New Strategies for Enantioselective Syntheses of 1-Alkyl- and 1,4-Dialkyl-1,2,3,4-tetrahydroisoquinolines: Diastereoselective Additions of Nucleophiles and Electrophiles to Isoquinoline Mediated by an Easily Resolved and Recycled Chiral Transition Metal Auxiliary

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Abstract: The chiral rhenium isoquinoline complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\textit{iso}\text{-}NC_9H_7)]^+$ TfO^- (**1**) and $(CH_3)_3SiCH_2Li$ give the addition product $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}CH{=}CHC(CH)_4CCHCH_2Si(CH_3)_3)$ (**2**) in 71% yield as a 94:6 *SS,RR/SR,RS* diastereomer mixture. Similar reactions with RMgX (R = $(CH_3)_2CH$, CH_3CH_2, $C_6H_5CH_2$, $CH_3(CH_2)_2$, CH_3, $CH_3(CH_2)_3$) give analogous adducts (**3–8**) as 89–82:11–18 diastereomer mixtures. Reactions of **2** and ROTf (R = H/D, $(CH_3)_3SiCH_2$, CH_3) give alkyl-1,4-dihydroisoquinoline complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N{=}CHCHRC(CH)_4CCHCH_2Si(CH_3)_3)]^+$ TfO^- in 84–72% yields as 94:6 diastereomer mixtures. Related complexes are prepared from **3–5** and HOTf. These react with $NaBH_4/CH_3OH$ to give alkyl-1,2,3,4-tetrahydroisoquinoline complexes, which are in turn treated with $(CH_3CH_2)_4N^+$ CN^- to give $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (**17**) and the title compounds. A reaction sequence starting with (+)-(*S*)-**1** and $(CH_3)_3SiCH_2Li$ yields (+)-(*SS*)-$NHCH_2CH(CH_2Si(CH_3)_3)C(CH)_4CCHCH_2Si(CH_3)_3$ (84% overall, 88% ee) and (+)-(*S*)-**17** (82%, >98% ee). Other optically active alkyl tetrahydroisoquinolines are similarly prepared. Complexes **17** and (+)-(*S*)-**17** are converted to $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ ($CH_3OTf/NaBH_4$; 88–53%) and thence to **1** or (+)-(*S*)-**1** (92–74%, >98% ee). A crystal structure and other data confirm the configurations assigned to the preceding compounds.

The isoquinoline alkaloids are the most abundant group of naturally occurring nitrogenous bases and exhibit a wide range of useful pharmacological properties.[1,2] Both 1,4-dihydroisoquinolines and 1,2,3,4-tetrahydroisoquinolines commonly feature substituted heterocyclic rings with one or more carbon stereocenters. Hence, there is considerable interest in the development of enantioselective syntheses.[3–6] Surprisingly, there are few protocols for the elaboration of isoquinoline itself, which constitutes a very inexpensive starting material, into nonracemic hydroisoquinolines.

Unsaturated organic compounds are frequently activated toward nucleophilic attack upon coordination to a transition metal, and the addition products are often amenable to further functionalization. Thus, we were attracted by the potential of chiral transition metal auxiliaries for the sequential, stereoselective derivatization of isoquinoline and other aromatic nitrogen heterocycles.[6] In earlier studies, we synthesized numerous adducts of the chiral rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (I) with aldehydes and ketones.[7–9] These underwent diastereoselective nucleophilic additions, and the intermediate alkoxide complexes could be converted to alcohols or esters thereof with high enantiomeric purities.

We sought to extend these investigations to unsaturated nitrogen donor ligands. In predecessor efforts, we prepared adducts of I with saturated amines and aromatic nitrogen heterocycles in both racemic and enantiomerically pure form.[10,11] We also synthesized the corresponding neutral amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}RR')$ as models for anticipated addition products.[12] Studies of acyclic and cyclic imine complexes of I were undertaken

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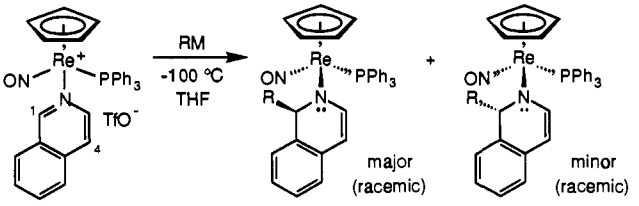
Scheme I. Additions of Nucleophiles to the Isoquinoline Complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(iso\text{-}NC_9H_7)]^+ TfO^-$ (**1**)



1 (*SS,RR*)-**2** or (*SR,RS*)**3-9** (*SR,RS*)-**2** or (*SS,RR*)**3-9**

product	RM[a]	reaction temperature[b] (°C)	ratio[c] (%de)	^{31}P NMR[d] δ, ppm
2	$(CH_3)_3SiCH_2Li$	−55	94:6 (88)	14.4:20.4
2	$(CH_3)_3SiCH_2MgCl$	20	80:20 (60)	14.4:20.4
3	$(CH_3)_2CHMgCl$	−100	89:11 (78)	15.3:20.4
4	CH_3CH_2MgBr	−100	89:11 (78)	15.5:20.4
5	$C_6H_5CH_2MgCl$	−100	88:12 (76)	15.3:20.8
6	$CH_3(CH_2)_2MgCl$	−100	87:13 (74)	15.7:20.6
7	CH_3MgCl	20	84:16 (68)[e]	15.5:20.5
8	$CH_3(CH_2)_3MgCl$	−100	82:18 (64)	15.7:20.7
9	$CH_2{=}CHCH_2MgBr$	−100	73:27 (46)	15.4:20.6

[a] Added at −100 °C. [b] Temperature at which **1** is consumed on the time scale of minutes. [c] In some cases, transients (18.6–18.8 ppm) are minor (**2**), major (**3, 8**), or exclusive (**4, 6**) kinetic products. Diastereomer ratios and chemical shifts of **3**, **4**, **6**, and **8** are measured after warming from −45 °C to −20 °C. Transients did not reappear upon cooling. [d] Chemical shifts are slightly temperature dependent. [e] At 76% conversion.

concurrently.[13,14] In the following narrative, we show that I is an effective and easily recycled chiral auxiliary for the introduction of new stereocenters onto the heterocyclic ring of isoquinoline and that 1-alkyl- and 1,4-dialkyl-1,2,3,4-tetrahydroisoquinolines can be isolated in high yields and enantiomeric excesses. The stereoelectronic basis for asymmetric induction is also analyzed in detail.

Results

1. Nucleophilic Additions to Coordinated Isoquinoline. A THF solution of the previously characterized isoquinoline complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(iso\text{-}NC_9H_7)]^+ TfO^-$ (**1**)[11,15] was cooled to −100 °C (Scheme I). Then $(CH_3)_3SiCH_2Li$ was added (1.0 equiv). Separate ^{31}P-NMR-monitored experiments showed that reaction was slow at −100 °C but complete within a few minutes at −55 °C. A 94:6 mixture of two products formed (14.4/20.4 ppm).[16] However, a small amount of a transient species was detected (18.5 ppm, up to 16%), and possible structures are discussed below. Solvent was removed from a sample at 0 °C, and the residue was dissolved in THF-d_8 at −20 °C. A ^1H NMR spectrum showed an identical mixture (δ −0.37/−0.26, 5.18/5.03; $Si(CH_3)_3$, C_5H_5). The homology of resonances indicated that the products were rhenium/carbon configurational diastereomers.

Workup gave the 1,2-addition product, enamido complex **2**, in 71% yield as a 94:6 mixture of *SS,RR/SR,RS* diastereomers (Scheme I).[17] Complex **2** was characterized by microanalysis and IR and NMR ($^1H/^{13}C/^{31}P$) spectroscopy, as summarized in the Experimental Section. It exhibited ^{31}P NMR chemical shift and IR ν_{NO} values similar to those of secondary amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\dot{N}RR')$.[12] The NCH=CH linkage gave ^1H NMR resonances at δ 5.92 and 4.83 ($^3J_{HH}$ = 6.3 Hz) and ^{13}C NMR resonances at 154.3 (d, $^3J_{CP}$ = 3.0 Hz) and 99.3 ppm. Configurations were assigned crystallographically, as described below. When solutions of **2** were kept at room temperature, epimerization slowly occurred.[18-20]

The generality of this diastereoselective addition was probed. Data for NMR-monitored reactions of **1** and other carbon nucleophiles are summarized in Scheme I. With one exception, 89–82:11–18 mixtures of diastereomeric 1,2-addition products (**3–9**) were obtained. The major diastereomers gave upfield ^{31}P NMR resonances (14.4–15.7 ppm), and the minor diastereomers gave downfield resonances (20.4–20.8 ppm), as observed for **2**. Configurations were assigned accordingly and confirmed for **5** as described below.[17]

Several trends are evident in Scheme I. First, reaction of the Grignard reagent $(CH_3)_3SiCH_2MgCl$ was much slower than that of $(CH_3)_3SiCH_2Li$. Diastereoselectivity decreased, presumably due to the higher temperature required. However, the secondary Grignard reagent $(CH_3)_2CHMgCl$ rapidly reacted at −100 °C. A transient species dominated, but only 1,2-addition products remained when the sample was warmed to −20 °C (89:11). The primary Grignard reagents CH_3CH_2MgBr, $CH_3(CH_2)_2MgCl$, and $CH_3(CH_2)_3MgCl$ behaved similarly. The benzylic and allylic Grignard reagents $C_6H_5CH_2MgCl$ and $CH_2{=}CHCH_2MgBr$ gave only 1,2-addition products at −100 °C, but the diastereoselectivity diminished in the latter case (73:27). Surprisingly, CH_3MgCl was the least reactive nucleophile, and some product epimerized at high conversions.[20]

Exploratory reactions with other alkyl lithium reagents gave either poorer yields of 1,2-addition products (CH_3CH_2Li, C_6H_5Li) or lower diastereoselectivities (CH_3Li). The Grignard reagent CH_3MgBr effected chiefly substitution at rhenium to give the known methyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**10**).[21] Copper reagents gave either no reaction (C_6H_5Cu) or very slow reactions ($(CH_3)_2CuLi$) at room temperature. Thus, many carbon nucleophiles add to **1** with good diastereoselectivities. However, the best cation choice (Li, MgBr, MgCl, etc.) appears arbitrary, and some optimization may be necessary.

2. Electrophilic Additions to Enamido Complexes. Organic enamines, $R_2NCH{=}CR'R''$, readily combine with electrophiles at either carbon or nitrogen. *N*-Metallo derivatives such as **2–9** would be expected to be even more reactive. Hence, **2** was generated in THF (94:6 *SS,RR/SR,RS*) and treated with HOTf (1.0 equiv) at 0 °C. Workup gave the carbon protonation product, 1-alkyl-1,4-dihydroisoquinoline complex **11**, in 84% yield, as depicted in Scheme II (top). NMR spectra showed **11** to be a 94:6 mixture of diastereomers (88% de), and retention of configuration was presumed. The sample was characterized analogously to **2** and exhibited spectroscopic properties typical of imine complexes of the rhenium fragment I.[13,14] These included

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(15) Abbreviations: (a) $TfO^- = CF_3SO_3^-$. (b) hfc = 3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato. (c) BNPPA = 1,1′-binaphthyl-2,2′-diylphosphoric acid.

(16) Isomer ratios are normalized to 100, and error limits on each integer are generally ±2. However, *SS,RR/SR,RS* ratios for **2** are accurate to ±1, on the basis of the replicate data and multiple NMR criteria utilized.

(17) (a) The absolute configuration at rhenium is specified first and is assigned as reported earlier.[11] Note that the carbon configurations in **2–9** depend upon the alkyl group ($CH_2Si > C_{aryl}$ but $C_{aryl} > CH_2C$; Scheme I). In compounds with more than one carbon stereocenter, that of the higher priority carbon is given first (*C*–N > *C*–C–N). (b) The enamido nitrogens in **2–9** are also formal stereocenters. However, inversion barriers should be <8 kcal/mol.[12]

(18) Amido complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\dot{N}RR')$ have been shown to lose configuration at rhenium in the dark slightly above room temperature.[12b] The mechanism involves initial PPh_3 ligand dissociation.

