a**. The solvent was evaporated and the residue distilled: 25.5 g (87%) of colorless liquid. B.p. 98°/0.2 Torr. IR (neat): 3280 (OH, NH). ^{1}H-NMR ($CHCl_3$): 1.12 (*d*, 3 H); 2.24–2.84 (complex *m*, 8 H, OH, NH, CH_2); 2.30 (*s*, CH_3); 2.45 (*s*, CH_3); 3.81 (*m*, CH). Anal. calc. for $C_7H_{18}N_2O$: C 57.5, H 12.4, N 19.2; found: C 57.3, H 12.4, N 19.5.

(2RS)-1-{N-Methyl-N-[2-(methylamino)ethyl]amino}butan-2-ol (**20b**). As described for **20a**, **20b** was prepared from 176.3 g (2 mol) of **8** and 36.0 g (186 mmol) of **19b** in 400 ml of MeOH (2 h at 35°). The residue was distilled twice to give 49.3 g of colorless liquid. A small quantity of unidentified side products was removed by mixing a soln. of the crude product in 100 ml of toluene with 3.5 g of benzaldehyde and 0.1 g of acidic ion-exchange resin (*IR 120*) for 3 h at 70°. The mixture was filtered, the solvent evaporated, and the residue distilled: 42.7 g (67%) of colorless liquid. B.p. 97–98°/2 Torr. IR (neat): 3400 (OH, NH). ^{1}H-NMR ($CDCl_3$): 0.93 (*t*, CH_3); 1.43 (*m*, 2 H, CH_2); 2.30 (*s*, CH_3); 2.45 (*s*, CH_3); 2.46–2.84 (complex *m*, 6 H, CH_2); 3.91 (*m*, CH). Anal. calc. for $C_8H_{20}N_2O$: C 60.0, H 12.6, N 17.5; found: C 60.0, H 12.6, N 17.8.

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[8]) Correct elemental analysis for N was not obtained; calc.: N 5.2; found: N 6.0.

(2RS)-1-{N-Methyl-N-[2-(methylamino)ethyl]amino}hex-5-en-2-ol (**20c**). As described for **20a**, **20c** was prepared from 176.3 g (2 mol) of **8** and 50.0 g (510 mmol) of **19c** in 400 ml of MeOH (2 h at 40°). The residue was distilled: 68.5 g (71%) of colorless liquid. B.p. 96–98°/0.02 Torr. IR ($CHCl_3$): 3280 (OH, NH). ^{1}H-NMR ($CDCl_3$): 1.46 (*m*, 2 H, CH_2); 2.06–2.83 (complex overlapping *m*, 8 H, CH_2); 2.30 (*s*, CH_3); 2.44 (*s*, CH_3); 3.65 (*m*, CH); 4.99 (*m*, CH_2=CH); 5.85 (*m*, CH_2=C*H*). Anal. calc. for $C_{10}H_{22}N_2O$: C 64.5, H 11.8, N 15.1; found: C 64.3, H 12.0, N 15.3.

(2RS)-1-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}propan-2-ol (**21a**). As described for (*R,S*)-**11**, **21a** was prepared from 3.20 g (5 mmol) of (*R,S*)-**10**, 52.80 g (150 mmol) of **20a**, and 50 ml of MeOH (heated 18 h at reflux temp.). The residue was purified by CC twice (SiO_2, MeOH; SiO_2, acetone): 2.28 g (63%) of yellowish-orange viscous liquid. The diastereoisomer mixture was not separable on TLC (MeOH): R_f 0.32. $[\alpha]_D^{22} = -314.4$ (*c* = 0.567, $CHCl_3$). IR (KBr): 3380 (OH). ^{1}H-NMR ($CDCl_3$): 1.07, 1.09 (2 *d*, 3 H each[9]), CpCCH_3); 1.17 (*d*, CH_3); 1.65, 1.67 (2 *s*, 3 H each[9]), CpCNCH_3); 1.69–2.17 (complex *m*, 4 H, CH_2); 2.04 (*s*, CH_3N); 2.25 (*m*, 1 H); 2.44 (*m*, 1 H); 2.95 (br. *s*, OH); 3.49 (*m*, 1 H, Cp); 3.64 (overlapping *m*, 2 H, Cp, C*H*OH); 3.94 (*m*, 1 H, Cp); 4.07 (*m*, 2 H, Cp); 4.16 (*m*, 1 H, CpC*H*); 4.37 (*m*, 2 H, Cp); 7.03–7.52 (complex *m*, 20 H). Anal. calc. for $C_{43}H_{48}FeN_2OP_2$: C 71.1, H 6.7, N 3.9; found: C 70.8, H 6.8, N 3.8.

(2RS)-1-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}butan-2-ol (**21b**). As described for (*R,S*)-**11**, **21a** was prepared from 6.4 g (10 mmol) of (*R,S*)-**10**, 42.0 g (263 mmol) of **20b**, and 100 ml of MeOH (heated 20 h at reflux temp.). The residue was purified by CC (SiO_2, AcOEt): 6.2 g (83%) of yellowish-orange viscous liquid. $[\alpha]_D^{22} = -302.52$ (*c* = 0.515, $CHCl_3$). IR (KBr): 3400 (OH). ^{1}H-NMR ($CDCl_3$): 0.93 (*t*, CH_3); 1.15 (*d*, CpCCH_3); 1.36 (*m*, CHCH_2CH$_3$); 1.65, 1.66 (2 *s*, 3 H each[9]), CpCNCH_3); 1.83 (complex *m*, 4 H, CH_2); 2.05 (*s*, CH_3N); 2.23 (*m*, 1 H); 2.41 (*m*, 1 H); 3.40 (*m*, C*H*OH); 3.48 (*m*, 1 H, Cp); 3.63 (*m*, 1 H, Cp); 3.93 (*m*, 1 H, Cp); 4.05 (*m*, 2 H, Cp); 4.15 (*m*, CpC*H*); 4.35 (*m*, 2 H, Cp); 7.00–7.50 (complex *m*, 20 H). Anal. calc. for $C_{44}H_{50}FeN_2OP_2$: C 71.4, H 6.8, N 3.8; found: C 71.5, H 6.8, N 4.2.

(2RS)-1-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}hex-5-en-2-ol (**21c**). As described for (*R,S*)-**11**, **21c** was prepared from 6.4 g (10 mmol) of (*R,S*)-**10**, 63.0 g (339 mmol) of **20c**, and 100 ml of MeOH (heated 24 h at reflux temp.). The residue was purified twice by CC (SiO_2, EtOH): 6.5 g (85%) of yellowish-orange viscous liquid. $[\alpha]_D^{22} = -302.99$ (*c* = 0.535, $CHCl_3$). IR ($CHCl_3$): 3400 (OH). ^{1}H-NMR ($CDCl_3$): 1.15 (*d*, CpCCH_3); 1.40 (*m*, 2 H, CH_2); 1.65, 1.66 (2 *s*, 3 H each[9]), CpCNCH_3); 1.70–2.50 (complex overlapping *m*, 8 H, CH_2); 2.05 (*s*, CH_3N); 3.48 (*m*, 2 H, Cp, C*H*OH); 3.63 (*m*, 1 H, Cp); 3.94 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.15 (*m*, CpC*H*); 4.35 (*m*, 2 H, Cp); 4.99 (*m*, CH_2=CH); 5.85 (*m*, CH_2=C*H*); 7.00–7.50 (complex *m*, 20 H). Anal. calc. for $C_{44}H_{50}FeN_2OP_2$: C 72.1, H 6.8, N 3.7; found: C 71.8, H 6.9, N 3.4.

(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl Benzoate (**22a**). To a soln. of 363 mg (0.5 mmol) of **21a** in 10 ml of Et_2O were added sequentially 202 mg (2 mmol) of Et_3N and 104.3 mg (0.8 mmol) of benzoyl chloride. The mixture was stirred at r.t. for 1 h, the resultant precipitate removed by filtration, the filtrate extracted with H_2O (2 × 20 ml), the org. phase dried ($MgSO_4$), and evaporated, and the residue purified by CC (SiO_2, Et_2O): 290 mg (70%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -267.19$ (*c* = 0.448, $CHCl_3$). IR (KBr): 1715 (C=O). ^{1}H-NMR ($CDCl_3$): 1.15 (unresolved *d*, CpCCH_3); 1.29 (*d*, CH_3CHO); 1.67 (*s*, CpCNCH_3); 1.79 (*m*, 2 H, CH_2); 2.10 (*s*, CH_3N); 2.27 (*m*, 1 H); 2.41 (*m*, 3 H); 3.50 (*m*, 1 H, Cp); 3.63 (*m*, 1 H, Cp); 3.91 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.15 (*m*, CpC*H*CH$_3$); 4.35 (*m*, 2 H, Cp); 5.15 (*m*, CH$_3$C*H*O); 7.03–8.03 (complex *m*, 25 H). Anal. calc. for $C_{50}H_{52}FeN_2O_2P_2$: C 72.3, H 6.3, N 3.4; found: C 72.0, H 6.5, N 3.3.

