A New Family of Chelating Diphosphines with Transition-Metal and Carbon Stereocenters in the Backbone: A Second-Generation Rhenium-Containing System

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The less stable Re=C isomer of the enantiomerically pure benzylidene complex (*S*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CHPh)]$^+BF_4^-$ ((*S*)-(*sc*)-**6**) and PPh_2H react to give the phosphonium salt ($S_{Re}S_C$)-[(η^5-C_5H_5)Re(NO)(PPh_3)(CH(Ph)PPh_2H)]$^+BF_4^-$ (($S_{Re}S_C$)-**7**; 91%), as confirmed by a crystal structure of the racemate. Reaction with *t*-BuOK gives the phosphine ($S_{Re}S_C$)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH(Ph)PPh_2) (($S_{Re}S_C$)-**8**; 73%). An analogous sequence with the more stable Re=C isomer ((*S*)-(*ac*)-**6**) but at −60 °C gives ($S_{Re}R_C$)-**8** (58%). NMR experiments show that the intermediate ($S_{Re}R_C$)-**7** epimerizes to ($S_{Re}S_C$)-**7** above −20 °C, and the mechanism has been analyzed. Reactions of ($S_{Re}S_C$)- and ($S_{Re}R_C$)-**8** with *t*-BuLi and then PPh_2Cl give the title diphosphines ($S_{Re}S_C$)- and ($S_{Re}R_C$)-(η^5-$C_5H_4PPh_2$)Re(NO)(PPh_3)(CH(Ph)PPh_2) (84−89%). Additions of $[Rh(NBD)_2]^+PF_6^-$ give the heterobimetallic chelate complexes ($S_{Re}S_C$)- and ($S_{Re}R_C$)-[(η^5-$C_5H_4PPh_2$)Re(NO)(PPh_3)(μ-CH(Ph)PPh_2)Rh(NBD)]$^+PF_6^-$ (87−91%). In efforts to access similar compounds with $ReCPh_2PPh_2$ linkages, the chlorobenzene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(ClPh)]$^+BF_4^-$ and $NNCPh_2$ have been reacted. Instead of the target Re=CPh_2 adduct, the diphenyldiazomethane complex [(η^5-C_5H_5)Re(NO)(PPh_3)($NNCPh_2$)]$^+BF_4^-$ (73%) has been isolated and crystallographically characterized.

Introduction

Over the last 10 years, there has been rapidly increasing interest in the synthesis of chiral, ferrocene-based chelating ligands.[1] Many useful applications of their metal complexes in enantioselective organic synthesis have been developed. For some transformations, these constitute the catalysts of choice. Efforts have more recently been extended to nonferrocene metal fragments.[2−8] Besides extrapolations to other metallocenes[1a] and our work described below,[6−8] examples include (η^6-arene)$Cr(CO)_3$,[2] (η^5-C_5R_5)$M(CO)_3$ (M = Mn, Re),[3,4] and (η^5-C_5R_5)Co(η^4-C_4R_4)[5] based chiral chelating ligands. Apropos to the diverse architectural possibilities inherent in such templates, all three types of stereogenic elements (centers, planes, axes) have been employed, often in combination.

A wide variety of chelating diphosphines that are chiral by virtue of carbon or phosphorus stereocenters are known.[9] We described the first family of chelating diphosphines that are chiral by virtue of a transition-metal stereocenter, as depicted in formulas **1** and **2** (Scheme 1).[6] These feature a chiral rhenium fragment in the backbone and are easily obtained in enantiomerically pure form. The rhodium adducts **3** and **4** were found to be excellent catalyst precursors for asymmetric hydrogenations of protected dehydroamino acids.[6] The activities, lifetimes, and enantioselectivities with **3** compared well with the best systems in the literature. However, the enantioselectivities with **4** were somewhat lower. Here, the rhenium stereocenter is one methylene group further removed from one coordinating PPh_2 group and the active rhodium center.