(19) For reactions of the epimerized compounds (*SR,RS*)-**2** and (*RS*)-**2**, see: Dewey, M. A. Ph.D. Thesis, University of Utah, 1991. The latter has been rigorously shown to form by inversion at rhenium.

(20) Rates of epimerization were measured by ^{31}P NMR at 55 °C in THF as previously described.[12b] Equilibrium ratios (*SR,RS/SS,RR* unless noted) and rate constants (s^{-1}) were as follows: **2**, 5:95 (*SS,RR/SR,RS*), 5×10^{-4}; **3**, 2:98, 5×10^{-3}; **4**, 6:94, 5×10^{-4}; **5**, 4:96, 9×10^{-4}; **6**, 5:95, 7×10^{-4}; **9**, 2:98, 8×10^{-4}. Note that lithium or magnesium salts are present and may affect equilibria and rates.

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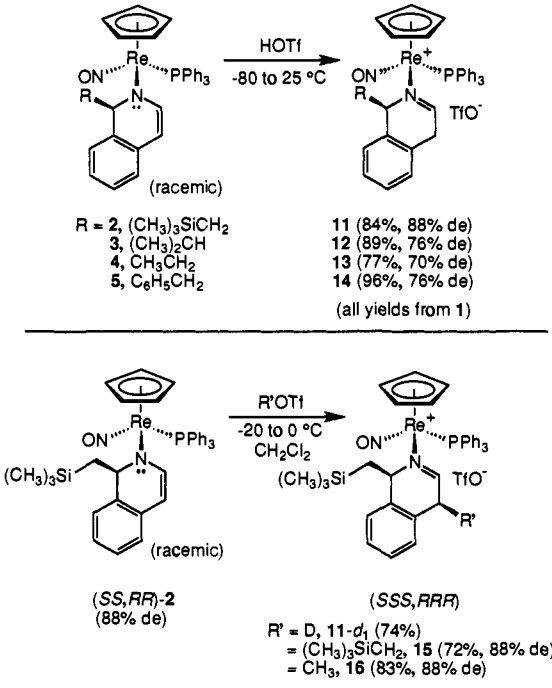
Scheme II. Syntheses of Alkyl-1,4-dihydroisoquinoline Complexes



downfield CH=N ^{1}H and ^{13}C NMR resonances ($CDCl_3$: δ 8.01; 181.0 ppm) and an IR ν_{NO} value of 1686 cm^{-1}.

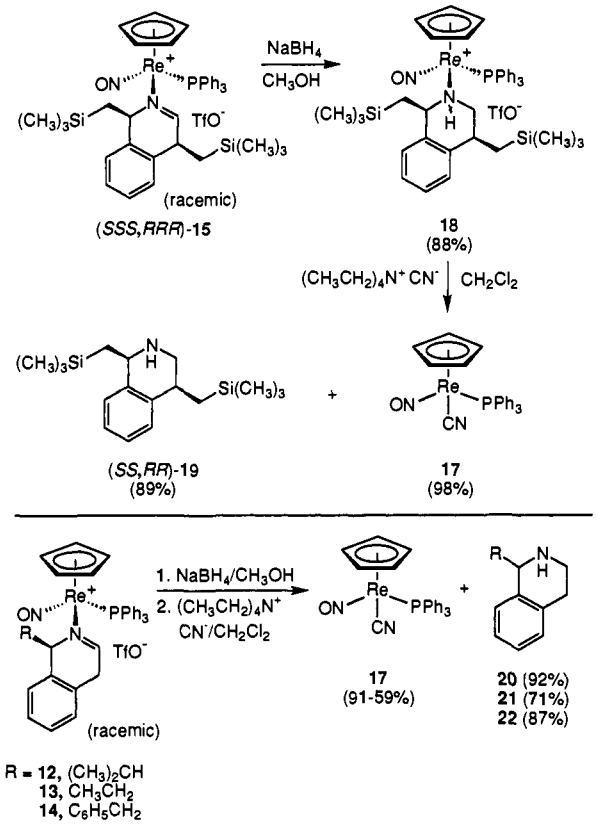
Next, the enamido complexes **3–5** were isolated in crude form and treated with HOTf in CH_2Cl_2 at –80 °C. The corresponding 1-alkyl-1,4-dihydroisoquinoline complexes **12–14** were isolated in 77–96% yields as 88–85:12–15 mixtures of diastereomers (76–70% de), as shown in Scheme II (top). These samples, which were converted to known organic compounds as described below, were characterized by IR and ^{1}H and ^{31}P NMR. With **12** and **14**, diastereomeric excesses closely matched those of the precursors **3** and **5** in Scheme I. With **13**, a slight diminution was observed. This was attributed to epimerization during the removal of solvent from **4**.[18,20]

As noted above, one advantage of auxiliary-based methodologies for enantioselective syntheses is the potential for controlling configurations of a *sequence* of new stereocenters. Thus, we sought to investigate similar reactions with nonprotic electrophiles. These would generate a *second* carbon stereocenter. First, **2** (94:6 *SS,RR/SR,RS*) was treated with the deuterated acid DOTf (Scheme II, bottom). Workup gave **11**-d_1 in 74% yield as a 93:7 mixture of Re/C_1 diastereomers. Integration of the CHD ^{1}H NMR resonances of the major diastereomer (*SS,RR*) indicated a 97:3 mixutre of H/D isotopomers. Configurations were assigned by analogy to the following alkylation reactions.

Complex **2** was next treated with the alkyl triflates $(CH_3)_3SiCH_2OTf$ and CH_3OTf in CH_2Cl_2 at –23 °C (3 equiv; Scheme II (bottom)). Workup gave the 1,4-dialkyl-1,4-dihydroisoquinoline complexes **15** and **16** in 72–83% yields as 94:6 mixtures of *SSS,RRR/SRR,RSS* diastereomers.[17] These were characterized analogously to **2**. Both reactions were monitored by ^{31}P NMR (–20 °C), but no other diastereomers were observed. Thus, alkylation gives a single configuration at the new carbon stereocenter. The stereochemistry of (*SSS,RRR*)-**15** was established crystallographically, as described below. The crystal structure of (*SRR,RSS*)-**15** was also determined, as reported elsewhere.[19]

3. Racemic Alkyl-1,2,3,4-tetrahydroisoquinolines. Attention was turned to liberating 1,2,3,4-tetrahydroisoquinolines from the preceding complexes. We have shown that amine complexes [(η^5-C_5H_5)Re(NO)(PPh_3)(NRR'R'')]$^+$ TfO^- and cyanide ion react to give free amines and the cyanide complex (η^5-C_5H_5)Re(NO)-(PPh_3)(CN) (**17**)[22] with retention of configuration at rhenium.[10,11] Thus, we sought to reduce the CH=N linkages in representative 1,4-dihydroisoquinoline complexes from Scheme II. Since this introduces a tetravalent nitrogen stereocenter, twice as many diastereomers can potentially be observed.[17b] Hence, we did not attempt to fully characterize these compounds.

Scheme III. Syntheses of Racemic Alkyl-1,2,3,4-tetrahydroisoquinolines



Next, the dihydroisoquinoline complex **15** (94:6 *SSS,RRR/SRR,RSS*) and $NaBH_4$ were reacted in methanol at room temperature (Scheme III (top)). Workup gave the tetrahydroisoquinoline complex **18** in 88% yield, which was characterized by microanalysis, IR, and ^{31}P NMR. Presumably, hydride adds to the imine carbon to give an intermediate amido complex,[12] which is protonated by the solvent. Next, **18** and the cyanide salt $(CH_3CH_2)_4N^+$ CN^- (1.5 equiv) were combined in CH_2Cl_2. Workup gave the diastereomerically pure free amine, 1,4-dialkyl-1,2,3,4-tetrahydroisoquinoline (*SS,RR*)-**19**, in 89% yield. The cyanide complex **17** was also isolated in 98% yield. The former was characterized by microanalysis and ^{1}H/^{13}C NMR, and the latter was characterized by IR and ^{1}H/^{31}P NMR.

Next, the dihydroisoquinoline complexes **12–14** and $NaBH_4$ were combined in methanol at –80 °C (Scheme III (bottom)). The resulting crude tetrahydroisoquinoline complexes were directly reacted with $(CH_3CH_2)_4N^+$ CN^-. Workups gave the previously characterized 1-alkyl-1,2,3,4-tetrahydroisoquinolines **20–22**[23] in 71–92% yields as spectroscopically pure oils. Their ^{1}H NMR spectra closely matched those given in the literature. The cyanide complex **17** was also isolated in 91–59% yields.

4. Optically Active Compounds. We sought to demonstrate the utility of the preceding reactions for the preparation of nonracemic alkyl-1,2,3,4-tetrahydroisoquinolines. Thus, the previously reported optically active isoquinoline complex (+)-(*S*)-**1** (>98% ee)[11] and $(CH_3)_3SiCH_2Li$ were reacted at –100 °C

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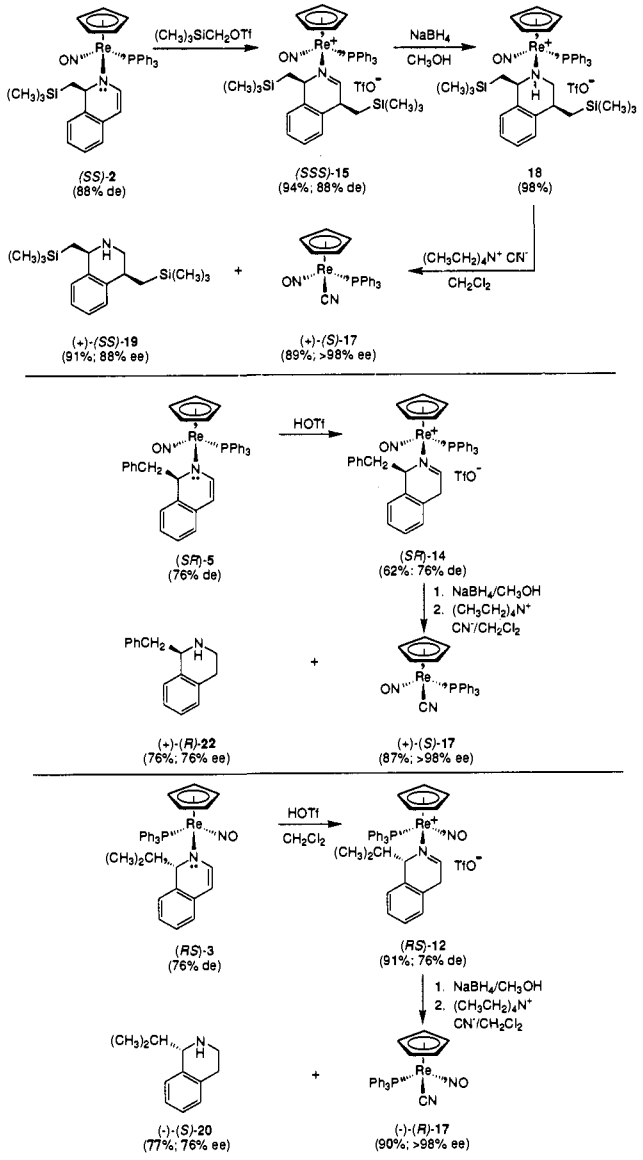
(23) (a) Scully, F. E., Jr.; Schlager, J. J. *Heterocycles* **1982**, *19*, 653. (b) Gray, N. M.; Cheng, B. K.; Mick, S. J.; Lair, C. M.; Contreras, P. C. *J. Med. Chem.* **1989**, *32*, 1242.