(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl Butanoate (**22b**). As described for **22a**, **22b** was prepared from 363 mg (0.5 mmol) of **21a**, 202 mg (2 mmol) of Et_3N, and 79.2 mg (0.8 mmol) of butanoyl chloride in 15 ml of Et_2O (30 min at r.t.). The mixture was extracted with sat. $NaHCO_3$ soln. (2 × 5 ml), the org. phase dried ($MgSO_4$) and evaporated, and the residue purified by CC (SiO_2, Et_2O): 240 mg (60%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -286.65$ (*c* = 0.487, $CHCl_3$). IR (KBr): 1720 (C=O). ^{1}H-NMR ($CDCl_3$): 0.93 (*t*, CH_3); 1.14 (overlapping *m*, CpCCH_3, CH_3CHO); 1.58–2.41 (complex overlapping *m*, 10 H); 1.65 (*s*, CpCNCH_3); 2.07 (*s*, CH_3N); 2.25 (*t*, CH_2COO); 3.49 (*m*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.96 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.14 (*m*, CpC*H*CH$_3$); 4.36 (*m*, 2 H, Cp); 4.90 (*m*, CH$_3$C*H*O); 7.00–7.51 (complex *m*, 20 H). Anal. calc. for $C_{47}H_{56}FeN_2O_2P_2$: C 70.6, H 7.0, N 3.5; found: C 71.0, H 6.5, N 3.5.

Bis{(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl} Hexanedioate (**22c**). As described for **22a**, **22c** was prepared from 726 mg

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[9]) The number of protons indicated is that for a single diastereoisomer. The overall proton integration was consistent with a 1:1 diastereoisomer mixture.

(1 mmol) of **21a**, 0.625 ml (1 mmol) of 1.6M BuLi in hexane, and 91.5 mg (0.5 mmol) of hexanedioyl dichloride in 20 ml of Et_2O (30 min at r.t.). The residue was purified by CC (SiO_2, Et_2O): 470 mg (60%) of viscous yellowish-orange liquid. R_f (AcOEt) 0.40. $[\alpha]_D^{22} = -292.66$ ($c = 0.463$, $CHCl_3$). IR (KBr): 1728 (C=O). ^{1}H-NMR ($CDCl_3$): 1.13 (overlapping *m*, 2 CpCCH_3, 2 CH_3CHO); 1.62 (*s*, 2 CpCNCH_3); 1.67–2.46 (complex overlapping *m*, 20 H, CH_2); 2.07 (*s*, 2 CH_3N); 3.47 (*s*, 2 H, Cp); 3.64 (*m*, 2 H, Cp); 3.79 (*m*, 2 H, Cp); 4.07 (*s*, 4 H, Cp); 4.35 (*s*, 4 H, Cp); 4.49 (*m*, 2 CpC*H*CH_3); 4.93 (*m*, 2 CH_3C*H*O); 7.00–7.58 (complex *m*, 40 H). Anal. calc. for $C_{92}H_{102}Fe_2N_4O_4P_4$: C 70.7, H 6.6, N 3.6; found: C 70.4, H 6.6, N 3.7.

Bis{(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl} Decanedioate (**22d**). As described for **13**, **22d** was prepared from 726 mg (1 mmol) of **21a**, 0.625 ml (1 mmol) of 1.6M BuLi in hexane, and 119.5 mg (0.5 mmol) of decanedioyl dichloride in 20 ml of Et_2O (30 min at r.t.). The residue was purified twice by CC (SiO_2, Et_2O): 440 mg (54%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -285.69$ ($c = 0.496$, $CHCl_3$). IR (KBr): 1725 (C=O). ^{1}H-NMR ($CDCl_3$): 1.13 (overlapping *d*, 12 H, 2 CpCCH_3); 1.28 (complex *m*, 12 H); 1.48–2.58 (complex overlapping *m*, 16 H, CH_2); 1.58 (*s*, 2 CpCNCH_3); 2.07 (*s*, 2 CH_3N); 3.47 (*s*, 2 H, Cp); 3.60 (*m*, 2 H, Cp); 4.05 (*m*, 4 H); 4.13 (*s*, 2 H); 4.35 (*s*, 4 H); 4.43 (*m*, 2 H); 4.88 (*m*, 2 CH_3C*H*O); 7.00–7.56 (complex *m*, 40 H). Anal. calc. for $C_{96}H_{110}Fe_2N_4O_4P_4$: C 71.2, H 6.9, N 3.5; found: C 70.9, H 6.9, N 3.5.

(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl N-*Phenylcarbamate* (**22e**). As described for **17a**, **22e** was prepared from 363 mg (0.5 mmol) of **21a** and 71.4 mg (0.6 mmol) of phenyl isocyanate in 10 ml of THF (1 day at r.t.). The residue was purified by CC (SiO_2, CH_2Cl_2/Et_2O 1:1): 320 mg (76%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -269.22$ ($c = 0.484$, $CHCl_3$). IR ($CHCl_3$): 3380, 3310 (NH), 1728 (C=O). ^{1}H-NMR ($CDCl_3$): 1.15 (2 overlapping *d*, 3 H each[9]), CpCCH_3); 1.23 (2 *d*, 3 H each[9]), CH_3CHO); 1.67 (*s*, CpCNCH_3); 1.75–2.41 (complex overlapping *m*, 6 H, CH_2); 2.08 (*s*, CH_3N); 3.48 (*s*, 1 H, Cp); 3.63 (*m*, 1 H, Cp); 3.93 (*m*, 1 H, Cp); 4.06 (*s*, 2 H, Cp); 4.15 (*m*, CpC*H*CH_3); 4.35 (*m*, 2 H, Cp); 4.88 (*m*, CH_3C*H*O); 6.65 (*m*, NH); 7.00–7.60 (complex *m*, 25 H). Anal. calc. for $C_{50}H_{53}FeN_3O_2P_2$: C 71.0, H 6.3, N 5.0; found: C 70.9, H 6.5, N 5.0.

(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl N-*Butylcarbamate* (**22f**). As described for **17a**, **22f** was prepared from 363 mg (0.5 mmol) of **21a** and 59.4 mg (0.6 mmol) of butyl isocyanate in 10 ml of THF (1 day at r.t.). The residue was purified twice by chromatography (SiO_2, CH_2Cl_2/Et_2O 1:1 followed by CH_2Cl_2/Et_2O 3:1): 300 mg (73%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -276.34$ ($c = 0.465$, $CHCl_3$). IR ($CHCl_3$): 3410, 3340 (NH), 1715 (C=O). ^{1}H-NMR ($CDCl_3$): 0.92 (2 *t*, 3 H each[9]), CH_3); 1.07 (overlapping *d*, CpCCH_3, CH_3CHO); 1.33 (complex *m*, 2 H); 1.45 (complex *m*, 2 H); 1.67 (*s*, CpCNCH_3); 1.75 (complex *m*, 2 H); 2.08 (*s*, CH_3N); 2.20–2.40 (complex overlapping *m*, 4 H); 3.15 (*m*, C(O)NHCH_2); 3.50 (*s*, 1 H, Cp); 3.62 (*s*, 1 H, Cp); 3.95 (*m*, 1 H, Cp); 4.06 (*s*, 2 H, Cp); 4.15 (*m*, CpC*H*CH_3); 4.35 (*s*, 2 H, Cp); 4.63 (*m*, NH); 4.76 (*m*, CH_3C*H*O); 7.03–7.50 (complex *m*, 20 H). Anal. calc. for $C_{48}H_{57}FeN_3O_2P_2$: C 69.8, H 7.0, N 5.1; found: C 69.4, H 7.2, N 5.3.

(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl N-*Octadecylcarbamate* (**22g**). As described for **17a**, **22g** was prepared from 363 mg (0.5 mmol) of **21a** and 177 mg (0.6 mmol) of octadecyl isocyanate in 10 ml of THF (2 days at r.t.). The residue was purified by CC (SiO_2, Et_2O): 440 mg (86%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -199.34$ ($c = 0.465$, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, CH_3); 1.15 (overlapping *d*, CpCCH_3, CH_3CHO); 1.20 (complex overlapping *m*, 30 H, CH_2); 1.46 (*m*, NHCH_2CH_2); 1.66 (*s*, CpCNCH_3); 1.70–2.46 (complex overlapping *m*, 6 H); 2.08 (*s*, CH_3N); 3.11 (*m*, C(O)NHCH_2); 3.49 (*m*, 1 H, Cp); 3.63 (*m*, 1 H, Cp); 3.93 (*m*, 1 H, Cp); 4.06 (*s*, 2 H, Cp); 4.16 (*m*, CpC*H*CH_3); 4.35 (*m*, 2 H, Cp); 4.76 (overlapping *m*, NH, CH_3C*H*O); 7.01–7.58 (complex *m*, 20 H). Anal. calc. for $C_{62}H_{85}FeN_3O_2P_2$: C 72.9, H 8.4, N 4.1; found: C 72.7, H 8.4, N 4.2.

Bis{(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}-ethyl}-N-methylamino}-1-methylethyl} N,N-*(Hexane-1,6-diyl)dicarbamate* (**22h**). As described for **17a**, **22h** was prepared from 726 mg (1 mmol) of **21a** and 76 mg (0.6 mmol) of hexane-1,6-diyl diisocyanate in 20 ml of THF (3 days at r.t.). The residue was purified by CC (SiO_2, acetone): 200 mg (28%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -274.17$ ($c = 0.453$, $CHCl_3$). IR ($CHCl_3$): 3420, 3340 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 1.16 (overlapping *d* and *d*, 2 CpCCH_3, 2 CH_3CHO); 1.32 (*m*, 4 H); 1.49 (*m*, 4 H); 1.67 (*s*, 2 CpCNCH_3); 1.70–2.46 (complex overlapping *m*, 6 H); 2.08 (*s*, 2 CH_3N); 3.11 (*m*, 2 C(O)NHCH_2); 3.48 (*s*, 2 H, Cp); 3.62 (*m*, 2 H, Cp); 3.93 (*m*, 2 H, Cp); 4.06 (*s*, 4 H, Cp); 4.15 (*m*, 2 CpC*H*CH_3); 4.35 (*s*, 4 H, Cp); 4.75 (*m*, 2 CH_3C*H*O, 2 NH); 7.03–7.58 (complex *m*, 40 H).