We wondered whether enantioselectivities might improve if the methylene group in diphosphine **2** and rhodium/rhenium chelate **4** were replaced by a carbon stereocenter. In this paper, we report enantioselective and diastereoselective syntheses of two such new diphosphines and chelates, which feature CHPh moieties of

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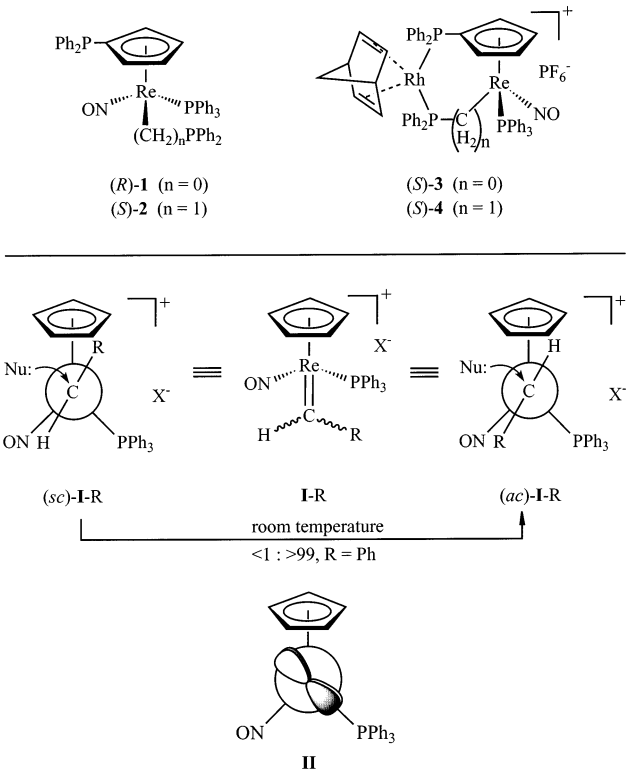
Scheme 1. Previously Characterized Complexes and Equilibria



opposite configurations. Reactions directed at related targets are also described. Applications to enantioselective hydrosilylations of ketones and hydrogenations of protected dehydroamino acids are detailed in the following paper.[10] To provide context for our synthetic planning, the following background is given.

A key step in the synthesis of **2** is the reaction of the secondary phosphine PPh_2H and the methylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+BF_4^-$ to give the phosphonium salt $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2H)]^+BF_4^-$.[6a] Deprotonation with *t*-BuOK yields $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2)$, a monophosphine donor ligand that is itself effective for metal-catalyzed reactions.[11] Many analogous alkylidene complexes, $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+X^-$ (**I**-R), are easily prepared.[12−14] These can exist as two Re=CHR geometric isomers, as illustrated by (*sc*)-**I**-R and (*ac*)-**I**-R in Scheme 1. Both rhenium−carbon conformations maximize overlap of the =CHR π-acceptor orbital and the rhenium fragment HOMO shown in **II**. Importantly, either isomer can be accessed with high selectivity. However, the latter is more stable, and equilibration occurs on the time scale of hours at room temperature. Each undergoes highly diastereoselective nucleophilic additions, with predominant attack opposite to the bulky PPh_3 ligand.[12,13,15]

Such alkylidene complexes are generally weaker electrophiles and Lewis acids than the methylidene complex. Accordingly, with nucleophiles that are weaker Lewis bases, reversible reactions can be observed.[15] The addition of the triarylphosphine P(*p*-tol)$_3$ to the ethylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHCH_3)]^+PF_6^-$ is a case in point. As assayed by low-temperature NMR, each Re=$CHCH_3$ isomer gives a different diastereomer of an addition product with a $ReCH(CH_3)P$ linkage. However, one is sterically more congested and isomerizes to the other at ambient temperature.[15] All of the preceding phenomena are manifested in the sequences described below.

Results

1. First Diastereomer Series. The benzyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2Ph)$ (**5**) is easily accessed in racemic and enantiomerically pure forms.[12,16] The crystal structure shows the rhenium−carbon conformation depicted in idealized structure **III** (Scheme 2).[16] A variety of NMR and computational data indicate this to be the most stable conformation in solution.[17] The phenyl group occupies the least congested interstice, between the small nitrosyl and medium-sized cyclopentadienyl ligands. The interstice between the bulky PPh_3 ligand and the nitrosyl ligand, which features a L−Re−L′ angle of ca. 90°, is the most congested.

As shown in Scheme 2, racemic **5** or (*S*)-**5**[18] and $Ph_3C^+BF_4^-$ were combined in CH_2Cl_2 at −60 °C to generate the corresponding benzylidene complexes (*sc*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHPh)]^+BF_4^-$ ((*sc*)-**6** and (*S*)-(*sc*)-**6**). Then PPh_2H was added. Workups at room temperature gave the diastereomerically pure phosphonium salts $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(Ph)PPh_2H)]^+BF_4^-$ ($(S_{Re}S_C,R_{Re}R_C)$- and ($S_{Re}S_C$)-**7**) as orange needles in 83−91% yields. These were indefinitely stable in air, and configurations were assigned in accord with the mode of addition in Scheme 1.[12,13,15] The sequence with (*S*)-**5** was repeated in an NMR tube. Only the *sc* Re=CHPh isomer of (*S*)-**6** was detected (^{31}P NMR), and **7** formed as a 96.6:3.4 mixture of $S_{Re}S_C/S_{Re}R_C$ diastereomers. Such stereoselectivity is typical (94:6 for PMe_3),[12] and the minor diastereomer is characterized below.