Scheme IV. Syntheses of Optically Active Alkyl-1,2,3,4-tetrahydroisoquinolines



as in Scheme I. The resulting enamido complex **2** (94:6 *SS*/*SR*; 88% de) was treated with $(CH_3)_3SiCH_2OTf$ *in situ* at −23 °C (Scheme IV (top)). Workup afforded the dihydroisoquinoline complex **15** in 94% yield (94:6 *SSS*/*SRR*; 88% de). Reactions with $NaBH_4$/methanol and $(CH_3CH_2)_4N^+$ CN^- gave the 1,4-dialkyl-1,2,3,4-tetrahydroisoquinoline (+)-(*SS*)-**19** and the cyanide complex (+)-(*S*)-**17**[10] in 89% and 87% yields. A ^1H NMR spectrum of the latter in the presence of the chiral shift reagent (+)-Eu(hfc)$_3$[15] indicated an enantiomeric excess of >98%. Hence, there is no loss of configuration at rhenium at any stage in the reaction sequence. A ^1H NMR spectrum of (+)-(*SS*)-**19** in the presence of the shift reagent (−)-BNPPA[15,24] indicated an enantiomeric excess of 88%, in accord with the diastereomeric composition of the precursors. The compound was also characterized by microanalysis, optical rotation,[25] and ^1H NMR.

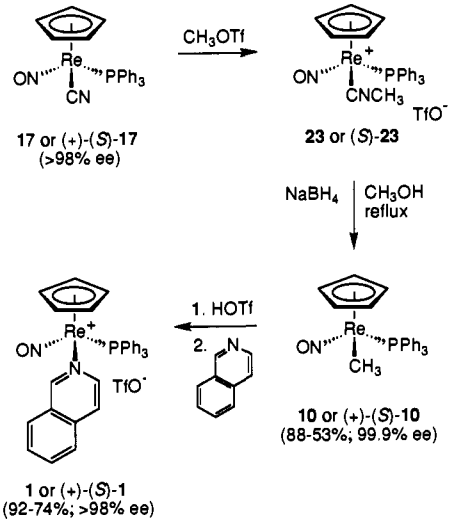
Next, (+)-(*S*)-**1** and $C_6H_5CH_2MgCl$ were combined at −100 °C as in Scheme I. The resulting enamido complex **5** (88:12 *SR*/*SS*; 76% de) and HOTf were reacted at −80 °C (Scheme IV (middle)). Workup afforded the dihydroisoquinoline complex **14** in 62% yield (88:12 *SR*/*SS*; 76% de). Reactions with $NaBH_4$/methanol and $(CH_3CH_2)_4N^+$ CN^- gave the cyanide complex (+)-(*S*)-**17** in 87% yield and >98% ee and the previously characterized compound (+)-(*R*)-1-benzyl-1,2,3,4-tetrahydroisoquinoline ((+)-(*R*)-**22**)[26] in 76% yield and 76% ee ((−)-BNPPA). Importantly, this confirms the configurations given for **5** in Scheme I and provides further support for the other assignments.

As a control, we sought to prepare an alkyl tetrahydroisoquinoline of the opposite configuration. Thus, the enantiomeric isoquinoline complex (−)-(*R*)-**1** and $(CH_3)_2CHMgCl$ were combined at −100 °C as in Scheme I. The resulting enamido complex **3** (88:12 *RS*/*RR*; 76% de) and HOTf were reacted at −80 °C (Scheme IV (bottom)). Workup afforded the dihydroisoquinoline complex **12** in 91% yield (88:12 *RS*/*RR*; 76% de). Analogous

Table I. Summary of Crystallographic Data for (*SSS*,*RRR*)-**15**·$(C_6H_6)_{1.5}$

molecular formula	$C_{41}H_{49}F_3N_2O_4PReSSi_2\cdot(C_6H_6)_{1.5}$
molecular weight	1113.44
crystal system	triclinic
space group	$P\bar{1}$ (no. 2)
cell dimensions (16 °C)	
a, Å	14.461(2)
b, Å	16.725(2)
c, Å	12.936(1)
α, deg	104.19(2)
β, deg	111.73(2)
γ, deg	103.14(2)
V, Å^3	2635.79
Z	2
d_{calc}, g/cm^3 (16 °C)	1.403
d_{obs}, g/cm^3 (22 °C)	1.397
crystal dimensions, mm	0.40 × 0.38 × 0.25
radiation, Å	Mo Kα (0.71073)
data collection method	θ–2θ
scan speed, deg/min	3.0
reflections measured	9561
range/indices (*h*,*k*,*l*)	0,17, −19,19, −13,13
scan range	$K_{\alpha 1}$ − 1.3 to $K_{\alpha 2}$ +1.6
2θ limit, deg	3.0–50.0
total bkdg time/scan time	0.0
no. of reflections between std	97
total unique data	9273
observed data, $I > 3\sigma(I)$	7609
abs coefficient, cm^{-1}	25.0
min transmission, %	61.71
max transmission, %	99.99
no. of variables	578
goodness of fit	1.1952
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0432
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.0570
Δ/σ (max)	0.006
$\Delta\rho$ (max), e/Å^3	0.941, 0.14 Å from Re

Scheme V. Recycling of the Chiral Rhenium Auxiliary



(24) Shapiro, M. J.; Archinal, A. E.; Jarema, M. A. *J. Org. Chem.* **1989**, *54*, 5826. All assays utilized 0.4–0.5 equiv of (−)-BNPPA.

(25) Dewey, M. A.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2390.

(26) Meyers, A. I.; Fuentes, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 117.

$NaBH_4$ reduction and cyanide ion displacement gave the cyanide complex (-)-(*R*)-**17** in 90% yield and >98% ee and (-)-(*S*)-1-isopropyl-1,2,3,4-tetrahydroisoquinoline ((-)-(*S*)-**20**) in 77% yield and 76% ee ((-)-BNPPA).

5. Recycling of the Chiral Metal Auxiliary. In order to maximize the utility of the preceding transformations, we sought to recycle the racemic and optically active cyanide complexes **17** to the corresponding isoquinoline complexes **1**. The latter are in turn prepared from the racemic and optically active methyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**10**) via intermediate triflate complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OTf)$, as shown in Scheme V.[11] We noted that cyanide complexes can often be alkylated at nitrogen to give isonitrile complexes.[27] Furthermore, the carbonyl complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$ can be reduced to **10** with $NaBH_4$.[21] Hence, we sought to convert **17** to an analogous isonitrile complex and attempt similar reductions.

Thus, **17** and CH_3OTf were reacted in benzene (Scheme V). Workup gave the new methyl isonitrile complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CNCH_3)]^+ TfO^-$ (**23**) in 93% yield. Complex **23** was characterized as described for **2**. It exhibited a characteristic IR ν_{CN} band at 2192 cm^{-1} (m, KBr) and a Re*C*N ^{13}C NMR absorption at 129.5 ppm (d, J_{CP} = 10.1 Hz, $CDCl_3$; assigned by ^{13}C labeling). The preceding reaction was repeated, and the crude product was refluxed with $NaBH_4$ in methanol. Workup gave the methyl complex **10** in 88% overall yield. Analogous reactions of (+)-(*S*)-**17** gave (+)-(*S*)-**10** in 53% overall yield. HPLC analysis[28] established an enantiomeric excess of >99.9%.

6. Crystal Structure of a 1,4-Dialkyl-1,4-dihydroisoquinoline Complex. In order to verify the configurations of the preceding compounds, a sample of **15** was crystallized to diastereomeric purity. Data were collected on the resulting solvate, (*SSS*,*RRR*)-**15**·$(C_6H_6)_{1.5}$, as outlined in Table I. Refinement (Experimental Section) gave the structures shown in Figure 1. Atomic coordinates and selected bond lengths, bond angles, and torsion angles are summarized in Tables II–III. Hydrogen atom positions were calculated.

Figure 1 confirms the identity of the product assigned as (*SSS*,*RRR*)-**15** in Scheme II and clearly illustrates the *cis* relationship of the 1,4-((trimethylsilyl)methyl) substituents. The heterocyclic ring adopts a boat conformation, with both silylmethyl groups in pseudoaxial positions.[29] Also, the imine hydrogen (CH=N, H27) and one triflate ion oxygen (O2) are separated by a distance (2.49 Å) close to the sum of their van der Waals radii (2.6 Å). The crystal structures of two acyclic imine complexes of I have been determined, but analogous contacts were not observed.[13] The N=C linkage in (*SSS*,*RRR*)-**15** is *anti* to the Re—NO bond, as indicated by the N—Re—N=C torsion angle of 160.9(6)°. A similar conformation is found in one of the other structurally characterized imine complexes (∠N—Re—N=C 161.6(5)°), and this feature has been analyzed in detail.[13] All three compounds exhibit similar N=C bond lengths (1.258(6) Å vs 1.272(5)–1.275(5) Å), but the Re–N bond in (*SSS*,*RRR*)-**15** is slightly longer (2.150(4) Å vs 2.112(3)–2.097(3) Å).

Discussion

1. Stereochemistry of Nucleophilic Addition. The addition of carbon nucleophiles to C1 of free isoquinoline can be effected.[30]

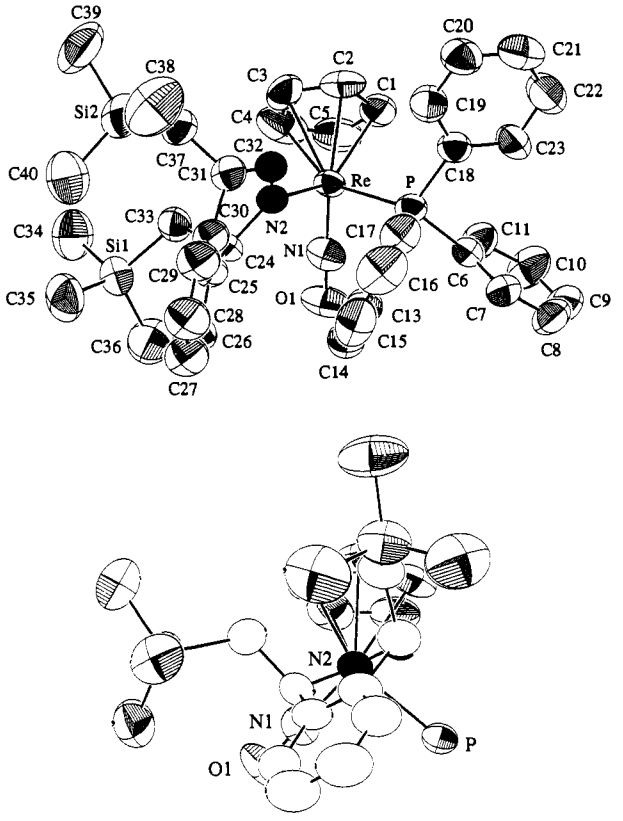


Figure 1. Structure of the cation of 1,4-dialkyl-1,4-dihydroisoquinoline complex (*SSS*,*RRR*)-**15**·$(C_6H_6)_{1.5}$: (top) numbering diagram; (bottom) Newman-type projection with phenyl rings omitted.

However, the cationic rhenium complex **1** and other N-derivatized isoquinolines[5,6] are much more reactive. These rate trends, and the site of attack, have been previously analyzed theoretically.[30a] Indeed, extended Hückel MO calculations on **1** establish a high LUMO coefficient at C1 of the isoquinoline ligand.[31] However, the formation of transients during some of the additions in Scheme I suggests that attack can also occur at a second location.

The π faces of free isoquinoline are rendered diastereotopic upon coordination to the rhenium fragment I. The data in Scheme I show that one face is distinctly more reactive toward nucleophiles. Logically, there is a rough correlation of diastereoselectivity with the bulk of the nucleophile. However, analysis of the mechanism of asymmetric induction is complicated by the transients. One possibility is that the transients form reversibly and that product stereochemistry is determined solely by the direction of attack upon C1 of the isoquinoline ligand. Another possibility is that initial 1,4- or 1,6-addition occurs, followed by a nondissociative migration of the alkyl group to C1. Other sites of attack, such as the nitrosyl or cyclopentadienyl ligands, also have precedent.[32] However, we believe that such species would likely have ^{31}P NMR chemical shifts outside of the range observed. Importantly, diastereoselectivities for nucleophiles that do not give transients (e.g., $C_6H_5CH_2MgCl$) are similar to those that do give transients (e.g., CH_3CH_2MgCl).

(27) Fehlhammer, W. P.; Fritz, M. *Chem. Rev.* **1993**, *93*, 1243.

(28) Ramsden, J. A.; Garner, C. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 1631.