(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-ethylethyl N-*Methylcarbamate* (**22i**). As described for **17a**, **22i** was prepared from 370 mg (0.5 mmol) of **21b**, 57 mg (1.0 mmol) of methyl isocyanate, and 5 mg of dibutyltin dilaurate in 10 ml of THF (24 h

at r.t.). The residue was purified twice by CC (SiO_2, Et_2O; SiO_2, AcOEt): 360 mg (90%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -282.00$ ($c = 0.511$, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 0.88 (*m*, CH_3); 1.15 (*d*, CpCCH_3); 1.46 (*m*, CH_3CH_2); 1.65 (*s*, CpCNCH_3); 1.76 (*m*, 2 H); 2.08 (*s*, CH_3N); 2.23 (*m*, 3 H); 2.40 (*m*, 3 H); 2.76 (2 overlapping *d*, 3 H each[9]), CH_3NH); 3.49 (*m*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.95 (*m*, 1 H, Cp); 4.05 (*m*, 2 H, Cp); 4.13 (*m*, 1 H, CpC*H*CH_3); 4.45 (*m*, 2 H, Cp); 4.66 (*m*, CH_2CHO); 4.76 (*m*, NH); 7.00–7.50 (complex *m*, 20 H). Anal. calc. for $C_{46}H_{53}FeN_3O_2P_2$: C 69.3, H 6.7, N 5.3; found: C 68.9, H 6.8, N 5.4.

(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-ethylethyl N-*Octadecylcarbamate* (**22j**). As described for **17a**, **22j** was prepared from 370 mg (0.5 mmol) of **22b**, 295 mg (1.0 mmol) of octadecyl isocyanate, and 5 mg of dibutyltin dilaurate in 20 ml of THF (48 h at r.t.). The residue was purified twice by CC (SiO_2, Et_2O; SiO_2, Et_2O/CH_2Cl_2 1:1): 430 mg (93%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -227.25$ ($c = 0.480$, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 0.80 (overlapping *t*, 2 CH_3); 1.15 (*d*, CpCCH_3); 1.26–1.46 (complex *m*, 34 H); 1.65 (*s*, CpCNCH_3); 1.75 (*m*, 2 H); 2.07 (*s*, CH_3N); 2.23 (*m*, 3 H); 2.40 (*m*, 1 H); 3.13 (*dt*, C(O)NHCH_2); 3.48 (*m*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.95 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.13 (*m*, CpC*H*CH_3); 4.35 (*m*, 2 H, Cp); 4.65 (*m*, CH_2CHO); 4.73 (br. *s*, NH); 7.08–7.50 (complex *m*, 20 H). Anal. calc. for $C_{63}H_{87}FeN_3O_2P_2$: C 73.0, H 8.5, N 4.1; found: C 73.1, H 8.2, N 4.1.

Bis{(1RS)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-ethylethyl} N,N'-*(Hexane-1,6-diyl)dicarbamate* (**22k**). As described for **17a**, **22k** was prepared from 740 mg (1 mmol) of **22b**, 85 mg (1.0 mmol) of hexane-1,6-diyl diisocyanate, and 5 mg of dibutyltin dilaurate in 20 ml of THF (3 days at r.t.). The residue was purified twice by CC (SiO_2, acetone; SiO_2, AcOEt/acetone 1:1): 300 mg (36%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -276.68$ ($c = 0.430$, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, 2 CH_3); 1.15 (*d*, 2 CpCCH_3); 1.31 (*m*, 4 H); 1.46 (*m*, 8 H); 1.65 (*s*, 2 CpCNCH_3); 1.75 (*m*, 4 H); 2.06 (*s*, 2 CH_3N); 2.23 (*m*, 6 H); 2.40 (*m*, 2 H); 3.13 (*m*, 2 C(O)NHCH_2); 3.48 (*s*, 2 H, Cp); 3.60 (*s*, 2 H, Cp); 3.95 (*s*, 2 H, Cp); 4.06 (*m*, 4 H, Cp); 4.13 (*m*, 2 CpC*H*CH_3); 4.34 (*s*, 4 H, Cp); 4.65 (*m*, CH_2CHO); 4.76 (br. *s*, 2 NH); 7.00–7.50 (complex *m*, 20 H). Anal. calc. for $C_{96}H_{112}FeN_3O_2P_2$: C 69.8, H 6.8, N 5.1; found: C 69.4, H 7.0, N 5.3.

(1RS)-1-{{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}methyl}pent-4-en-1-yl N-*Methylcarbamate* (**22l**). As described for **17a**, **22l** was prepared from 383 mg (0.5 mmol) of **21c**, 57 mg (1.0 mmol) of methyl isocyanate, and 5 mg of dibutyltin dilaurate in 10 ml of THF (20 h at r.t.). The residue was purified twice by CC (SiO_2, Et_2O): 250 mg (67%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -281.33$ ($c = 0.450$, $CHCl_3$). IR ($CHCl_3$): 3455 (NH), 1712 (C=O). ^{1}H-NMR ($CDCl_3$): 1.15 (*m*, CpCCH_3): 1.53–2.40 (complex overlapping *m*, 10 H); 1.65 (*s*, CpCNCH_3); 2.02 (*s*, CH_3N); 3.13 (*dt*, C(O)NHCH_3); 3.42 (*m*, 1 H, Cp); 3.59 (*m*, 1 H, Cp); 3.84 (*m*, 1 H, Cp); 4.02 (*m*, 2 H, Cp); 4.12 (*m*, CpC*H*CH_3); 4.29 (*m*, 2 H, Cp); 4.68 (*m*, CH_2CHO, NH); 4.93 (*m*, CH_2=CH); 5.81 (*m*, CH_2=C*H*); 7.00–7.60 (complex *m*, 20 H). Anal. calc. for $C_{48}H_{55}FeN_3O_2P_2$: C 70.0, H 6.7, N 5.1; found: C 69.6, H 6.7, N 5.3.

(1RS)-1-{{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}methyl}pent-4-en-1-yl N-*Octadecylcarbamate* (**22m**). As described for **17a**, **22m** was prepared from 383 mg (0.5 mmol) of **22c**, 295 mg (1.0 mmol) of octadecyl isocyanate, and 5 mg of dibutyltin dilaurate in 10 ml of THF (2 days at r.t.). The residue was purified twice by CC (SiO_2, CH_2Cl_2/acetone 4:1; SiO_2, CH_2Cl_2/acetone 2:1): 340 mg (63%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -215.35$ ($c = 0.430$, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 0.89 (*t*, CH_3); 1.15 (*d*, CpCCH_3); 1.25 (complex *m*, 30 H); 1.47–1.83 (complex overlapping *m*, 8 H); 1.65 (*s*, CpCNCH_3); 2.07 (*s*, CH_3N); 2.23 (*m*, 3 H); 2.38 (*m*, 1 H); 3.13 (*dt*, C(O)NHCH_2); 3.48 (*m*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.95 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.13 (*m*, CpC*H*CH_3); 4.35 (*m*, 2 H, Cp); 4.64 (*m*, CH_2CHO); 4.72 (*m*, NH); 4.98 (*m*, CH_2=CH); 5.81 (*m*, CH_2=CH); 7.03–7.50 (complex *m*, 20 H). Anal. calc. for $C_{65}H_{89}FeN_3O_2P_2$: C 73.5, H 8.5, N 4.0; found: C 73.4, H 8.5, N 4.1.

Tris{2-{N-{2-{N-{(1R)-1-[(S)-1',2-bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}ethyl} Benzene-1,3,5-tricarboxylate (**23**). As described for **13**, **23** was prepared from 772 mg (1 mmol) of (*R,S*)-**11**, 0.625 ml (1 mmol) of 1.6M BuLi in hexane, and 88 mg (0.33 mmol) of benzene-1,3,5-tricarbonyl trichloride (prepared from benzene-1,3,5-tricarboxylic acid and oxalyl chloride) in 20 ml of Et_2O (18 h at r.t.). The residue was purified twice by CC (SiO_2, acetone; alumina act. III, AcOEt): 410 mg (55%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -294.92$ ($c = 0.433$, $CHCl_3$). IR (KBr): 1720. ^{1}H-NMR ($CDCl_3$): 1.14 (*d*, 3 CpCCH_3); 1.67 (*s*, 3 CpCNCH_3); 1.79 (complex *m*, 6 H, CH_2); 2.15 (*s*, 3 CH_3N); 2.35 (*m*, 3 H); 2.43 (*m*, 3 H); 2.57 (*m*, 3 NCH_2CH_2O); 3.48 (*s*, 3 H, Cp); 3.61 (*s*, 3 H, Cp); 3.95 (*s*, 3 H, Cp); 4.06 (*m*, 6 H, Cp); 4.15 (*dq*, 3 CpC*H*CH_3); 4.29 (*t*, 3 NCH_2CH_2O); 4.35 (*m*, 6 H, Cp); 7.05–52 (complex *m*, 60 H). Anal. calc. for $C_{132}H_{138}Fe_3N_6O_6P_6$: C 70.2, H 6.2, N 3.7; found: C 70.3, H 6.1, N 3.8.

(−)-(2R)-3-{N-Methyl-N-[2-(methylamino)ethyl]amino}propan-2-ol ((*R*)-**26**). As described for **20a**, (*R*)-**26** was prepared from 44.1 g (0.5 mol) of **8** and 4.15 g (71 mmol) of (+)-(*R*)-**24** in 75 ml of MeOH (2 h at r.t.). The

residue was distilled: 7.20 g (69%) of colorless liquid. B.p. 61°/0.1 Torr. $[\alpha]_D^{22} = -74.29$ ($c = 1.019$, $CHCl_3$). IR (neat): 3300 (OH, NH). ^{1}H-NMR ($CHCl_3$): 1.12 (*d*, 3 H); 2.24–2.84 (complex *m*, 8 H, OH, NH, CH_2); 2.30 (*s*, CH_3); 2.45 (*s*, CH_3); 3.81 (*m*, CH). Anal. calc. for $C_7H_{18}N_2O$: C 57.5, H 12.4, N 19.2; found: C 57.1, H 12.5, N 19.6.