The crystal structure of ($S_{Re}S_C,R_{Re}R_C$)-**7** was determined as summarized in Table 1 and the Experimental Section. The molecular structure, shown in Figure 1, confirmed the diastereomer assignment. Note that the rhenium−carbon conformation accommodates the larg-

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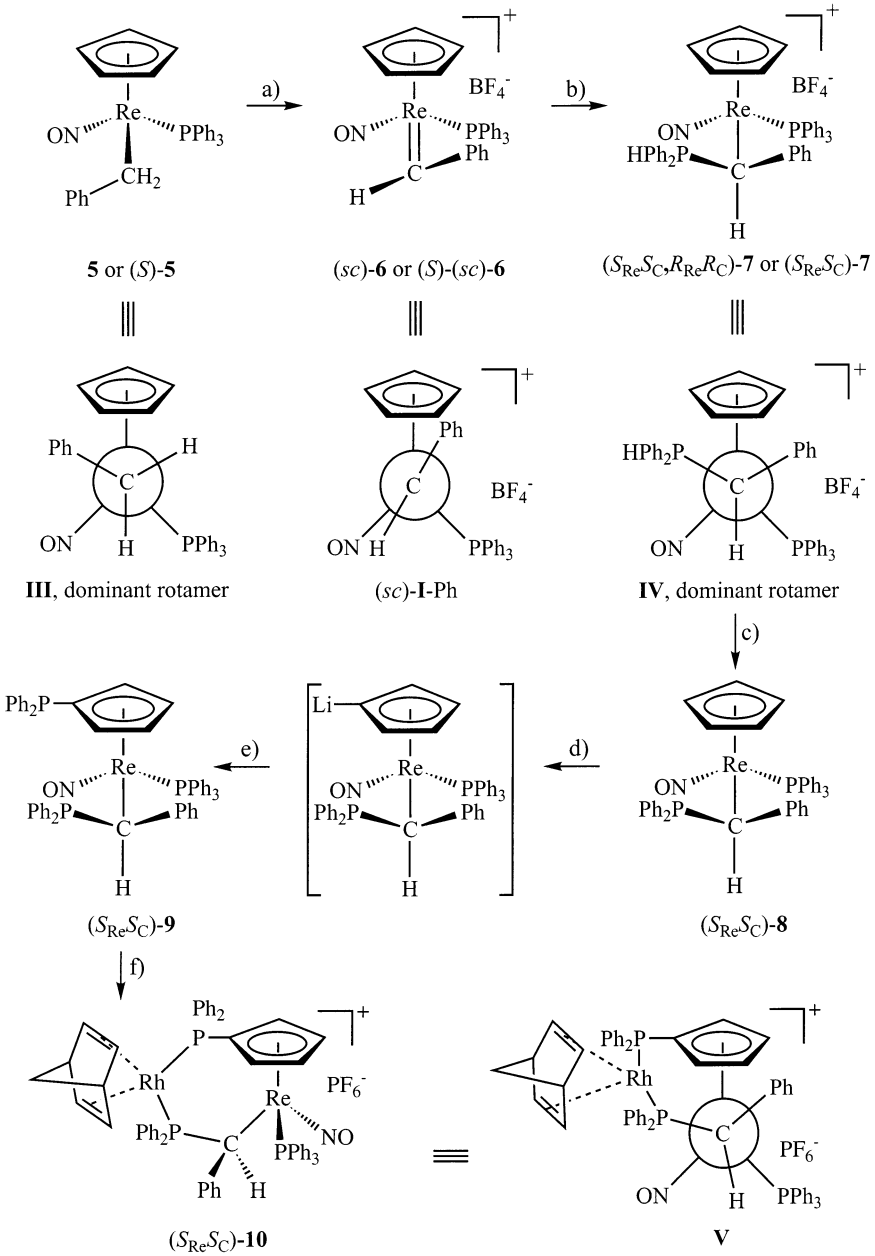
(18) (a) Nonracemic compounds in the two series of diastereomers (Schemes 2 and 3) were prepared from opposite enantiomers of benzyl complex **5**. For ease of comparison (including previous papers involving similar compounds),[6−8] the configurations for the diastereomers in Scheme 3 have been inverted in the text, tables, and graphics. The Experimental Section describes the syntheses as they were actually conducted. In other words, the $R_{Re}S_C$ complexes in the Experimental Section are represented as $S_{Re}R_C$ enantiomers elsewhere in the paper. (b) The basis for assigning *R*/*S* descriptors has been summarized earlier.[6a]