(29) (a) A search of the Cambridge Structural Database located one 1,4-dihydroisoquinoline and one 1,4-dihydronaphthalene that did not contain additional fused rings (Weidner, R.; Maas, G.; Würthwein, E.-U. *Chem. Ber.* **1989**, *122*, 1711. Zimmerman, H. E.; Cassel, J. M. *J. Org. Chem.* **1989**, *54*, 3800). Both exhibited boat conformations. (b) MM2 calculations were conducted on the free 1,4-dialkyl-1,4-dihydroisoquinoline ligand with the CAChe Worksystem 3.0 (CAChe Scientific, Beaverton, Oregon). All trial structures minimized to the boat conformation found in (*SSS*,*RRR*)-**15**, but with the pseudoaxial trimethylsilyl groups rotated *syn* to the N=C linkage.

(30) (a) Dyke, S. F.; Kinsman, R. G. In *Isoquinolines*; Grethe, G., Ed.; The Chemistry of Heterocyclic Compounds; Taylor, E. C., Weissberger, A., Series Eds.; Wiley: New York, 1981; Vol. 38, Part 1, pp 29–39. (b) Nair, M. D.; Premila, M. S. In *Isoquinolines*; Kathawala, F. G., Coppola, G. M., Schuster, H. F., Eds.; The Chemistry of Heterocyclic Compounds; Taylor, E. C., Weissberger, A., Series Eds.; Wiley: New York, 1990; Vol. 38, Part 2, pp 65–69.

(31) MO calculations were conducted on a CAChe worksystem[29b] utilizing the two isoquinoline ligand geometries shown in Scheme VI. The PPh_3 ligand conformation was fixed as in the crystal structure of **1**.

(32) (a) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992; pp 281–285. (b) Forschner, T. C.; Corella, J. A., II; Cooper, N. J. *Organometallics* **1990**, *9*, 2478. Analogs of the cyclopentadienyl addition reactions reported in this paper have been observed with complexes of I.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters for (*SSS,RRR*)-**15**·$(C_6H_6)_{1.5}$[a]

atom	x	y	z	B (Å²)
Re	0.22928(2)	0.22283(2)	0.15337(3)	3.851(7)
P	0.2063(1)	0.2332(1)	0.3282(2)	4.06(5)
Si1	0.5797(2)	0.3708(2)	0.1264(2)	5.91(7)
Si2	0.6534(2)	0.0628(2)	0.2757(3)	7.90(9)
O1	0.2806(5)	0.4135(4)	0.2086(6)	7.4(2)
N1	0.2638(5)	0.3360(4)	0.1883(6)	5.0(2)
N2	0.3879(4)	0.2245(4)	0.2465(5)	3.9(1)
C1	0.0620(6)	0.1281(6)	0.0320(8)	6.3(3)
C2	0.1307(8)	0.0768(6)	0.0503(8)	6.5(3)
C3	0.1972(7)	0.0975(7)	-0.0010(8)	6.7(3)
C4	0.175(1)	0.1633(8)	-0.0471(8)	8.8(4)
C5	0.0948(8)	0.1791(6)	-0.0261(8)	7.1(3)
C6	0.1363(5)	0.3067(5)	0.3587(7)	4.4(2)
C7	0.1539(6)	0.3502(6)	0.4736(7)	5.4(2)
C8	0.0896(7)	0.3947(6)	0.4930(8)	6.5(3)
C9	0.0058(7)	0.3953(6)	0.3982(9)	7.0(3)
C10	-0.0123(7)	0.3544(7)	0.285(1)	7.6(3)
C11	0.0541(6)	0.3103(6)	0.2631(8)	5.8(2)
C12	0.3306(5)	0.2767(5)	0.4664(6)	4.3(2)
C13	0.3997(6)	0.3600(6)	0.4922(7)	5.6(2)
C14	0.4999(7)	0.3944(7)	0.5934(8)	7.1(3)
C15	0.5278(8)	0.3494(8)	0.6636(9)	8.3(4)
C16	0.4617(9)	0.2683(8)	0.6377(9)	8.7(4)
C17	0.3638(7)	0.2307(6)	0.5389(8)	6.4(3)
C18	0.1299(6)	0.1312(5)	0.3301(7)	4.7(2)
C19	0.1591(7)	0.0578(6)	0.3148(8)	6.0(2)
C20	0.1013(8)	-0.0191(6)	0.3161(9)	6.6(3)
C21	0.0123(9)	-0.0256(6)	0.3326(9)	7.5(3)
C22	-0.0180(8)	0.0435(7)	0.346(1)	8.4(4)
C23	0.0402(6)	0.1238(6)	0.3440(9)	6.6(3)
C24	0.4788(5)	0.2998(5)	0.2633(6)	4.3(2)
C25	0.5793(6)	0.3167(5)	0.3720(7)	4.7(2)
C26	0.6480(6)	0.4022(6)	0.4411(8)	6.1(3)
C27	0.7390(7)	0.4215(7)	0.5437(9)	7.4(3)
C28	0.7577(8)	0.3490(8)	0.579(1)	8.3(4)
C29	0.6906(7)	0.2658(7)	0.5124(9)	7.0(3)
C30	0.5977(6)	0.2485(6)	0.4057(7)	5.2(2)
C31	0.5168(6)	0.1566(5)	0.3349(7)	5.2(2)
C32	0.4067(6)	0.1616(5)	0.2765(7)	4.6(2)
C33	0.4895(6)	0.2827(6)	0.1457(7)	5.1(2)
C34	0.5450(9)	0.3324(8)	-0.0347(9)	8.7(4)
C35	0.7211(8)	0.3854(9)	0.209(1)	8.7(4)
C36	0.557(1)	0.4760(7)	0.170(1)	9.4(4)
C37	0.5320(6)	0.0955(6)	0.2367(8)	6.2(3)
C38	0.675(1)	0.023(1)	0.395(1)	12.9(6)
C39	0.6273(9)	-0.0253(9)	0.138(1)	11.8(4)
C40	0.7731(9)	0.156(1)	0.312(1)	12.5(6)
C41	0.285(1)	-0.149(1)	0.203(1)	14.7(6)
C42	0.955(1)	0.732(1)	0.318(2)	17.4(7)
C43	0.870(2)	0.7478(9)	0.322(1)	13.8(6)
C44	0.780(1)	0.701(1)	0.232(1)	13.4(5)
C45	0.771(1)	0.642(1)	0.140(1)	15.2(7)
C46	0.853(1)	0.631(1)	0.136(1)	18.2(6)
C47	0.947(1)	0.667(1)	0.224(2)	26.4(9)
C48	0.948(1)	0.424(1)	0.008(1)	11.8(6)
C49	1.062(1)	0.477(1)	0.089(1)	10.8(5)
C50	1.110(1)	0.550(1)	0.080(1)	11.7(6)
S	0.2483(3)	-0.1356(2)	0.0824(4)	12.0(2)
O2	0.2528(9)	-0.0496(6)	0.138(1)	11.5(5)
O3	0.150(1)	-0.1973(9)	0.009(1)	14.3(6)
O4	0.3351(9)	-0.139(1)	0.044(1)	13.8(5)
F1	0.3035(9)	-0.2441(7)	0.176(1)	13.0(5)
F2	0.223(1)	-0.1764(9)	0.241(1)	14.1(5)
F3	0.382(1)	-0.117(1)	0.277(1)	21.2(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table III. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) in (*SSS,RRR*)-**15**·$(C_6H_6)_{1.5}$[a]

Re–N2	2.150(4)	C27–C28	1.44(1)
Re–P	2.376(1)	C28–C29	1.342(9)
Re–N1	1.738(5)	C29–C30	1.431(8)
N1–O1	1.203(5)	C30–C31	1.507(7)
Re–C1	2.248(5)	C31–C32	1.521(7)
Re–C2	2.278(5)	C31–C37	1.542(8)
Re–C3	2.328(6)	Si1–C33	1.866(6)
Re–C4	2.280(7)	Si1–C34	1.852(8)
Re–C5	2.211(6)	Si1–C35	1.845(7)
N2–C24	1.504(6)	Si1–C36	1.854(8)
N2–C32	1.258(6)	Si2–C37	1.885(6)
C24–C25	1.509(7)	Si2–C38	1.77(1)
C24–C33	1.550(7)	Si2–C39	1.857(8)
C25–C26	1.378(7)	Si2–C40	1.86(1)
C25–C30	1.363(8)	P–C6	1.822(5)
C26–C27	1.378(9)	P–C12	1.829(5)
		P–C18	1.821(5)
N2–Re–P	89.6(1)	C26–C25–C30	120.6(5)
N2–Re–N1	96.4(2)	C25–C30–C31	119.8(5)
P–Re–N1	91.7(2)	C30–C31–C37	118.1(5)
Re–N1–O1	175.7(4)	C25–C24–C33	114.4(5)
Re–N2–C24	117.6(3)	C32–C31–C37	107.4(4)
Re–N2–C32	122.8(3)	C33–Si1–C36	110.6(3)
C24–N2–C32	119.2(4)	C34–Si1–C35	107.2(4)
N2–C24–C25	111.2(4)	C34–Si1–C36	109.4(4)
N2–C32–C31	125.0(5)	C35–Si1–C36	111.1(4)
N2–C24–C33	109.2(4)	C33–Si1–C34	106.0(3)
C24–C25–C26	119.2(6)	C33–Si1–C35	112.3(3)
C24–C25–C30	120.0(4)	C37–Si2–C38	111.2(4)
C25–C26–C27	121.6(6)	C37–Si2–C39	105.9(4)
C26–C27–C28	117.5(6)	C37–Si2–C40	111.1(4)
C27–C28–C29	121.0(6)	C38–Si2–C39	110.5(5)
C28–C29–C30	119.7(7)	C38–Si2–C40	110.8(6)
C25–C30–C29	119.6(5)	C39–Si2–C40	107.2(5)
C29–C30–C31	120.5(6)	C24–C33–Si1	120.7(4)
C30–C31–C32	109.3(4)	C31–C37–Si2	120.6(4)
P–Re–N2–C24	-117.8(5)	N1–Re–N2–C24	-26.1(5)
P–Re–N2–C32	69.2(6)	N1–Re–N2–C32	160.9(6)

[a] Bond lengths and angles involving the phenyl rings have been omitted.

The crystal structure of **1** has been previously determined, and a portion is illustrated in Scheme VI.[11] The Re–NC_9H_7 bond adopts a solid-state conformation in which the fused benzenoid ring is roughly *anti* to the nitrosyl ligand, as shown in Newman projection II. Nucleophiles preferentially add to σ-ketone complexes of **I** from a direction opposite the bulky PPh_3 ligand.[8a,9] However, analogous attack upon II would give the minor diastereomers in Scheme I. Consequently, we propose that the alternative Re–NC_9H_7 rotamer **III**, in which the benzenoid ring is *syn* to the nitrosyl ligand, is more reactive. As analyzed earlier,[11] it is probable that III dominates in solution.