(−)-(2S)-3-{N-Methyl-N-[2-(methylamino)ethyl]amino}propan-2-ol ((*S*)-**26**). As described for **20a**, (*S*)-**26** was prepared from 88.2 g (1 mol) of **8** and 8.29 g (142 mmol) of (−)-(*S*)-**24** in 150 ml of MeOH (2 h at r.t.). The residue was distilled: 14.7 g (68%) of colorless liquid. B.p. 61–63°/0.1 Torr. $[\alpha]_D^{22} = +75.47$ ($c = 1.011$, $CHCl_3$). IR (neat): 3300 (OH, NH). ^{1}H-NMR ($CHCl_3$): 1.12 (*d*, 3 H); 2.24–2.84 (complex *m*, 8 H, OH, NH, CH_2); 2.30 (*s*, CH_3); 2.45 (*s*, CH_3); 3.81 (*m*, CH). Anal. calc. for $C_7H_{18}N_2O$: C 57.5, H 12.4, N 19.2; found: C 57.0, H 12.5, N 19.5.

(−)-(1R)-2-{N-Methyl-N-[2-(methylamino)ethyl]amino}-1-phenylethanol ((*R*)-**27**). As described for **20a**, (*R*)-**27** was prepared from 88.2 g (1 mol) of **8** and 25.0 g (208 mmol) of (−)-(*R*)-**25** in 200 ml of MeOH (3 h at 45–50°). The residue was distilled twice: 30.1 g (70%) of colorless liquid. B.p. 102–106°/0.002 Torr. $[\alpha]_D^{22} = -72.40$ ($c = 0.913$, $CHCl_3$). IR (neat): 3300 (OH, NH). ^{1}H-NMR ($CDCl_3$): 2.36 (*s*, CH_3); 2.43 (*s*, CH_3); 2.46–2.83 (complex overlapping *m*, 6 H, CH_2); 4.70 (*m*, CH); 7.16–7.41 (complex *m*, 5 H). Anal. calc. for $C_{12}H_{20}N_2O$: C 69.2, H 9.7, N 13.5; found: C 68.7, H 9.6, N 13.6.

(+)-(1S)-2-{N-Methyl-N-[2-(methylamino)ethyl]amino}-1-phenylethanol ((*S*)-**27**). As described for **20a**, (*S*)-**27** was prepared from 88.2 g (1 mol) of **8** and 20.0 g (166 mmol) of (+)-(*S*)-**25** in 200 ml of MeOH (2 h at 45–50°). The residue was distilled twice: 26.2 g (76%) of colorless liquid. B.p. 105–108°/0.004 Torr. $[\alpha]_D^{22} = +75.70$ ($c = 0.778$, $CHCl_3$). IR (neat): 3300 (OH, NH). ^{1}H-NMR ($CDCl_3$): 2.36 (*s*, CH_3); 2.43 (*s*, CH_3); 2.46–2.83 (complex overlapping *m*, 6 H, CH_2); 4.70 (*m*, CH); 7.16–7.41 (complex *m*, 5 H). Anal. calc. for $C_{12}H_{20}N_2O$: C 69.2, H 9.7, N 13.5; found: C 68.7, H 9.8, N 13.6.

(2R)-1-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}propan-2-ol ((*R,R,S*)-**29**). As described for (*R,S*)-**11**, (*R,R,S*)-**29** was prepared from 3.20 g (5 mmol) of (*R,S*)-**10**, 7.70 g (48 mmol) of (*R*)-**26**, and 50 ml of MeOH (heated 20 h at reflux temp.). The residue was purified by CC (SiO_2, EtOH): 2.85 (79%) of yellowish-orange viscous liquid. $[\alpha]_D^{22} = -338.52$ ($c = 0.501$, $CHCl_3$). IR ($CHCl_3$): 3400 (OH). ^{1}H-NMR ($CDCl_3$): 1.09 (*d*, CpCCH_3); 1.17 (*d*, CH_3); 1.67 (*s*, CpCNCH_3); 1.85 (*m*, 3 H, CH_2); 2.09 (*s*, CH_3N); 2.12 (complex *m*, 1 H, CH_2); 2.25 (*m*, 1 H); 2.46 (*m*, 1 H); 3.50 (*m*, 1 H, Cp); 3.66 (overlapping *m*, 2 H, Cp, CH_3CHO); 3.94 (*m*, 1 H, Cp); 4.07 (*m*, 2 H, Cp); 4.17 (*dq*, 1 H, Cp); 4.37 (*m*, 2 H, Cp); 7.05–7.60 (complex *m*, 20 H). Anal. calc. for $C_{43}H_{48}FeN_2OP_2$: C 71.1, H 6.7, N 3.9; found: C 70.8, H 6.6, N 4.0.

(2S)-1-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-propan-2-ol ((*R,S,S*)-**29**). As described for (*R,S*)-**11**, (*R,S,S*)-**29** was prepared from 3.20 g (5 mmol) of (*R,S*)-**10**, 14.10 g (96 mmol) of (*S*)-**26**, and 50 ml of MeOH (heated 18 h at reflux temp.). The residue was purified by CC (SiO_2, EtOH): 3.00 (83%) of yellowish-orange viscous liquid. $[\alpha]_D^{22} = -305.78$ ($c = 0.467$, $CHCl_3$). IR ($CHCl_3$): 3400 (OH). ^{1}H-NMR ($CDCl_3$): 1.07 (*d*, CpCCH_3); 1.15 (*d*, CH_3); 1.67 (*s*, CpCNCH_3); 1.72 (*m*, 1 H, CH_2); 1.94 (complex *m*, 3 H, CH_2); 2.05 (*s*, CH_3N); 2.25 (*dt*, 1 H); 2.40 (*dt*, 1 H); 3.49 (*m*, 1 H, Cp); 3.66 (overlapping *m*, 2 H, Cp, CH_3CHO); 3.94 (*m*, 1 H, Cp); 4.07 (*m*, 2 H, Cp); 4.16 (*dq*, CpCH); 4.36 (*m*, 2 H, Cp); 7.05–7.60 (complex *m*, 20 H). Anal. calc. for $C_{43}H_{48}FeN_2OP_2$: C 71.1, H 6.7, N 3.9; found: C 70.7, H 6.8, N 4.0.

(2R)-1-{N-{2-{N-{(1S)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}propan-2-ol ((*S,R,S*)-**29**). As described for (*R,S*)-**11**, (*S,R,S*)-**29** was prepared from 1.92 g (3 mmol) of (*S,S*)-**10**, 4.6 g (31 mmol) of (*R*)-**26**, and 30 ml of MeOH (heated 18 h at reflux temp.). The residue was purified by CC (neutral alumina, act. IV, toluene followed by Et_2O; SiO_2, EtOH): 1.35 (62%) of yellowish-orange viscous liquid. $[\alpha]_D^{22} = -374.81$ ($c = 0.401$, $CHCl_3$). IR ($CHCl_3$): 3400 (OH). ^{1}H-NMR ($CDCl_3$): 1.09 (*d*, 3 H); 1.34 (*d*, 3 H); 2.15 (*s*, CH_3N); 2.19 (*s*, CH_3N); 2.20–2.45 (complex overlapping *m*, 6 H); 3.42 (*m*, 1 H, Cp); 3.54 (*m*, 1 H, Cp); 3.72 (overlapping *m*, 2 H, CpC*H*CH_3, CH_3CHO); 4.06 (*m*, 1 H, Cp); 4.14 (*m*, 1 H, Cp); 4.25 (*m*, 1 H, Cp); 4.46 (*m*, 2 H, Cp); 7.10–7.48 (complex *m*, 20 H). Anal. calc. for $C_{43}H_{48}FeN_2OP_2$: C 71.1, H 6.7, N 3.9; found: C 70.9, H 6.9, N 4.1.

(2S)-1-{N-{2-{N-{(1S)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}propan-2-ol ((*S,S,S*)-**29**). As described for (*R,S*)-**11**, (*S,S,S*)-**29** was prepared from 1.92 g (3 mmol) of (*S,S*)-**10**, 9.6 g (67 mmol) of (*S*)-**26**, and 50 ml of MeOH (heated 18 h at reflux temp.). The residue was purified by CC (neutral alumina, act. IV, toluene followed by Et_2O; twice SiO_2, EtOH): 1.41 (65%) of yellowish-orange viscous liquid. $[\alpha]_D^{22} = -343.82$ ($c = 0.429$, $CHCl_3$). IR ($CHCl_3$): 3400 (OH). ^{1}H-NMR ($CDCl_3$): 1.09 (*d*, 3 H); 1.35 (*d*, 3 H); 2.12 (*s*, CH_3N); 2.13–2.59 (complex overlapping *m*, 6 H); 2.19 (*s*, CH_3N); 3.41 (*m*, 1 H, Cp); 3.54 (*m*, 1 H, Cp); 3.74 (overlapping *m*, 2 H, CpC*H*CH_3, CH_3CHO); 4.04 (*m*, 1 H, Cp); 4.14 (*m*, 1 H, Cp); 4.25 (*m*, 1 H, Cp); 4.44 (*m*, 2 H, Cp); 7.08–7.52 (complex *m*, 20 H). Anal. calc. for $C_{43}H_{48}FeN_2OP_2$: C 71.1, H 6.7, N 3.9; found: C 70.8, H 6.7, N 3.9.