Scheme 2. Series of Reactions Involving the Thermodynamically More Stable Diastereomer of 7[a]



[a] Legend: (a) $Ph_3C^+BF_4^-$, CH_2Cl_2, −60 °C; (b) PPh_2H, −60 to 25 °C; (c) *t*-BuOK, THF, 25 °C; (d) *t*-BuLi, THF, −60 to −10 °C; (e) PPh_2Cl, THF, −60 to 25 °C; (f) $[Rh(NBD)_2]^+PF_6^-$, THF, 25 °C.

est group on carbon (PPh_2H) in the largest interstice on rhenium, and the smallest group (H) in the smallest interstice, per the idealized representation **IV** in Scheme 2. The crystal structure also showed a hydrogen bond between a fluorine of the BF_4^- anion and the PH moiety, as indicated by a F11−H54 distance of 2.43 Å (determined from a calculated hydrogen position). Similar hydrogen bonds have been found in related cationic secondary phosphine (RePHRR′) complexes.[19]

Deprotonation of ($S_{Re}S_C$)-**7** with *t*-BuOK gave the phosphine ($S_{Re}S_C$)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH(Ph)PPh_2) (($S_{Re}S_C$)-**8**) in 73% yield. Solid ($S_{Re}S_C$)-**8** could survive a few hours in air, but solutions had to be kept under inert atmospheres. All new compounds were characterized by IR, NMR (^{1}H, ^{13}C, ^{31}P), optical rotations, and microanalyses, as described in the Experimental Section. The ^{31}P NMR chemical shifts and coupling constants were particularly diagnostic of structure and are collected in Table 2 and analyzed below.

2. Second Diastereomer Series.[18] As shown in Scheme 3, a CH_2Cl_2 solution of the benzylidene complex (*S*)-(*sc*)-**6** was generated as described above and warmed to room temperature. This yields the opposite Re=CHPh geometric isomer, (*S*)-(*ac*)-**6**, in an equilibrium concentration of ≥99%.[12] The solution was cooled to −60 °C, and $HPPh_2$ was added to generate ($S_{Re}R_C$)-**7**. Subsequent addition of *t*-BuOK (−60 °C) gave the phosphine ($S_{Re}R_C$)-**8**, with a carbon configuration opposite to that in Scheme 2. Workup afforded ($S_{Re}R_C$)-**8** as an air-sensitive orange powder in 58% overall yield. The crude reaction mixtures contained at most 1−4% of the opposite diastereomer, as assayed by ^{1}H and ^{31}P NMR.

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Table 1. Summary of Crystallographic Data.

	($S_{Re}S_C$,$R_{Re}R_C$)-**7**	**12**·0.5CH_2Cl_2
mol formula	$C_{42}H_{37}BF_4NOP_2Re$	$C_{36.5}H_{31}BClF_4N_3OPRe$
mol wt	906.68	867.07
temp of collection, °C	−100(2)	−100(2)
diffractometer	KappaCCD	KappaCCD
radiation	Mo Kα	Mo Kα
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
unit cell dimens		
a (Å)	12.53970(10)	13.620(3)
b (Å)	16.4271(2)	12.110(2)
c (Å)	18.6437(3)	21.411(4)
β (deg)	106.9550(10)	104.79(3)
V (Å^3)	3673.50(8)	3414.6(12)
Z	4	4
D_c (g cm^{-3})	1.639	1.687
μ (mm^{-1})	3.451	3.741
cryst dimens, mm	0.30 × 0.20 × 0.20	0.35 × 0.30 × 0.30
θ range (deg)	1.70 ≤ θ ≤ 27.48	1.95 ≤ θ ≤ 27.48
range/indices (h,k,l)	−16 to +16; −21 to +21; −24 to +24	−17 to +17; −15 to +14; −27 to +27
no. of rflns	15 767	13 210
no. of unique data	8353	7810
no. of obsd data	6487 ($I > 2\sigma(I)$)	6635 ($I > 2\sigma(I)$)
no. of refined params	617	451
refinement	least squares on F^2	least squares on F^2
R_{int}	0.0276	0.0275
R indices ($I > 2\sigma(I)$)		
R1	0.0277	0.0291
wR2	0.0583	0.0558
R indices (all data)		
R1	0.0473	0.0372
wR2	0.0645	0.0622
goodness of fit	0.967	1.015
largest diff peak, hole (e Å^{-3})	1.632/−0.813	0.975/−1.210