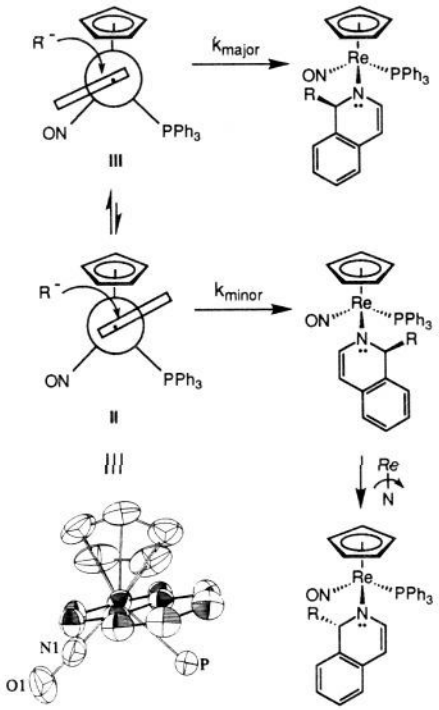
Interestingly, the *less* stable diastereomers of **2–9** preferentially form in Scheme I. Equilibrium ratios are in fact 6–2:94–98 in the *opposite* direction[20]—a fortuitous circumstance that allows either species to be accessed in high diastereomeric excess. The stabilities of related diastereomeric alkoxide complexes have been previously rationalized by the model in Scheme VIIA.[33] If *anti* conformations are maintained along the Ph_3P–Re–O–C–R_L linkage, which contains the bulkiest rhenium and carbon substituents, one diastereomer will experience a destabilizing steric interaction between the cyclopentadienyl ligand and the second largest carbon substituent (R_M). As shown in Scheme VIIB, a similar model also correctly predicts the relative stabilities of analogous amido complexes.[12b] However, equilibrium ratios are not as biased, and this treatment neglects any effect of the labile nitrogen stereocenter.[17b] These models can be extrapolated to **2–9**, as shown in Scheme VIIC. However, since equilibrium ratios are much higher, additional steric or electronic factors, likely involving the nitrogen stereocenter, are probably important.[34]

2. Stereochemistry of Electrophilic Addition. The reactions of enamido complex (*SS,RR*)-**2** and electrophiles in Scheme II (bottom) are also highly diastereoselective. Thus, one C=C face

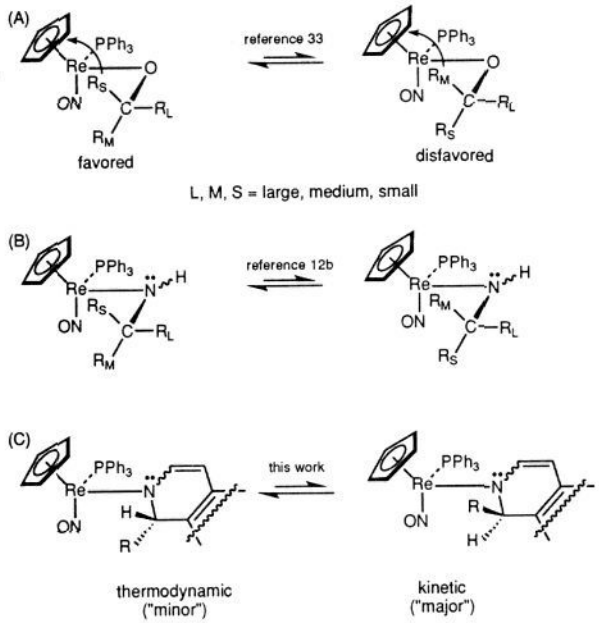
(33) Saura-Llamas, I.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 2136.

(34) The carbon configurations of any free alkyl 1,2,3,4-tetrahydroisoquinolines derived from epimerized **2–9** should be identical with those obtained from unepimerized samples. However, as has been verified for epimerized (*SS*)-**2**,[19] the configuration of the recovered rhenium auxiliary is opposite, and the enantiomeric purity is lower.

Scheme VI. Transition State Models for Nucleophilic Addition to Isoquinoline Complex **1**



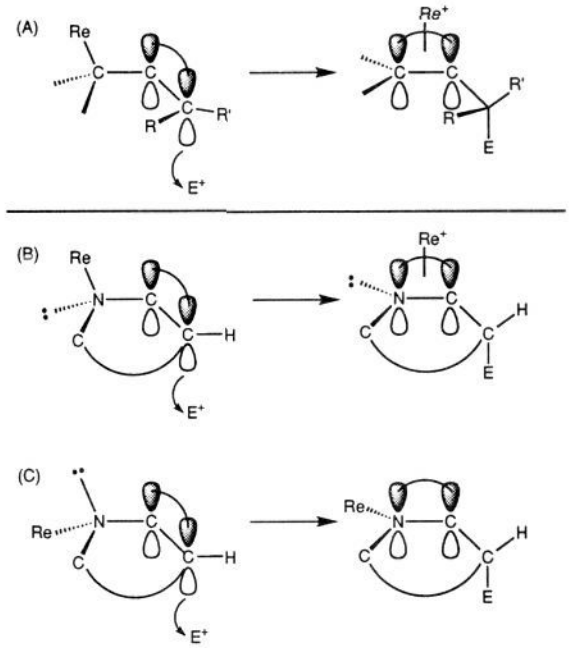
Scheme VII. Models for Diastereomeric Equilibria in (A) Alkoxide, (B) Amido, and (C) Enamido Complexes



is distinctly more reactive, and configuration can be controlled at a site with a 1,4 relationship to the chiral auxiliary. We have also observed efficient 1,4 asymmetric induction in additions of electrophiles to σ allyl complexes of **I**, $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CHR)$.[35] These afford cationic alkene complexes in which the configurations of the new tetravalent carbons are consistent with the transition-state model shown in Scheme VIIIA. The key feature is the *syn* alignment of the Re—C_α bond and the C=C π cloud, which maximizes the orbital interactions that render C_γ nucleophilic. The electrophile then attacks the C=C face *anti* to the Re—C_α bond.

(35) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191.

Scheme VIII. Transition State Models for Electrophilic Additions to (A) σ-Allyl Complexes and (B, C) Enamido Complexes



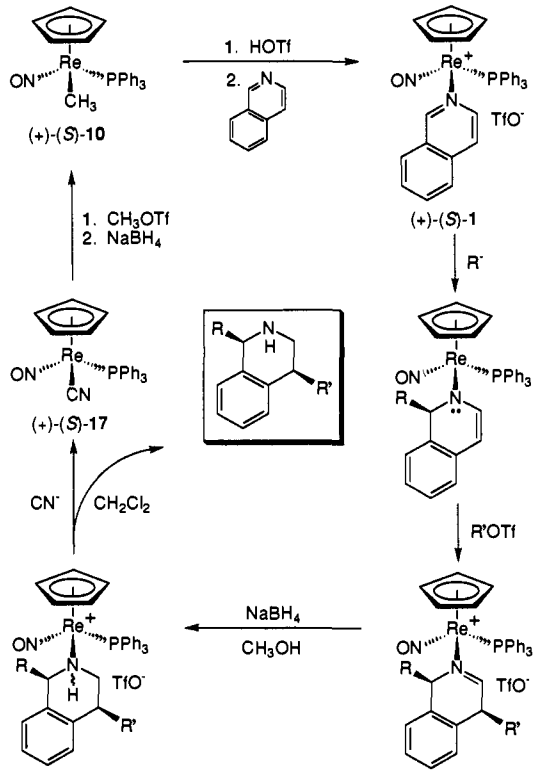
It is well-known that the nitrogen lone pair similarly participates in the C-alkylation of organic enamines. Hence, the alkylation of (*SS*,*RR*)-**2** could involve assistance of either the Re–N bond *or* the nitrogen lone pair, as sketched in Scheme VIIIB,C. Two complementary transition states can also be formulated in which the configurations of the enamido nitrogen stereocenters[17b] are inverted and the *syn* Re—N bond or nitrogen lone pair is moved to the bottom C=C face. Scheme VIIIB initially gives a π imine complex. However, on the basis of π/σ equilibria in aldehyde and ketone complexes of **I**,[7,8] it is unlikely that this would be prohibitively high in energy. Unfortunately, our present data do not distinguish between the models in Scheme VIIIB,C. Furthermore, the existing carbon stereocenter is likely a factor. Thus, in order to acquire baseline data, alkylations of simple *monocyclic* enamido complexes of **I** are presently under investigation.

3. Merits of Methodology. Practical application of the preceding transformations can be summarized as shown in Scheme IX. The following points deserve emphasis. First, the methyl complex **10** can be prepared in three steps from commercially available $Re_2(CO)_{10}$ via checked procedures.[21] A recent enhancement of one step[36] brings the overall yield to 57%. Resolution is easily effected en route in two steps and in 76% yield. All of *these reactions, and those in Scheme IX, are amenable to* multigram scales, as illustrated by the procedures given in the Experimental Section for **12** and **14**. Half-gram quantities of free alkyl-1,2,3,4-tetrahydroisoquinolines have been isolated, and this by no means constitutes a practical upper limit.

The chiral rhenium auxiliary is easily recovered from the reaction mixtures and recycled without loss of enantiomeric purity. Importantly, the yields of many steps in the preceding schemes remain unoptimized. At present, the overall yield of the 1,4-dialkyl-1,2,3,4-tetrahydroisoquinoline **19** from **1** is 40% (racemic) or 84% (optically active). This distinction is largely artificial, reflecting the fact that some steps were combined in the optically active series. Furthermore, simple modifications can potentially give enantiomerically pure alkyltetrahydroisoquinolines. One approach would entail the crystallization of intermediate

(36) Zhou, Y.; Dewey, M. A.; Gladysz, J. A. *Organometallics* **1993**, *12*, 3918.

Scheme IX. Summary of Enantioselective Syntheses of Alkyl-1,2,3,4-tetrahydroisoquinolines



1,4-dihydroisoquinoline complexes to diastereomeric purity, as was done for (*SSS,RRR*)-**15**.

There is also the possibility that Scheme IX can be modified to introduce additional stereocenters. For example, the $NaBH_4$ utilized to reduce 1,4-dihydroisoquinoline complexes **12–15** could be replaced by $NaBD_4$ or other nucleophiles, thereby functionalizing all carbons of the non-benzenoid ring. Indeed, other imine complexes of I undergo diastereoselective additions of carbon nucleophiles.[37] Finally, note that substitution at rhenium is required at two critical stages in Scheme IX. Such processes almost invariably occur with retention of configuration, and recent kinetic studies have established *associative* mechanisms.[38]

Other researchers have recently reported diastereoselective additions of carbon nucleophiles to chiral transition metal imine complexes.[39,40] In particular, Templeton has developed routes to enantiomerically pure chiral tungsten imine complexes, effected highly diastereoselective additions of hydride and cyanide nucleophiles, and isolated the corresponding free amines in the racemic series.[40] Also, Comins has described an organic chiral auxiliary that allows additions of methyl nucleophiles to C1 of isoquinoline in 72–60% de.[5] Other transition metal-based approaches to isoquinoline alkaloids have appeared.[41]

In summary, the above results exemplify the considerable potential of chiral transition metal auxiliaries in a currently important area of enantioselective organic synthesis. Further, such auxiliaries are readily amenable to modification and optimization. For example, replacement of the cyclopentadienyl or PPh_3 ligands in I by bulkier or electronically altered groups may afford enhanced stereoselectivities. Parallel investigations involving complexes of I and quinoline, and acyclic and monocyclic unsaturated nitrogen donor ligands, are currently in progress and will be reported in due course.[37]

Experimental Section

General Data. General procedures were identical with those in a previous paper.[13,42] Chemicals were obtained as follows: CH_3OH, $CHCl_3$ (Mallinckrodt), C_6D_6 (Isotec), CH_3OTf, $(CH_3)_3SiCH_2OTf$, (–)-BNPPA, (+)-Eu(hfc)$_3$ (Aldrich), $NaBH_4$ (Alfa), and silica gel (Baker, 60–200 mesh) were used as received;[15] RMgX and RLi reagents (Aldrich)were standardized before use;[43] DOTf was prepared from Tf_2O (distilled from P_2O_5) and D_2O (1:1, ampule, 4.5 days, until homogeneous) and then distilled and analyzed for isotopic purity by ^1H NMR.[44] Other materials were acquired as described earlier.[13]

(η^5-C_5H_5)Re(NO)(PPh$_3$)(ÑCH=CHC(CH)$_4$CCHCH$_2$Si(CH$_3$)$_3$) (2). A Schlenk flask was charged with [(η^5-C_5H_5)Re(NO)(PPh$_3$)(*iso*-NC_9H_7)]$^+$ TfO$^-$ (**1**;[11] 0.155 g, 0.189 mmol), THF (10 mL), and a stir bar and cooled to –100 °C (ethanol/N_2(l)). Then $(CH_3)_3SiCH_2Li$ (0.378 mL, 0.189 mmol, 0.48 M in pentane) was added dropwise with stirring. The orange solution turned deep red. The flask was transferred to a –23 °C bath (CCl_4/CO_2). After 0.5 h, an oil pump vacuum was applied, and the cold bath was removed.[45] The resulting residue was extracted with CH_2Cl_2/hexane (13.5 mL, 20:80 v/v). The extract was slowly concentrated to ca. 5 mL under oil pump vacuum. A red solid formed, and the sample was kept at –20 °C for 12 h. The solid was collected by filtration, washed with pentane, and dried under oil pump vacuum to give **2** (0.103 g, 0.135 mmol, 71%; 94:6 *SS,RR/SR,RS*),[16,17] mp 182–184 °C dec. Anal. Calcd for $C_{36}H_{38}N_2OPReSi$: C, 56.97; H, 4.91. Found: C, 56.79; H, 5.06. IR (cm^{-1}, KBr) ν_{NO} 1650 vs.