(1R)-2-{N-{2-{N-{(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-phenylethanol ((*R,R,S*)-**30**). As described for (*R,S*)-**11**, (*R,R,S*)-**30** was prepared from 3.2 g (5

mmol) of (*R,S*)-**10**, 30.0 g (144 mmol) of (*R*)-**27**, and 50 ml of MeOH (heated 24 h at reflux temp.). The residue was purified twice by CC (SiO_2, EtOH; SiO_2, Et_2O): 2.7 g (69%) of yellowish-orange viscous liquid. $[\alpha]_D^{22} = -326.37$ ($c = 0.512$, $CHCl_3$). IR (KBr): 3360 (OH). ^{1}H-NMR ($CDCl_3$): 1.18 (*d*, CpCCH_3); 1.68 (*s*, CpCNCH_3); 1.88 (complex *m*, 2 H, CH_2); 2.13 (*s*, CH_3N); 2.28 (complex *m*, 3 H); 2.46 (*m*, 1 H); 3.48 (*m*, 1 H, Cp); 3.65 (*m*, 1 H, Cp); 3.91 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.16 (*dq*, CpC*H*); 4.36 (*m*, 2 H, Cp); 4.50 (*m*, PhC*H*O); 7.28–7.51 (complex *m*, 25 H). Anal. calc. for $C_{48}H_{50}FeN_2OP_2$: C 73.1, H 6.4, N 3.6; found: C 72.7, H 6.3, N 3.6.

(1S)-2-{N-{*2-*{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-phenylethanol* ((*R,S,S*)-**30**). As described for (*R,S*)-**11**, (*R,S,S*)-**30** was prepared from 3.2 g (5 mmol) of (*R,S*)-**10**, 26.0 g (125 mmol) of (*S*)-**27**, and 50 ml of MeOH (heated 24 h at reflux temp.). The residue was purified twice by CC (SiO_2, EtOH; SiO_2, Et_2O): 2.9 g (73%) of yellowish-orange viscous liquid. $[\alpha]_D^{22} = -278.33$ ($c = 0.540$, $CHCl_3$). IR (KBr): 3360 (OH). ^{1}H-NMR ($CDCl_3$): 1.18 (*d*, CpCCH_3); 1.68 (*s*, CpCNCH_3); 1.98 (complex *m*, 2 H, CH_2); 2.13 (*s*, CH_3N); 2.25 (complex *m*, 3 H); 2.44 (*m*, 1 H); 3.48 (*m*, 1 H, Cp); 3.65 (*m*, 1 H, Cp); 3.91 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.17 (*dq*, CpC*H*); 4.36 (*m*, 2 H, Cp); 4.55 (*m*, PhC*H*O); 7.00–7.53 (complex *m*, 25 H). Anal. calc. for $C_{48}H_{50}FeN_2OP_2$: C 73.1, H 6.4, N 3.6; found: C 73.0, H 6.4, N 3.6.

(1R)-1-{N-{*2-*{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-methylethyl* N-*Octadecylcarbamate* ((*R,R,S*)-**31a**). As described for **17a**, (*R,R,S*)-**31a** was prepared from 363 mg (0.5 mmol) of (*R,R,S*)-**29**, 295 mg (1 mmol) of octadecyl isocyanate, and 5 mg of dibutyltin dilaurate in 20 ml of THF (2 days at r.t.). The residue was purified 3 times by CC (neutral alumina, act. III, CH_2Cl_2; twice with SiO_2, AcOEt): 430 mg (84%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -222.06$ ($c = 0.485$, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, CH_3); 1.15 (overlapping *d*, CpCCH_3, CH_3CHO); 1.26 (complex overlapping *m*, 30 H, CH_2); 1.46 (*m*, NHCH$_2$CH_2); 1.66 (*s*, CpCNCH_3); 1.78–2.40 (complex overlapping *m*, 6 H); 2.06 (*s*, CH_3N); 3.13 (*m*, C(O)NHCH_2); 3.50 (*m*, 1 H, Cp); 3.63 (*m*, 1 H, Cp); 3.95 (*m*, 1 H, Cp); 4.06 (*s*, 2 H, Cp); 4.15 (*dq*, CpC*H*CH$_3$); 4.35 (*m*, 2 H, Cp); 4.75 (overlapping *m*, 2 H, NH, CH$_3$C*H*O); 7.03–7.51 (complex *m*, 20 H). Anal. calc. for $C_{62}H_{85}FeN_3O_2P_2$: C 72.9, H 8.4, N 4.1; found: C 73.0, H 8.5, N 4.2.

(1S)-1-{N-{*2-*{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-methylethyl* N-*Octadecylcarbamate* ((*R,S,S*)-**31a**). As described for **17a**, (*R,S,S*)-**31a** was prepared from 363 mg (0.5 mmol) of (*R,S,S*)-**29**, 295 mg (1 mmol) of octadecyl isocyanate, and 5 mg of dibutyltin dilaurate in 20 ml of THF (2 days at r.t.). The residue was purified 3 times by CC (neutral alumina, act. III, CH_2Cl_2; SiO_2, AcOEt; SiO_2, Et_2O): 350 mg (69%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -233.65$ ($c = 0.419$, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, CH_3); 1.15 (overlapping *d*, CpCCH_3, CH_3CHO); 1.20 (complex overlapping *m*, 30 H, CH_2); 1.46 (*m*, NHCH$_2$CH_2); 1.66 (*s*, CpCNCH_3); 1.70–2.46 (complex overlapping *m*, 6 H); 2.08 (*s*, CH_3N); 3.11 (*m*, C(O)NHCH_2); 3.49 (*m*, 1 H, Cp); 3.63 (*m*, 1 H, Cp); 3.93 (*m*, 1 H, Cp); 4.06 (*s*, 2 H, Cp); 4.16 (*m*, CpC*H*CH$_3$); 4.35 (*m*, 2 H, Cp); 4.76 (overlapping *m*, NH, CH$_3$C*H*O); 7.01–7.58 (complex *m*, 20 H). Anal. calc. for $C_{62}H_{85}FeN_3O_2P_2$: C 72.9, H 8.4, N 4.1; found: C 72.8, H 8.4, N 4.2.

(1R)-1-{N-{*2-*{N-{*(1S)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-methylethyl* N-*Octadecylcarbamate* ((*S,R,S*)-**31a**). As described for **17a**, (*S,R,S*)-**31a** was prepared from 363 mg (0.5 mmol) of (*S,R,S*)-**29**, 295 mg (1 mmol) of octadecyl isocyanate, and 5 mg of dibutyltin dilaurate in 20 ml of THF (20 h at r.t.). The residue was purified by CC (neutral alumina, act. IV, CH_2Cl_2; SiO_2, Et_2O): 390 mg (76%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -247.14$ ($c = 0.420$, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, CH_3); 1.19 (*d*, CH_3); 1.25 (complex overlapping *m*, 33 H); 1.45 (*m*, NHCH$_2$CH_2); 2.17 (*s*, CH_3N); 2.20 (*s*, CH_3N); 2.22–2.51 (complex overlapping *m*, 6 H); 3.14 (*m*, C(O)NHCH_2); 3.42 (*m*, 1 H, Cp); 3.51 (*m*, 1 H, Cp); 3.69 (*dq*, CpC*H*CH$_3$); 4.04 (*m*, 1 H, Cp); 4.09 (*m*, 1 H, Cp); 4.26 (*m*, 1 H, Cp); 4.40 (*m*, 1 H, Cp); 4.45 (*m*, 1 H, Cp); 4.66 (*m*, 1 H); 4.87 (*m*, 1 H); 7.10–7.46 (complex *m*, 20 H). Anal. calc. for $C_{62}H_{85}FeN_3O_2P_2$: C 72.9, H 8.4, N 4.1; found: C 72.9, H 8.5, N 4.3

(1S)-1-{N-{*2-*{N-{*(1S)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-methylethyl* N-*Octadecylcarbamate* ((*S,S,S*)-**31a**). As described for **17a**, (*S,S,S*)-**31a** was prepared from 363 mg (0.5 mmol) of (*S,S,S*)-**29**, 295 mg (1 mmol) of octadecyl isocyanate, and 5 mg of dibutyltin dilaurate in 20 ml of THF (20 h at r.t.). The residue was purified by CC (neutral alumina, act. IV, CH_2Cl_2; SiO_2, Et_2O): 390 mg (76%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -250.11$ ($c = 0.443$, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, CH_3); 1.20 (*d*, CH_3); 1.25 (complex overlapping *m*, 33 H); 1.45 (*m*, NHCH$_2$CH_2); 2.19 (*s*, CH_3N); 2.20 (*s*, CH_3N); 2.24–2.52 (complex overlapping *m*, 6 H); 3.14 (*m*, C(O)NHCH_2); 3.42 (*m*, 1 H, Cp); 3.51 (*m*, 1 H, Cp); 3.69 (*dq*, CpC*H*CH$_3$); 4.04 (*m*, 1 H, Cp); 4.09 (*m*, 1 H, Cp); 4.26 (*m*, 1 H, Cp); 4.40 (*m*, 1 H, Cp); 4.45 (*m*, 1 H, Cp); 4.66 (*m*, 1 H); 4.89 (*m*, 1 H); 7.10–7.45 (complex *m*, 20 H). Anal. calc. for $C_{62}H_{85}FeN_3O_2P_2$: C 72.9, H 8.4, N 4.1; found: C 72.9, H 8.7, N 4.4.