NMR, (*SS,RR*)-**2** (–20 °C, THF-d_8): ^1H, 7.52–7.08 (m, 3C_6H_5), 6.94–6.86 (m, 2H of C_6H_4), 6.83–6.77 (m, 1H of C_6H_4), 6.58–6.51 (m, 1H of C_6H_4), 5.92 (d, J = 6.3, CH=C*H*N), 5.22 (s, C_5H_5), 4.83 (d, J = 6.3, C*H*=CHN), 4.72 (dd, J = 3.3, 11.8, CHH'C*H*N), 1.59 (dd, J = 11.8, 13.8, C*H*H'CHN), 0.46 (dd, J = 3.3, 13.8, CH*H*'CHN), –0.31 (s, Si(CH$_3$)$_3$); $^{13}C\{^1H\}$, 154.3 (d, J = 3.0, CH=*C*HN), PPh at 136.5 (d, J = 49.2, *i*), 135.0 (d, J = 10.0, *o*), 130.9 (s, *p*), 129.1 (d, J = 10.5, *m*); C_6H_4 at 134.7 (s), 128.1 (s), 126.2 (s), 125.2 (s), 122.1 (s), 121.2 (s); 99.3 (s, *C*H=CHN), 91.9 (s, C_5H_5), 73.0 (s, CHH'*C*HN), 20.2 (s, *C*HH'CHN), –0.75 (s, Si(CH$_3$)$_3$); $^{31}P\{^1H\}$, 14.6 (s). NMR, (*SR,RS*)-**2** (THF-d_8):[46] ^1H, 7.72–7.29 (m, 3C_6H_5), 6.93–6.75 (m, 3H of C_6H_4), 6.61–6.54 (m, 1H of C_6H_4), 5.90 (d, J = 6.4, CH=C*H*N), 5.07 (s, C_5H_5), 4.90 (dd, J = 3.5, 11.6, CHH'C*H*N), 4.63 (d, J = 6.4, C*H*=CHN), 1.61 (dd, J = 11.6, 13.9, C*H*H'CHN), 0.94 (dd, J = 3.5, 13.9, CH*H*'CHN), –0.20 (s, Si(CH$_3$)$_3$); $^{13}C\{^1H\}$, 152.0 (d, J = 4.6, CH=*C*HN), PPh at 136.1 (d, J = 51.8, *i*), 134.7 (d, J = 10.5, *o*), 131.0, (s, *p*), 129.1 (d, J = 10.1, *m*); C_6H_4 at 134.9 (s), 127.8 (s), 126.3 (s), 125.7 (s), 122.2 (s), 121.0 (s); 97.1 (s, *C*H=CHN), 92.2 (s, C_5H_5), 77.5 (s, CHH'*C*HN), 22.4 (s, *C*HH'CHN), –0.60 (s, Si(CH$_3$)$_3$); $^{31}P\{^1H\}$, 20.1 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(N=CHCH$_2$C(CH)$_4$CCHCH$_2$Si-(CH$_3$)$_3$)]$^+$ TfO$^-$ (11). Complex **1** (0.199 g, 0.242 mmol), THF (13 mL), and $(CH_3)_3SiCH_2Li$ (0.484 mL, 0.242 mmol, 0.48 M in pentane) were combined in a procedure analogous to that given for **2**. The flask was transferred to a 0 °C bath. Then HOTf (0.021 mL, 0.24 mmol) was added with stirring. Solvent was removed under oil pump vacuum, and the residue was extracted with CH_2Cl_2 (10 mL). The extract was filtered,

(37) Stark, G. A., University of Utah, unpublished data.
(38) Dewey, M. A.; Zhou, Y.; Liu, Y.; Gladysz, J. A. *Organometallics*, **1993**, *12*, 3924.
(39) Martin, G. C.; Boncella, J. M.; Wucherer, E. J. *Organometallics* **1991**, *10*, 2804.
(40) (a) Feng, S. G.; Templeton, J. L. *Organometallics* **1992**, *11*, 1295. (b) Caldarelli, J. L.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10097.
(41) Davies, S. G. *J. Organomet. Chem.* **1990**, *400*, 223.

(42) (a) NMR spectra were recorded at ambient temperature (unless noted) on 300-MHz spectrometers and referenced as follows: ^1H (δ) $CHCl_3$ (7.24), THF-d_8 (3.58, 1.73), $CHDCl_2$ (5.32), or internal TMS (0.00); $^{13}C\{^1H\}$ (ppm) $CDCl_3$ (77.0), CD_2Cl_2 (53.8), THF-d_8 (67.4, 25.3); $^{31}P\{^1H\}$ external 85% H_3PO_4 (0.0 ppm). Chemical shifts are in δ (^1H) or ppm (^{13}C, ^{31}P), and coupling constants (J) are in Hz. All ^1H NMR couplings are to ^1H, and all ^{13}C NMR couplings are to ^{31}P, unless noted. PPh carbon assignments were made as described in: Buhro, W. E.; Georgiou, S.; Fernández, J. M.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1986**, *5*, 956. (b) Except for $CH_2Si(CH_3)_3$ derivatives, melting points and microanalyses were not acquired for rhenium complexes that were mixtures of diastereomers.
(43) (a) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87. (b) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165.
(44) Bakoss, H. J.; Ranson, R. J.; Roberts, R. M. G.; Sadri, A. R. *Tetrahedron* **1982**, *38*, 623.
(45) Solvent is generally removed at as low a temperature as possible to avoid epimerization of the enamido complexes at rhenium.[18,20]
(46) (a) These data were acquired on a sample obtained as described in footnote 18. (b) Complete NMR data for (*SR,RS*)-**11** and (*SRR,RSS*)-**15** are similarly available.[19]

and solvent was removed under oil pump vacuum. The oil was triturated with ether (20 mL). The resulting yellow powder was collected by filtration and dried under oil pump vacuum to give **11** (0.185 g, 0.203 mmol, 84%; 94:6 *SS,RR/SR,RS*), mp 205–207 °C dec. Anal. Calcd for $C_{37}H_{39}F_3N_2O_4PReSSi$: C, 48.83; H, 4.32. Found: C, 48.58; H, 4.43. IR (cm^{-1}, KBr) ν_{NO} 1686 vs.

NMR, (*SS,RR*)-**11** ($CDCl_3$): ^1H, 8.01 (dd, J_{HH} = 5.3, J_{HP} = 1.1, CH=N), 7.36–7.18 (m, 12H of $3C_6H_5$), 7.13–7.03 (m, 3H of $3C_6H_5$, 3H of C_6H_4), 6.97–6.92 (m, 1H of C_6H_4), 5.59 (s, C_5H_5), 5.06 (dd, J = 2.5, 12.7, CHH'C*H*N), 3.99 (d, J = 21.4, C*H*H'CH=N), 3.42 (dd, J = 5.3, 21.4, CH*H'*CH=N), 1.27 (dd, J = 2.5, 13.9, C*H*H'CHN), 0.92 (dd, J = 12.7, 13.9, CH*H'*CHN), –0.11 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$, 181.0 (d, J = 3.4, CH=N), PPh at 133.2 (d, J = 10.5, *o*), 131.1 (s, *p*), 130.4 (d, J = 55.5, *i*), 128.9 (d, J = 10.5, *m*); C_6H_4 at 136.5 (s), 128.6 (s), 127.8 (s), 126.3 (s), 125.3 (s);[47] 120.6 (q, J_{CF} = 320.3, CF_3), 92.4 (s, C_5H_5), 75.3 (s, CHH'*C*HN), 36.0 (s, *C*HH'CH=N), 23.6 (s, *C*HH'CHN), –0.93 (s, $Si(CH_3)_3$); $^{31}P\{^1H\}$, 18.7 (s).[46b]

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N{=}CHCH_2C(CH)_4CCHCH(CH_3)_2)]^+$ TfO^- (12). **A.** Complex **1** (2.207 g, 2.466 mmol), THF (80 mL), and $(CH_3)_2CHMgCl$ (1.37 mL, 2.47 mmol, 1.8 M in THF) were combined in a procedure analogous to that given for **2**. The flask was transferred to a –23 °C bath. After 1 h, solvent was removed under oil pump vacuum.[45] The residue was cooled to –80 °C (acetone/CO_2), and CH_2Cl_2 (60 mL) and HOTf (0.436 mL, 4.93 mmol; dropwise, with stirring) were added. The cold bath was removed. After 1 h, solvent was removed by rotary evaporation. The residue was extracted with $CHCl_3$ (80 mL). The extract was filtered through Celite. Solvent was removed from the filtrate by rotary evaporation. The residue was triturated with ether (50 mL). The resulting orange powder was collected by filtration, washed with hexane, and dried under oil pump vacuum to give **12** (1.903 g, 2.198 mmol, 89%; 88:12 *SR,RS/SS,RR*).[42b] IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1693 vs. **B.** Complex (–)-(*R*)-**1** (2.628 g, 3.198 mmol; >98% ee),[11] $(CH_3)_2CHMgCl$ (2.0 mL, 4.00 mmol, 2.0 M in THF), and HOTf (0.57 mL, 6.441 mmol) were combined in a procedure analogous to A. A similar workup gave **12** (2.522 g, 2.913 mmol, 91%; 88:12 *RS/RR*).[48a]

NMR ($CDCl_3$, *SR,RS/SS,RR*): ^1H, 8.54/8.44 (br s/br s, $w_{1/2}$ = 15 Hz, CH=N), 7.57–6.93 (m, $3C_6H_5$, C_6H_4), 5.73/5.53 (s/s, C_5H_5), 4.75/5.10 (br s/br s, $w_{1/2}$ = 12 Hz, CHC*H*N), 4.14/4.38 (d/d, J = 23.5/15.8, C*H*H'CH=N), 3.45/3.33 (d/d, J = 23.5/15.8, CH*H'*CH=N), 2.84–2.73/2.66–2.59 (m/m, C*H*$(CH_3)_2$), 1.14/0.92 (d/d, J = 7.1/6.8, CH-(C*H*$_3$)C'H$_3$), 0.59/0.26 (d/d, J = 6.8/6.8, CH(CH$_3$)C'*H*$_3$); $^{31}P\{^1H\}$, 18.4/18.0 (s/s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N{=}CHCH_2C(CH)_4CCHCH_2CH_3)]^+$ TfO^- (13). Complex **1** (0.565 g, 0.687 mmol), THF (30 mL), and CH_3CH_2MgBr (0.859 mL, 0.687 mmol, 0.8 M in THF) were combined in a procedure analogous to that given for **2**. The flask was transferred to a –45 °C bath (CH_3CN/CO_2). After 1 h, solvent was removed under oil pump vacuum.[45] The residue was cooled to –80 °C, and CH_2Cl_2 (30 mL) and HOTf (0.061 mL, 0.69 mmol; dropwise, with stirring) were added. The cold bath was removed. After 1 h, solvent was removed by rotary evaporation. The residue was extracted with $CHCl_3$ (60 mL). The extract was filtered through Celite. Solvent was removed from the filtrate by rotary evaporation. The residue was triturated with ether (30 mL). The resulting orange powder was collected by filtration, washed with ether, and dried under oil pump vacuum to give **13** (0.449 g, 0.527 mmol, 77%; 85:15 *SR,RS/SS,RR*).[42b] IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1693 vs.