(1R)-1-{N-{*2-*{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-methylethyl* N-*Methylcarbamate* ((*R,R,S*)-**31b**). As described for **17a**, (*R,R,S*)-**31b** was prepared

from 363 mg (0.5 mmol) of (*R,R,S*)-**29**, 57 mg (1 mmol) of methyl isocyanate, and 5 mg of dibutyltin dilaurate in 20 ml of THF (20 h at r.t.). The residue was purified 3 times by CC (neutral alumina, act. III, CH_2Cl_2/Et_2O 95:5; SiO_2, AcOEt; SiO_2): 300 mg (77%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -293.98$ ($c = 0.465$, $CHCl_3$). IR ($CHCl_3$): 3460 (NH), 1710. ^{1}H-NMR ($CDCl_3$): 1.16 (overlapping *d*, CpCCH_3, CH_3CHO); 1.66 (*s*, CpCNCH_3); 1.80–2.41 (complex overlapping *m*, 6H); 2.08 (*s*, CH_3N); 2.76 (*d*, C(O)NHCH_3); 3.50 (*m*, 1H, Cp); 3.64 (*m*, 1H, Cp); 3.93 (*m*, 1H, Cp); 4.06 (*s*, 2H, Cp); 4.15 (*m*, CpC*H*CH$_3$); 4.35 (*m*, 2H, Cp); 4.76 (overlapping *m*, NH, CH$_3$C*H*O); 7.01–7.50 (complex *m*, 20 H). Anal. calc. for $C_{45}H_{51}FeN_3O_2P_2$: C 69.0, H 6.6, N 5.4; found: C 69.0, H 6.6, N 5.6.

(1S)-1-{N-{*2-*{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-methylethyl* N-*Methylcarbamate* ((*R,S,S*)-**31b**). As described for **17a**, (*R,S,S*)-**31b** was prepared from 363 mg (0.5 mmol) of (*R,S,S*)-**29**, 57 mg (1 mmol) of methyl isocyanate, and 5 mg of dibutylin dilaurate in 20 ml of THF (2 days ar r.t.). The residue was purified 3 times by CC (neutral alumina, act. III, CH_2Cl_2; SiO_2, AcOEt; SiO_2, Et_2O followed by AcOEt): 250 mg (64%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -296.26$ ($c = 0.454$, $CHCl_3$). IR ($CHCl_3$): 3460 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 1.15 (overlapping *d*, CpCCH_3, CH_3CHO); 1.68 (*s*, CpCNCH_3); 1.75–2.46 (complex overlapping *m*, 6 H); 2.08 (*s*, CH_3N); 2.75 (*d*, C(O)NHCH_3); 3.48 (*m*, 1 H, Cp); 3.65 (*m*, 1 H, Cp); 3.91 (*m*, 1 H, Cp); 4.06 (*s*, 2 H, Cp); 4.15 (*m*, CpC*H*CH$_3$); 4.35 (*m*, 2 H, Cp); 4.63 (*m*, NH); 4.78 (*m*, CH$_3$C*H*O); 7.03–7.58 (complex *m*, 20 H). Anal. calc. for $C_{45}H_{51}FeN_3O_2P_2$: C 69.0, H 6.6, N 5.4; found: C 68.8, H 6.6, N 5.5.

(1R)-1-{N-{*2-*{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-phenylethyl* N-*Octadecylcarbamate* ((*R,R,S*)-**32a**). As described for **17a**, (*R,R,S*)-**32a** was prepared from 394 mg (0.5 mmol) of (*R,R,S*)-**30**, 295 mg (1.0 mmol) of octadecyl isocyanate, and 5 mg of dibutyltin dilaurate in 20 ml of THF (40 h at r.t.). The residue was purified twice by CC (SiO_2, Et_2O; SiO_2, CH_2Cl_2/Et_2O 3:1): 350 mg (65%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -219.86$ (*c*, 0.423, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710 C=O). ^{1}H-NMR ($CDCl_3$: 0.88 (*t*, 3 H); 1.15 (unresolved *d*, CpCCH_3); 1.25 (complex *m*, 30 H); 1.45 (complex *m*, 2 H); 1.65 (*s*, CpCNCH_3); 1.81 (complex *m*, 2 H); 2.13 (*s*, CH_3N); 2.20–2.43 (overlapping *m*, 3 H); 2.67 (*dd*, 1 H); 3.11 (*m*, NHCH_2); 3.48 (*m*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.93 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.13 (*m*, CpC*H*CH$_3$); 4.35 (*m*, 2 H, Cp); 4.85 (*m*, NH); 5.68 (*dd*, PhC*H*O); 7.03–7,51 (complex *m*, 25 H). Anal. calc. for $C_{67}H_{87}FeN_3O_2P_2$: C 74.2, H 8.1, N 3.9; found: C 74.3, H 8.0, N 4.2.

(1S)-1-{N-{*2-*{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-phenylethyl* N-*Octadecylcarbamate* ((*R,S,S*)-**32a**). As described for **17a**, (*R,S,S*)-**32a** was prepared from 394 mg (0.5 mmol) of (*R,S,S*)-**30**, 295 mg (1.0 mmol) of octadecyl isocyanate, and 5 mg of dibutylin dilaurate in 20 ml of THF (24 h at r.t.). The residue was purified twice by CC (SiO_2, CH_2Cl_2/Et_2O; SiO_2, CH_2Cl_2/Et_2O 3:1): 320 mg (59%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -211.45$ ($c = 0.428$, $CHCl_3$). IR ($CHCl_3$): 3440 (NH), 1710. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, 3 H); 1.13 (*d*, CpCCH_3); 1.26 (complex *m*, 30 H); 1.43 (complex *m*, 2 H); 1.63 (*s*, CpCNCH_3); 1.85 (br. complex *m*, 2 H); 2.13 (*s*, CH_3N); 2.21 (*m*, 1 H); 2.39 (*m*, 2 H); 2.64 (*dd*, 1 H); 3.10 (*m*, NHCH_2, 2 H); 3.48 (*m*, 1 H, Cp); 3.60 (*m*, 1 H, Cp); 3.95 (*m*, 1 H, Cp); 4.05 (*m*, 2 H, Cp); 4.12 (*m*, CpC*H*CH$_3$); 4.33 (*m*, 2 H, Cp); 4.71 (*m*, NH); 5.63 (*dd*, PhC*H*O); 6.96–7.50 (complex *m*, 25 H). Anal. calc. for $C_{67}H_{87}FeN_3O_2P_2$: C 74.2, H 8.1, N 3.9; found: C 74.0, H 8.0, N 4.0.

(1R)-1-{N-{*2-*{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-phenylethyl* N-*Methylcarbamate* ((*R,R,S*)-**32b**). As described for **17a**, (*R,R,S*)-**32b** was prepared from 394 mg (0.5 mmol) of (*R,R,S*)-**30**, 57 mg (1.0 mmol) of methyl isocyanate, and 5 mg of dibutylin dilaurate in 20 ml of THF (24 h at r.t.). The residue was purified (3 ×) by CC (SiO_2, Et_2O; SiO_2, Et_2O/i-PrOH 9:1, SiO_2, Et_2O): 180 mg (43%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -280.28$ ($c = 0.436$, $CHCl_3$). IR ($CHCl_3$): 3450 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 1.15 (unresolved *d*, CpCCH_3); 1.65 (*s*, CpCNCH_3); 1.81 (complex *m*, 2 H); 2.14 (*s*, CH_3N); 2.23–2.43 (overlapping *m*, 3 H); 2.69 (partially obscured *dd*, 1 H); 2.75 (*d*, NHCH_3); 3.49 (*m*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.91 (*m*, 1 H, Cp); 4.05 (*m*, 2 H, Cp); 4.12 (*m*, CpC*H*CH$_3$); 4.35 (*m*, 2 H, Cp); 4.83 (*m*, NH); 5.65 (*dd*, PhC*H*O); 7.00–7.58 (complex *m*, 25 H). Anal. calc. for $C_{50}H_{53}FeN_3O_2P_2$: C 71.0, H 6.3, N 5.0; found: C 70.7, H 6.3, N 5.0.

(1S)-1-{N-{*2-*{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-phenylethyl* N-*Methylcarbamate* ((*R,S,S*)-**32b**). As described for **17a**, (*R,S,S*)-**32b** was prepared from 394 mg (0.5 mmol) of (*R,S,S*)-**30**, 57 mg (1.0 mmol) of methyl isocyanate, and 5 mg of dibutylin dilaurate in 20 ml of THF (6 h at r.t.). The residue was purified twice by CC (SiO_2, CH_2Cl_2/Et_2O 95:5; SiO_2, Et_2O): 270 mg (64%) of a viscous yellowish-orange liquid. $[\alpha]_D^{22} = -221.42$ ($c = 0.422$, $CHCl_3$). IR ($CHCl_3$): 3450 (NH), 1710 (C=O). ^{1}H-NMR ($CDCl_3$): 1.15 (*d*, CpCCH_3); 1.65 (*s*, CpCNCH_3); 1.83 (br. complex *m*, 2 H); 2.14 (*s*, CH_3N); 2.23 (*m*, 1 H); 2.40 (overlapping *m*, 2 H); 2.67 (*dd*, 1 H); 2.73 (*d*, NHCH_3); 3.47 (*m*, 1 H, Cp); 3.63 (*m*, 1 H, Cp); 3.93 (*m*, 1

H, Cp); 4.05 (*m*, 2 H); 4.13 (*m*, CpC*H*CH$_3$); 4.35 (*m*, 2 H, Cp); 4.73 (*m*, NH); 5.66 (*dd*, PhC*H*O); 7.00–7.58 (complex *m*, 25 H). Anal. calc. for $C_{50}H_{53}FeN_3O_2P_2$: C 71.0, H 6.3, N 5.0; found: C 70.7, H 6.4, N 5.0.

*(1*R*)-1-*{N-{2-{N-{*(1*R*)-1-[(*S*)-1′,2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl N-[(1*R*)-1-(Naphthalen-1-yl)ethyl]carbamate* ((*R,R,R,S*)-**33**). As described for **17a**, (*R,R,R,S*)-**33** was prepared from 363 mg (0.5 mmol) of (*R,R,S*)-**29**, 197 mg (1 mmol) of (−)-(*R*)-1-(naphthalen-1-yl)ethyl isocyanate and 5 mg of dibutyltin dilaurate in 20 ml of THF (6 h at 50° followed by 20 h at 100° in pressure apparatus). The residue was purified 3 times by CC (neutral alumina, act. III, CH_2Cl_2; twice SiO_2, Et_2O): 220 mg (48%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -248.17$ ($c = 0.382$, $CHCl_3$). IR ($CHCl_3$): 3430 (NH), 1705 (C=O). ^{1}H-NMR ($CDCl_3$): 1.12 (overlapping *d*, 6 H); 1.63 (*d*, NpCHC*H*$_3$, 3 H); 1.65 (*s*, CpCNC*H*$_3$); 1.69–2.42 (complex overlapping *m*, 6 H); 2.07 (*s*, CH_3N); 3.49 (*m*, 1 H, Cp); 3.62 (*m*, 1 H, CP); 3.94 (*m*, 1 H, Cp); 4.05 (*s*, 2 H, Cp); 4.14 (*m*, CpCHC*H*$_3$); 4.33 (*m*, 2 H, Cp); 4.79 (*m*, CH_3CHO); 5.06 (br, *s*, NH); 5.64 (*m*, NPC*H*CH$_3$); 7.00–8.17 (complex *m*, 27 H). Anal. calc. for $C_{56}H_{59}FeN_3O_2P_2$: C 72.8, H 6.4, N 4.6; found: C 72.7, H 6.7, N 4.8.

*(1*R*)-1-*{N-{2-{N-{*(1*R*)-1-[(*S*)-1′,2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl N-[(1*S*)-1-(Naphthalen-1-yl)ethyl]carbamate* ((*R,R,S,S*)-**33**). As described for **17a**, (*R,R,S,S*)-**33** was prepared from 363 mg (0.5 mmol) of (*R,R,S*)-**29**, 197 mg (1 mmol) of (+)-(*S*)-1-(naphthalen-1-yl)ethyl isocyanate and 5 mg of dibutyltin dilaurate in 20 ml of THF (18 days at r.t. followed by 6 h at 50°). The residue was purified 3 times by CC (neutral alumina, act. III, CH_2Cl_2 twice SiO_2, Et_2O): 250 mg (54%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -252.25$ ($c = 0.423$, $CHCl_3$). IR ($CHCl_3$): 3430 (NH), 1705 (C=O). ^{1}H-NMR ($CDCl_3$): 1.09 (*d*, 3 H); 1.16 (*d*, 3 H); 1.60 (*s*, CpCNC*H*$_3$); 1.63 (*d*, NpCHC*H*$_3$); 1.73–2.33 (complex overlapping *m*, 6 H); 2.01 (*s*, CH_3N); 3.46 (*m*, 1 H, Cp); 3.60 (*m*, 1 H, Cp); 3.92 (*m*, 1 H, Cp); 4.05 (*m*, 2 H, Cp); 4.10 (*m*, CpC*H*CH$_3$); 4.31 (*m*, 2 H, Cp); 4.76 (*m*, CH_3CHO); 5.08 (br. *s*, NH); 5.64 (*m*, NpC*H*CH$_3$); 7.00–8.13 (complex *m*, 27 H). Anal. calc. for $C_{56}H_{59}FeN_3O_2P_2$: C 72.8, H 6.4, N 4.6; found: C 72.5, H 6.5, N 4.6.

*(1*S*)-1-*{N-{2-{N-{*(1*R*)-1-[(*S*)-1′,2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl N-[(1*R*)-1-(Naphthalen-1-yl)ethyl]carbamate* ((*R,S,R,S*)-**33**). As described for **17a**, (*R,S,R,S*)-**33** was prepared from 363 mg (0.5 mmol) of (*R,S,S*)-**29**, 197 mg (1 mmol) of (−)-(*R*)-1-(naphthalen-1-yl)ethyl isocyanate and 5 mg of dibutyltin dilaurate in 20 ml of THF (18 days at r.t. followed by 4 h at 100° in a pressure vessel). The residue was purified 3 times by CC (neutral alumina, act. IV, CH_2Cl_2 twice SiO_2, Et_2O): 300 mg (65%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -248.60$ ($c = 0.430$, $CHCl_3$). IR ($CHCl_3$): 3430 (NH), 1708 (C=O). ^{1}H-NMR ($CDCl_3$): 1.12 (*d*, 3 H); 1.19 (*d*, 3 H); 1.59 (*s*, CpCNC*H*$_3$); 1.63 (*d*, NpCHC*H*$_3$); 1.67–2.42 (complex overlapping *m*, 6 H); 2.04 (*s*, CH_3N); 3.49 (*m*, 1 H, Cp); 3.60 (*m*, 1 H, Cp); 3.95 (*m*, 1 H, Cp); 4.05 (*s*, 2 H, Cp); 4.12 (*m*, CpC*H*CH$_3$); 4.34 (*m*, 2 H, Cp); 4.80 (*m*, CH_3CHO); 5.01 (br. *s*, NH); 5.64 (*m*, NpC*H*CH$_3$); 7.00–8.17 (complex *m*, 27 H). Anal. calc. for $C_{56}H_{59}FeN_3O_2P_2$: C 72.8, H 6.4, N 4.6; found: C 72.6, H 6.6, N 4.6.

*(1*S*)-1-*{N-{2-{N-{*(1*R*)-1-[(*S*)-1′,2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl N-[(1*S*)-1-(Naphthalen-1-yl)ethyl]carbamate* ((*R,S,S,S*)-**33**). As described for **17a**, (*R,S,S,S*)-**33** was prepared from 363 mg (0.5 mmol) of (*R,S,S*)-**29**, 197 mg (1 mmol) of (+)-(*S*)-1-(naphthalen-1-yl)ethyl isocyanate and 5 mg of dibutyltin dilaurate in 20 ml of THF (18 days at r.t. followed by 4 h at 50°). The residue was purified 3 times by CC (neutral alumina, act. III, CH_2Cl_2 twice SiO_2, Et_2O): 290 mg (54%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -247.56$ ($c = 0.410$, $CHCl_3$). IR ($CHCl_3$): 3430 (NH), 1707 (C=O). ^{1}H-NMR ($CDCl_3$): 1.13 (overlapping *d*, 6 H); 1.63 (*d*, NpCHC*H*$_3$, 3 H); 1.65–2.42 (complex overlapping *m*, 9 H); 2.08 (*s*, CH_3N); 3.49 (*m*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.95 (*m*, 1 H, Cp); 4.06 (*s*, 2 H, Cp); 4.15 (*m*, CpC*H*CH$_3$); 4.33 (*m*, 2 H, Cp); 4.80 (*m*, CH_3CHO); 5.01 (br. *s*, NH); 5.64 (*m*, NpC*H*CH$_3$); 7.00–8.16 (complex *m*, 27 H). Anal. calc. for $C_{56}H_{59}FeN_3O_2P_2$: C 72.8, H 6.4, N 4.6; found: C 72.4, H 6.5, N 4.7.

*(1*R*)-1-*{N-{2-{N-{*(1*R*)-1-[(*S*)-1′,2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-methylethyl (2*R*)-2-Phenylbutanoate* ((*R,R,R,S*)-**34**). As described for **13**, (*R,R,R,S*)-**34** was prepared from 394 mg (0.5 mmol) of (*R,R,S*)-**30**, 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane, and 91 mg (0.5 mmol) of (−)-(*R*)-phenylbutanoyl chloride (prepared in a separate reaction from (−)-(*R*)-phenylbutanoic acid and oxalyl chloride) in 20 ml of Et_2O (acyl chloride added at −20°, then 2 h at r.t.). The residue was purified twice by CC (SiO_2, CH_2Cl_2/Et_2O 4:1): 350 mg (81%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -267.76$ ($c = 0.425$, $CHCl_3$). IR (KBr): 1725 (C=O). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.84 (*t*, CH_3); 1.10 (*d*, CpCC*H*$_3$); 1.57 (*s*, CpCNC*H*$_3$); 1.70 (complex overlapping *m*, 3 H); 1.94 (*s*, CH_3N); 2.04 (*m*, 2 H); 2.25 (*m*, 1 H); 2.30 (*dd*, $^2J_{AB} = 14$, $^3J_{AX} = 4.9$, 1 H); 2.51 (*dd*, $^2J_{AB} = 14$, $^3J_{BX} = 7.5$, 1 H); 3.48 (partially obscured *t*, C(O)PhC*H*Et); 3.49 (*m*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.94 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.09 (partially obscured *m*, CpC*H*CH$_3$); 4.34 (*m*, 2 H, Cp); 5.71 (*dd*, $^3J_{AX} = 4.9$, $^3J_{BX} = 7.5$, 1 H); 6.98–7.60 (complex *m*, 30 H). Anal. calc. for $C_{58}H_{60}FeN_2O_2P_2$: C 74.5, H 6.5, N 3.0; found: C 74.5, H 6.5, N 3.0.