NMR ($CDCl_3$, *SR,RS/SS,RR*): ^1H (partial), 9.58/9.35 (br s/br s, CH=N), 8.25–6.87 (m, $3C_6H_5$, C_6H_4), 5.65/5.45 (s/s, C_5H_5), 4.77/4.98 (br d/br d, J = 6.8/7.0, CHH'C*H*N), 2.18–1.90 (br m, C*H*H'CHN), 1.84–1.64 (br m, CH*H'*CHN), 0.81 (br t, J = 7.4, CH_3); $^{31}P\{^1H\}$, 18.6/18.9 (s/s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N{=}CHCH_2C(CH)_4CCHCH_2C_6H_5)]^+$ TfO^- (14). **A.** Complex **1** (2.362 g, 2.874 mmol), THF (120 mL), and $C_6H_5CH_2MgCl$ (2.00 mL, 3.48 mmol, 1.74 M in THF) were combined in a procedure analogous to that given for **2**. After 1 h, an oil pump vacum was applied, and the cold bath was removed.[45] The resulting residue was cooled to –80 °C, and CH_2Cl_2 (100 mL) and HOTf (0.510 mL, 5.76 mmol; dropwise, with stirring) were added. After 0.5 h, the cold bath was removed. After 0.5 h, solvent was removed by rotary evaporation. The residue was extracted with $CHCl_3$ (200 mL). The extract was filtered through Celite. Solvent was removed from the filtrate by rotary evaporation. The residue was triturated with ether/hexane (200 mL, 20:80 v/v). The resulting orange powder was collected by filtration, washed with hexane, and dried under oil pump vacuum to give **14** (2.525 g, 2.763 mmol, 96%; 88:12 *SR,RS/SS,RR*).[42b] IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1691 vs. **B.** Complex (+)-(*S*)-**1** (1.693 g, 2.060 mmol; >98% ee), THF (80 mL), $C_6H_5CH_2MgCl$ (1.43 mL, 2.49 mmol, 1.74 M in THF), and HOTf (0.183 mL) were combined in a procedure analogous to A. A similar workup gave **14** (1.168 g, 1.278 mmol, 62%; 88:12 *SR/SS*).[48a]

NMR ($CDCl_3$, *SR,RS/SS,RR*): ^1H (partial) 8.52 (d, J = 6.1, CH=N), 8.01–6.09 (m, $4C_6H_5$, C_6H_4), 5.00/5.25 (s/s, C_5H_5), 4.21 (dd, J = 3.4, 9.9, CHH'C*H*N); $^{31}P\{^1H\}$, 17.9/17.3 (s/s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N{=}CHCH(CH_2Si(CH_3)_3)C(CH)_4CCHCH_2Si(CH_3)_3)]^+$ TfO^- (15). **A.** A Schlenk flask was charged with **2** (0.182 g, 0.239 mmol), CH_2Cl_2 (3 mL), and a stir bar and cooled to –23 °C. Then $(CH_3)_3SiCH_2OTf$ (0.136 mL, 0.717 mmol; dropwise, with stirring) was added and the cold bath was removed. After 2 h, solvent was removed under oil pump vacuum. The residue was extracted with CH_2Cl_2 (5 mL). The extract was swirled over charcoal (15 min) and filtered. The filtrate was concentrated to ca. 2 mL, and hexane (30 mL) was slowly added with stirring. The resulting yellow precipitate was collected by filtration, washed with hexane, and dried under oil pump vacuum to give **15** (0.171 g, 0.172 mmol, 72%; 94:6 *SSS,RRR/SRR,RSS*), mp 220–222 °C dec. Anal. Calcd for $C_{41}H_{49}F_3N_2O_4PReSSi_2$: C, 49.43; H, 4.96. Found: C, 49.35; H, 4.98. IR (cm^{-1}, KBr) ν_{NO} 1686 vs. **B.** Complex (+)-(*S*)-**1** (0.648 g, 0.790 mmol), THF (50 mL), and $(CH_3)_3SiCH_2Li$ (1.320 mL, 0.792 mmol, 0.6 M in pentane) were combined in a procedure analogous to that given for **2**. The flask was transferred to a –23 °C bath (CCl_4/CO_2). After 0.5 h, an oil pump vacuum was applied, and the cold bath was removed.[45] The residue was cooled to –23 °C, and CH_2Cl_2 (5 mL) and $(CH_3)_3SiCH_2OTf$ (0.790 mL, 3.95 mmol; dropwise, with stirring) were added. The cold bath was removed. After 2 h, solvent was removed under oil pump vacuum. The residue was extracted with CH_2Cl_2 (25 mL). The extract was swirled over charcoal (15 min) and filtered. The filtrate was concentrated to ca. 3 mL and hexane (150 mL) was slowly added with stirring. The resulting brown precipitate was collected by filtration, washed with pentane, and dried under oil pump vacuum to give **15** (0.740 g, 0.743 mmol, 94%; 94:6 *SSS/SRR*).[48a]

NMR, (*SSS,RRR*)-**15** ($CDCl_3$): ^1H, 8.10 (d, J = 4.0, CH=N), 7.34–7.24 (m, 9H of $3C_6H_5$), 7.23–7.18 (m, 2H of C_6H_4), 7.17–7.07 (m, 6H of $3C_6H_5$), 7.01–6.94 (m, 2H of C_6H_4), 5.60 (s, C_5H_5), 4.83 (dd, J = 2.9, 12.5, CHH'C*H*N), 3.40 (ddd, J = 3.0, 4.0, 12.7, C*H*CH=N), 1.79 (dd, J = 2.9, 13.5, C*H*H'CHN), 1.62 (dd, J = 3.0, 13.5, C*H*H'CHCH=N), 0.94 (dd, J = 12.5, 13.5, CH*H'*CHN), 0.42 (dd, J = 12.7, 13.5, CH*H'*CHCH=N), –0.02 (s, $Si(CH_3)_3$), –0.04 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$, 184.6 (d, J = 3.5, CH=N), PPh at 133.2 (d, J = 10.6, *o*), 131.0 (s, *p*), 130.5 (d, J = 55.3, *i*), 129.0 (d, J = 10.7, *m*); C_6H_4 at 136.9 (s), 129.0 (s), 128.7 (s), 127.3 (s), 126.2 (s), 126.1 (s); 120.8 (q, J_{CF} = 320.0, CF_3), 92.9 (s, C_5H_5), 73.7 (s, CHH'*C*HN), 42.2 (s, *C*HCH=N), 30.4 (s, *C*HH'CHCH=N), 23.6 (s, *C*HH'CHN), –0.5 (s, $Si(CH_3)_3$), –0.6 (s, $Si(CH_3)_3$); $^{31}P\{^1H\}$, 16.9 (s).[46b]

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N{=}CHCH(CH_3)C(CH)_4CCHCH_2Si(CH_3)_3)]^+$ TfO^- (16). Complex **2** (0.243 g, 0.320 mmol), CH_2Cl_2 (4 mL), and CH_3OTf (0.109 mL, 0.960 mmol) were combined in a procedure analogous to that given for **15**. A similar workup gave **16** as a yellow powder (0.244 g, 0.264 mmol, 83%; 94:6 *SSS,RRR/SRR,RSS*), mp 201–202 °C dec. Anal. Calcd for $C_{38}H_{41}F_3N_2O_4PReSSi$: C, 49.39; H, 4.47. Found: C, 49.60; H, 4.64. IR (cm^{-1}, KBr) ν_{NO} 1681 vs.

NMR, (*SSS,RRR*)-**16** ($CDCl_3$): ^1H, 8.10 (d, J = 4.8, CH=N), 7.31–7.25 (m, 9H of $3C_6H_5$), 7.23–7.18 (m, 6H of $3C_6H_5$), 7.18–7.08 (m, 3H of C_6H_4), 6.97–6.90 (m, 1H of C_6H_4), 5.59 (s, C_5H_5), 4.87 (dd, J = 2.8, 13.0, CHH'C*H*N), 3.38 (dq, J = 4.8, 7.5, C*H*CH=N), 1.77 (dd, J = 2.8, 13.9, C*H*H'CHN), 1.46 (d, J = 7.5, CH_3CHCH=N), 0.78 (dd, J = 13.0, 13.9, CH*H'*CHN), –0.05 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$, 184.1 (s, CH=N), PPh at 133.2 (d, J = 10.3, *o*), 131.0 (s, *p*), 130.3 (d, J = 55.4, *i*), 129.0 (d, J = 10.8, *m*); C_6H_4 at 135.7 (s), 133.2 (s), 127.9 (s), 127.2 (s), 126.0 (s), 125.5 (s); 120.7 (q, J_{CF} = 320.4, CF_3), 92.8 (s, C_5H_5), 73.4 (s, CHH'*C*HN), 40.9 (s, *C*HCH=N), 31.8 (s, *C*H$_3$CHCH=N), 22.6 (s, *C*HH'CHN), –0.6 (s, $Si(CH_3)_3$); $^{31}P\{^1H\}$, 17.1 (s).

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NHCH_2CH(CH_2Si(CH_3)_3)C(CH)_4CCHCH_2Si(CH_3)_3)]^+$ TfO^- (18). A Schlenk flask was charged with **15** (0.380 g,

(47) One aromatic carbon resonance is (partially) obscured.
(48) Spectroscopic properties were idential with those of (a) the racemate; (b) an authentic sample.

0.381 mmol; 94:6 *SSS,RRR/SRR,RSS*), CH_3OH (10 mL), and a stir bar. Then $NaBH_4$ (0.144 g, 3.81 mmol) was added with stirring. After 0.75 h, solvent was removed under oil pump vacuum. The residue was extracted with CH_2Cl_2 (25 mL). The extract was filtered through Celite and concentrated to ca. 2 mL. Then ether/hexane (30 mL, 50:50 v/v) was added. An orange powder was nucleated by persistent scratching with a spatula, collected by filtration, washed with hexane, and dried under oil pump vacuum to give **18** (0.337 g, 0.338 mmol, 88%) as mixture of Re/C/C/N configurational diastereomers. Anal. Calcd for $C_{41}H_{51}F_3N_2O_4PReSSi_2$: C, 49.33; H, 5.15. Found: C, 49.49; H, 5.19. IR (cm^{-1}, CH_2Cl_2) ν_{NO} 1698 vs. $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 22.1/20.6/17.2 (s/s/s).

$NHCH_2CH(CH_2Si(CH_3)_3)C(CH)_4CCHCH_2Si(CH_3)_3$ (19). A. A Schlenk flask was charged with **18** (0.054 g, 0.054 mmol), CH_2Cl_2 (3 mL), and a stir bar. Then solid $(CH_3CH_2)_4N^+$ CN^- (0.013 g, 0.081 mmol) was added with stirring. After 1 h, solvent was removed under oil pump vacuum. The residue was flash chromatographed on a 20-cm silica gel column with ether (ca. 200 mL). Solvent was removed from the eluant by rotary evaporation. The resulting oil was triturated with ether/hexane (20 mL, 50:50 v/v), giving a yellow suspension that was filtered. Solvent was removed from the filtrate, and the yellow oil was distilled under oil pump vacuum (250 °C, Kugelrohr, CO_2(s) condenser) to give (*SS,RR*)-**19** as a colorless oil (0.015 g, 0.048 mmol, 89%). Anal. Calcd for $C_{17}H_{31}NSi_2$: C, 66.81; H, 10.22. Found: C, 66.99; H, 10.16. The solid removed by filtration was washed with hexane and dried under oil pump vacuum to give $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CN)$ (**17**, 0.030 g, 0.053 mmol, 98%).[22,48b] **B.** Nonracemic **15** (0.107 g, 0.107 mmol; 94:6 *SSS/SRR*), CH_3OH (10 mL), and $NaBH_4$ (0.040 g, 1.1 mmol) were combined in a procedure analogous to that given for **18**. A similar workup gave nonracemic **18** as a yellow powder (0.105 g, 0.105 mmol, 98%). A portion of this sample (0.035 g, 0.035 mmol), CH_2Cl_2 (5 mL), and $(CH_3CH_2)_4N^+$ CN^- (0.008 g, 0.053 mmol) were combined in a procedure analogous to A. After 0.5 h, solvent was removed under oil pump vacuum. The residue was dissolved in THF (20 mL). The solution was filtered through a 10-cm silica gel plug. The yellow eluate was concentrated to ca. 2 mL, and ether/hexane (60 mL, 50:50 v/v) was added with stirring. The resulting yellow powder was collected by filtration, washed with hexane, and dried under oil pump vacuum to give (+)-(*S*)-**17** (0.018 g, 0.031 mmol, 89%; >98% ee, (+)-Eu(hfc)$_3$).[10,48] The filtrate was flash chromatographed as in A to give (+)-(*SS*)-**19** as a colorless oil (0.010 g, 0.032 mmol, 91%; 88% ee, (–)-BNPPA),[15c,24] $[\alpha]^{23}_{589}$ 30 ± 1° (*c* 1.640 mg/mL, CH_2Cl_2).[25,48a] Anal. Found: C, 66.71; H, 10.20.