*(1*R*)-1-*{N-{2-{N-{*(1*R*)-1-[(*S*)-1′,2-Bis(diphenylphosphino)ferrocenyl]ethyl}-N-methylamino}ethyl}-N-methylamino}-1-phenylethyl (2*S*)-2-Phenylbutanoate* ((*R,R,S,S*)-**34**). As described for **13**, (*R,R,S,S*)-**34** was pre-

pared from 394 mg (0.5 mmol) of (*R,R,S*)-**30**, 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane, and 91 mg (0.5 mmol) of (+)-(*S*)-phenylbutanoyl chloride (prepared from (+)-(*S*)-phenylbutanoic acid and oxalyl chloride) in 20 ml of Et_2O (acyl chloride added at −20°, then 2 h at r.t.). The residue was purified twice by CC (SiO_2, CH_2Cl_2/Et_2O; 9:1 SiO_2, CH_2Cl_2/Et_2O 4:1): 310 mg (66%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -256.39$ ($c = 0.415$, $CHCl_3$). IR (KBr): 1725 (C=O). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.89 (*t*, CH_3); 1.14 (*d*, CpCCH_3); 1.64 (*s*, CpCNCH_3); 1.65–1.82 (complex overlapping *m*, 4 H); 1.95 (*m*, 1 H); 2.09 (*s*, CH_3N); 2.19 (*m*, 1 H); 2.27 (*dd*, $^2J_{AB} = 15$, $^3J_{AX} = 5$, 1 H); 2.37 (*m*, 1 H); 2.61 (*dd*, $^2J_{AB} = 15$, $^3J_{BX} = 10$, 1 H); 3.49 (*m*, 1 H, Cp); 3.51 (*t*, C(O)PhC*H*Et); 3.62 (*m*, 1 H, Cp); 3.94 (*m*, 1 H, Cp); 4.05 (*m*, 2 H, Cp); 4.12 (*dq*, CpC*H*CH_3); 4.35 (*m*, 2 H, Cp); 5.71 (*dd*, $^3J_{AX} = 4.9$, $^3J_{BX} = 7.5$, 1 H); 6.93–7.57 (complex *m*, 30 H). Anal. calc. for $C_{58}H_{60}FeN_2O_2P_2$: C 74.5, H 6.5, N 3.0; found: C 74.6, H 6.5, N 3.0.

(1S)-1-{N-{2-{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-phenylethyl (2R)-2-Phenylbutanoate* ((*R,S,R,S*)-**34**). As described for **13**, (*R,S,R,S*)-**34** was prepared from 394 mg (0.5 mmol) of (*R,S,S*)-**30**, 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane, and 91 mg (0.5 mmol) of (−)-(*R*)-phenylbutanoyl chloride (prepared from (−)-(*R*)-phenylbutanoic acid and oxalyl chloride) in 20 ml of Et_2O (acyl chloride added at −20°, then 2 h at r.t.). The residue was purified twice by CC (SiO_2, CH_2Cl_2/Et_2O; 4:1): 380 mg (81%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -250.99$ ($c = 0.455$, $CHCl_3$). IR (KBr): 1725 (C=O). ^{1}H-NMR ($CDCl_3$, 250 MHz): 0.81 (*t*, CH_3); 1.06 (*d*, CpCCH_3); 1.58 (*s*, CpCNCH_3); 1.70 (complex overlapping *m*, 3 H); 1.96–2.82 (complex overlapping *m*, 4 H); 2.04 (*s*, CH_3N); 2.51 (*dd*, $^2J_{AB} = 15$, $^3J_{AX} = 9$, 1 H); 3.42 (*m*, 1 H, Cp); 3.44 (*t*, C(O)PhC*H*Et); 3.54 (*m*, 1 H, Cp); 3.88 (*m*, 1 H, Cp); 4.00 (*m*, 2 H, Cp); 4.14 (*m*, CpC*H*CH_3); 4.28 (*m*, 2 H, Cp); 5.70 (*dd*, $^3J_{AX} = 5$, $^3J_{BX} = 9$, 1 H); 6.94–7.68 (complex *m*, 30 H). Anal. calc. for $C_{58}H_{60}FeN_2O_2P_2$: C 74.5, H 6.5, N 3.0; found: C 74.3, H 6.8, N 3.3.

(1S)-1-{N-{2-{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-phenylethyl (2S)-2-Phenylbutanoate* ((*R,S,S,S*)-**34**). As described for **13**, (*R,S,S,S*)-**34** was prepared from 394 mg (0.5 mmol) of (*R,S,S*)-**30**, 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane, and 91 mg (0.5 mmol) of (+)-(*S*)-phenylbutanoyl chloride (prepared from (+)-(*S*)-phenylbutanoic acid and oxalyl chloride) in 20 ml of Et_2O (acyl chloride added at −20°, then 2 h at r.t.). The residue was purified twice by CC (SiO_2, CH_2Cl_2/Et_2O 4:1): 390 mg (84%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -233.90$ ($c = 0.410$, $CHCl_3$). IR (KBr): 1725 (C=O). ^{1}H-NMR ($CDCl_3$): 0.83 (*t*, CH_3); 1.09 (*d*, CpCCH_3); 1.58 (*s*, CpCNCH_3); 1.64–1.80 (complex overlapping *m*, 3 H); 1.94 (*s*, CH_3N); 2.07 (*m*, 2 H); 2.22 (*m*, 1 H); 2.37 (*dd*, $^2J_{AB} = 15$, $^3J_{AX} = 5$, 1 H); 2.51 (*dd*, $^2J_{AB} = 15$, $^3J_{BX} = 7.5$, 1 H); 3.46 (*t*, C(O)PhC*H*Et); 3.47 (*m*, 1 H, Cp); 3.61 (*m*, 1 H, Cp); 3.94 (*m*, 1 H, Cp); 4.04 (*m*, 2 H, Cp); 4.11 (partially obscured *m*, CpC*H*CH_3); 4.34 (*m*, 2 H, Cp); 5.71 (*dd*, $^3J_{AX} = 5$, $^3J_{BX} = 7.5$, 1 H); 6.98–7.60 (complex *m*, 30 H). Anal. calc. for $C_{58}H_{60}FeN_2O_2P_2$: C 74.5, H 6.5, N 3.0; found: C 74.6, H 6.6, N 2.9.

(1R)-1-{N-{2-{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-phenylethyl Phenylacetate* ((*R,R,S*)-**35**). As described for **13**, (*R,R,S*)-**35** was prepared from 394 mg (0.5 mmol) of (*R,R,S*)-**30**, 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane, and 77 mg (0.5 mmol) of phenylacetyl chloride (prepared from phenylacetic acid and oxalyl chloride) in 20 ml of Et_2O (acyl chloride added at −20°, then 2 h at r.t.). The residue was purified twice by CC (SiO_2, CH_2Cl_2/Et_2O; 4:1): 310 mg (68%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -270.55$ ($c = 0.421$, $CHCl_3$). IR (KBr): 1730 (C=O). ^{1}H-NMR ($CDCl_3$,): 1.13 (*d*, CpCCH_3); 1.63 (*s*, CpCNCH_3); 1.77 (*m*, CH_2); 2.07 (*s*, CH_3N); 2.17 (*m*, 1 H); 2.30 (*dd*, $^2J_{AB} = 14$, $^3J_{AX} = 5$, 1 H); 2.37 (*m*, 1 H); 2.66 (*dd*, $^2J_{AB} = 14$, $^3J_{BX} = 10$, 1 H); 3.49 (*m*, 1 H, Cp); 3.62 (*m*, 1 H, Cp); 3.66 (*s*, PhCH_2); 3.94 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.12 (*dq*, CpC*H*CH_3); 4.34 (*m*, 2 H, Cp); 5.75 (*dd*, $^3J_{AX} = 5$, $^3J_{BX} = 10$, 1 H); 6.98–7.60 (complex *m*, 30 H). Anal. calc. for $C_{56}H_{56}FeN_2O_2P_2$: C 74.2, H 6.2, N 3.1; found: C 74.4, H 6.3, N 3.4.

(1S)-1-{N-{2-{N-{*(1R)-1-[(S)-1',2-Bis(diphenylphosphino)ferrocenyl]ethyl*}-N-*methylamino*}*ethyl*}-N-*methylamino*}*-1-phenylethyl Phenylacetate* ((*R,S,S*)-**35**). As described for **13**, (*R,S,S*)-**35** was prepared from 394 mg (0.5 mmol) of (*R,S,S*)-**30**, 0.313 ml (0.5 mmol) of 1.6M BuLi in hexane, and 77 mg (0.5 mmol) of phenylacetyl chloride (prepared from phenylacetic acid and oxalyl chloride) in 20 ml of Et_2O (acyl chloride added at −20°, then 2 h at r.t.). The residue was purified twice by CC (SiO_2, CH_2Cl_2/Et_2O; 4:1): 330 mg (73%) of viscous yellowish-orange liquid. $[\alpha]_D^{22} = -244.22$ ($c = 0.450$, $CHCl_3$). IR (KBr): 1730 (C=O). ^{1}H-NMR ($CDCl_3$,): 1.12 (*d*, CpCCH_3); 1.63 (*s*, CpCNCH_3); 1.70 (*m*, 1 H, CH_2); 1.85 (*m*, 1 H, CH_2); 2.07 (*s*, CH_3N); 2.17 (*m*, 1 H); 2.34 (*m*, 1 H); 2.37 (*dd*, $^2J_{AB} = 15$, $^3J_{AX} = 5$, 1 H); 2.60 (*dd*, $^2J_{AB} = 15$, $^3J_{BX} = 10$, 1 H); 3.49 (*m*, 1 H, Cp); 3.62 (*m*, 1 H, Cp); 3.64 (*s*, PhCH_2); 3.95 (*m*, 1 H, Cp); 4.06 (*m*, 2 H, Cp); 4.12 (*dq*, CpC*H*CH_3); 4.34 (*m*, 2 H, Cp); 5.78 (*dd*, $^3J_{AX} = 5$, $^3J_{BX} = 10$, 1 H); 7.00–7.50 (complex *m*, 30 H). Anal. calc. for $C_{56}H_{56}FeN_2O_2P_2$: C 74.2, H 6.2, N 3.1; found: C 74.0, H 6.4, N 3.3.

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