NMR, (*SS,RR*)-**19**: ^1H (C_6D_6) 7.28–7.10 (m, C_6H_4), 4.11 (dd, J = 9.9, 4.1, CH_2CHN), 2.96 (pseudo dq, J = 13.6, 4.6, 2H of $2CH_2Si$, NCH_2CH), 2.78 (pseudo sxt, J = 4.5, 1H of $2CH_2Si$, NCH_2CH), 1.30–1.04 (m, 5H of $2CH_2Si$, $HNCH_2CH$), –0.47 (s, $Si(CH_3)_3$), –0.67 (s, $Si(CH_3)_3$); $^{13}C\{^1H\}$ ($CDCl_3$) C_6H_4 at 141.8 (s), 141.6 (s), 128.4 (s), 125.9 (s), 125.8 (s), 125.5 (s); 53.9 (s, CHN), 47.8 (s, $CHCH_2N$), 34.3 (s, CH_2N), 25.6 (s, $SiCH_2$), 24.3 (s, $SiCH_2$), –0.5 (s, $Si(CH_3)_3$), –0.7 (s, $Si(CH_3)_3$).

$NHCH_2CH_2C(CH)_4CCHCH(CH_3)_2$ (20). A. A Schlenk flask was charged with **12** (2.522 g, 2.913 mmol; 88:12 *SR,RS/SS,RR*), CH_3OH (150 mL), and a stir bar and cooled to –80 °C. Then $NaBH_4$ (1.10 g, 29.1 mmol) was added with stirring, and the cold bath was removed. After 5 h, solvent was removed by rotary evaporation. The oily residue was extracted with CH_2Cl_2 (150 mL). The extract was filtered through Celite, and $(CH_3CH_2)_4N^+$ CN^- (0.472 g, 2.69 mmol) was added with stirring. After 4 h, solvent was removed by rotary evaporation. The residue was extracted with THF (150 mL). The extract was filtered through a silica gel plug. Solvent was removed by rotary evaporation to give an orange oil, which was triturated with ether/hexane (80 mL, 50:50 v/v). The resulting yellow powder was collected by filtration, washed with hexane, and dried under oil pump vacuum to give **17** (1.513 g, 2.656 mmol, 91%).[22,48b] Solvent was removed from the filtrate, and the orange oil was distilled under oil pump vacuum (200 °C, Kugelrohr, CO_2(s) condenser) to give **20** (0.472 g, 2.69 mmol, 92%) as a colorless oil with a ^1H NMR spectrum identical to that previously reported.[23b] **B.** Nonracemic **12** (1.135 g, 1.312 mmol; 88:12 *RS/RR*), CH_3OH (50 mL), and $NaBH_4$ (0.512 g, 13.1 mmol) were combined in a procedure analogous to A. After 1 h, solvent was removed by rotary evaporation. The residue was extracted with CH_2Cl_2 (150 mL). The extract was filtered through Celite and concentrated to ca. 1 mL. Ether/hexane (50 mL, 60:40 v/v) was added, and the resulting orange solid was collected by filtration, washed with hexane, and dried in air. The solid was transferred to a Schlenk flask, and $(CH_3CH_2)_4N^+$ CN^- (0.268 g, 1.72 mmol) and CH_2Cl_2 (70 mL) were added. The solution was stirred for 0.5 h, and solvent was removed by rotary evaporation. The residue was triturated with ether/hexane (25 mL, 20:80 v/v). The resulting orange suspension was filtered through a fine frit. Solvent was removed from the filtrate by rotary evaporation, and the orange oil was distilled as in procedure A to give (–)-(*S*)-**20** (0.177 g, 1.010 mmol, 77%; 76% ee, (–)-BNPPA)[24] as a colorless oil, $[\alpha]^{23}_{589}$ –48 ± 3° (*c* 1.200 mg/mL, CH_2Cl_2).[25,48b] The yellow solid removed by filtration was extracted with THF. The extract was chromatographed on a silica gel column. Solvent was removed from a yellow band to give (–)-(*R*)-**17** as a yellow powder (0.673 g, 1.18 mmol, 90%; >98% ee, (+)-Eu(hfc)$_3$).[48]

$NHCH_2CH_2C(CH)_4CCHCH_2CH_3$ (21). Complex **13** (1.351, 1.587 mmol; 85:15 *SR,RS/SS,RR*), CH_3OH (100 mL), and $NaBH_4$ (0.600 g, 15.9 mmol) were combined in a procedure analogous to that given for **20**. After 0.5 h, solvent was removed by rotary evaporation. The residue was extracted with CH_2Cl_2 (30 mL). The extract was filtered through Celite and concentrated to ca. 5 mL. Ether/hexane (50 mL, 40:60 v/v) was added. An orange powder was nucleated by persistent scratching with a spatula, collected by filtration, washed with hexane, and transferred to a Schlenk flask. Then $(CH_3CH_2)_4N^+$ CN^- (0.438 g, 2.80 mmol) and CH_2Cl_2 (100 mL) were added. The solution was stirred for 0.5 h, and workup analogous to that given for **20** afforded **17** as a yellow powder (0.533 g, 0.937 mmol, 59%)[48b] and the known compound **21** as a colorless oil (0.183, 1.13 mmol, 71%).[23a] ^1H NMR ($CDCl_3$): 7.86–6.87 (m, C_6H_4), 3.79 (m, CH_2CHN), 3.04–2.49 (m, CH_2CH_2N), 1.81–1.65 (m, CH_2CH_3), 1.02 (t, J = 7.3, CH_3).

$NHCH_2CH_2C(CH)_4CCHCH_2C_6H_5$ (22). A. Complex **14** (2.426 g, 2.654 mmol; 88:12 *SR,RS/SS,RR*), $NaBH_4$ (1.00 g, 26.5 mmol), and $(CH_3CH_2)_4N^+$ CN^- (0.438 g, 2.80 mmol) were reacted in a sequence analogous to that given for **20**. Similar workups gave **17** as a yellow powder (1.36 g, 2.39 mmol, 90%)[48b] and **22** as a colorless oil (0.514 g, 2.30 mmol, 87%) with a ^1H NMR spectrum identical to that previously reported.[23] **B.** Nonracemic **14** (0.285 g, 0.311 mmol; 88:12 *SR/SS*), $NaBH_4$ (0.117 g, 3.11 mmol), and $(CH_3CH_2)_4N^+$ CN^- (0.275 g, 1.76 mmol) were reacted in a sequence analogous to that given for (–)-(*S*)-**20**. Solvent was removed by rotary evaporation. The residue was triturated with ether/hexane (25 mL, 50:50 v/v). The resulting orange suspension was filtered through a fine frit. Solvent was removed from the filtrate by rotary evaporation, and the orange oil was distilled under oil pump vacuum (200 °C, Kugelrohr, CO_2(s) condenser) to give the known compound (+)-(*R*)-**22** as a colorless oil (0.053 g, 0.24 mmol, 76%; 76% ee, (–)-BNPPA).[24,48a] Complex (+)-(*S*)-**17** was isolated as a yellow powder (0.154 g, 0.271 mmol, 87%; >98% ee, (+)-Eu(hfc)$_3$) as in the procedure for (–)-(*S*)-**20**.

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CNCH_3)]^+$ TfO^- (23). A Schlenk flask was charged with **17** (0.109 g, 0.191 mmol), benzene (10 mL), and a stir bar. Then CH_3OTf (0.025 mL, 0.22 mmol) was added dropwise with stirring. After 3 h, solvent was removed under oil pump vacuum. The residue was triturated with ether (15 mL). The resulting yellow powder was collected by filtration and dried under oil pump vacuum to give **23** (0.133 g, 0.178 mmol, 93%), mp 152–153 °C dec. Anal. Calcd for $C_{27}H_{26}F_3N_2O_4PReS$: C, 42.56; H, 3.16. Found: C, 42.28; H, 3.08. IR (cm^{-1}, KBr) ν_{CN} 2192 m, ν_{NO} 1709 vs.

NMR: ^1H (CD_2Cl_2) 7.56–7.32 (m, 15H of $3C_6H_5$), 5.58 (s, C_5H_5), 3.61 (s, CH_3); $^{13}C\{^1H\}$ ($CDCl_3$) PPh at 133.0 (d, J = 11.2, *o*), 132.7 (d, J = ca. 55,[47] *i*), 131.6 (d, J = 2.3, *p*), 129.3 (d, J = 11.0, *m*); 120.8 (q, J_{CF} = 320.5, CF_3), 92.1 (s, C_5H_5), 31.2 (s, CH_3); $^{31}P\{^1H\}$ (CD_2Cl_2) 14.8 (s).[49]

$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (10). A. A Schlenk flask was charged with **17** (0.374 g, 0.656 mmol), benzene (50 mL), and a stir bar. Then CH_3OTf (0.082 mL, 0.72 mmol) was added with stirring. After 3 h, solvent was removed under oil pump vacuum. The residue was dissolved in CH_3OH (50 mL), and $NaBH_4$ (0.525 g, 7.20 mmol) was added. The solution was refluxed for 24 h. Solvent was removed under oil pump vacuum, and the residue was extracted with benzene (25 mL). The extract was filtered through a silica gel plug on a coarse frit. Hexane was added, and the resulting bright-orange powder was collected by filtration, washed with hexane, and dried under oil pump vacuum to give **10** (0.322 g, 0.577

(49) A sample of **23** was similarly prepared with a labeled $Re^{13}CN$ linkage. Partial NMR data ($CDCl_3$): $^{13}C\{^1H\}$, 129.5 (d, J = 10.1, ReCN), 31.2 (s, CH_3); ^1H, 3.63 (d, J_{HC} = 3.9, CH_3); $^{31}P\{^1H\}$, 14.7 (d, J_{PC} = 10.1). IR (cm^{-1}, KBr) $\nu_{^{13}CN}$ 2152 m.

mmol, 88%).[21,48b] **B.** Complex (+)-(*S*)-**17** (0.055 g, 0.097 mmol; >98% ee, (+)-Eu(hfc)$_3$),[10] benzene (10 mL), CH_3OTf (0.013 mL, 0.116 mmol), and $NaBH_4$ (0.110 g, 2.91 mmol) were combined in a procedure analogous to that given for **10**. A similar workup gave (+)-(*S*)-**10** as a bright-orange powder (0.029 g, 0.052 mmol, 53%; >99.9% ee, HPLC).[21,28,48]

Crystallography. Pentane was added by vapor diffusion to a benzene solution of **15** (94:6 *SSS,RRR/SRR,RSS*). Orange prisms formed, which were collected by filtration and dried under a N_2 flow to give (*SSS,RRR*)-**15**·$(C_6H_6)_{1.5}$. Anal. Calcd for $C_{41}H_{49}F_3N_2O_4PReSSi_2 \cdot (C_6H_6)_{1.5}$: C, 53.94; H, 5.25. Found: C, 53.64; H, 5.22. Data were collected on a Syntex P$\bar{1}$ diffractometer as outlined in Table I. Cell constants were obtained from 30 reflections with $20.0° < 2\theta < 28.0°$. The space group was determined from least squares refinement (no systematic absences). Lorentz, polarization, and absorption (ψ scans) corrections were applied. The structure was solved by standard heavy-atom techniques with the SDP/VAX package.[50] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure calculations but were not refined. The C_6H_6 molecules fully occupied two independent sites, one of which was on a crystallographic inversion center. Scattering factors, and values for $\Delta f'$ and $\Delta f''$, were taken from the literature.[51]

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Supplementary Material Available: Procedures for NMR-monitoring and deuterium-labeling experiments and tables of anisotropic thermal parameters for (*SSS,RRR*)-**15**·$(C_6H_6)_{1.5}$ (2 pages); tables of calculated and observed structure factors for (*SSS,RRR*)-**15**·$(C_6H_6)_{1.5}$ (22 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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