To best illustrate the stereochemical relationships, the structures of ($S_{Re}R_C$)-**7** and ($S_{Re}R_C$)-**8** in Scheme 3 are rendered analogously to those of diastereomers ($S_{Re}S_C$)-**7** and ($S_{Re}S_C$)-**8** in Scheme 2. However, this gives rhenium−carbon conformations in which a phenyl group occupies the most crowded rhenium interstice, as easily seen in **VIa**. Alternative conformations such as **VIb** (Figure 2), which feature hydrogen atoms in this position, are likely to be lower in energy. This equilibrium is further analyzed in the Discussion.

Attempts were made to isolate ($S_{Re}R_C$)-**7**. However, workups at room temperature always gave predominantly the diastereomer obtained in Scheme 2, ($S_{Re}S_C$)-**7**. Racemic complexes gave identical results. To check the stereochemical integrity of the addition, an isolated sample of the benzylidene complex (*S*)-(*ac*)-**6** was treated with PPh_2H in CD_2Cl_2 at −20 °C. Analysis by ^{1}H, ^{13}C, and ^{31}P NMR (−20 °C) showed only the expected ($S_{Re}R_C$)-**7** (>99%). When the sample was warmed to room temperature, equilibration commenced. Over 48 h at 25 °C, a >99:1 mixture of ($S_{Re}S_C$)-**7** and ($S_{Re}R_C$)-**7** formed. Solutions of ($S_{Re}R_C$)-**7** were similarly generated in $CDCl_3$, and isomerizations were monitored by NMR at eight temperatures between 15 and 55 °C.[20] First-order rate laws were observed.

Possible pathways for the equilibration of ($S_{Re}R_C$)-**7**, all of which involve the dissociation of PPh_2H, are analyzed in the Discussion. From a synthetic perspective, the key point is that the low-temperature deprotonation to ($S_{Re}R_C$)-**8** renders the phosphorus moiety a much poorer leaving group, and much more basic.

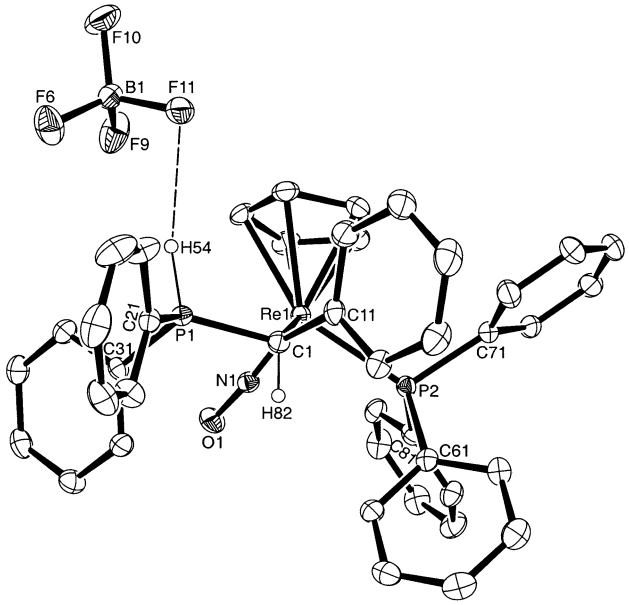


Figure 1. Molecular structure of ($S_{Re}S_C$,$R_{Re}R_C$)-**7**. Key interatomic distances (Å), bond angles (deg), and torsion angles (deg): Re1−C1 = 2.241(3), Re1−N1 = 1.743(3), Re1−P2 = 2.370(7), C1−P1 = 1.783(3), N1−O1 = 1.217(3), P1−H54 = 1.297(6), Re1−Cp(centroid) = 1.954, H54−F11 = 2.430, H54−F6 = 2.668, H54−F9 = 3.025, H54−F10 = 4.180; Re1−N1−O1 = 170.0(2), N1−Re1−P2 = 93.47(8), N1−Re1−C1 = 97.5(1), C1−Re1−P2 = 91.0(1), Re1−C1−P1 = 108.3(1), Re1−C1−C11 = 118.0(2), Re1−C1−H82 = 109.3, P1−C1−H82 = 103.1, C11−C1−H82 = 105.6, P1−C1−C11 = 111.4(2), C1−P1−C21 = 115.7(1), C1−P1−C31 = 111.2(1), C21−P1−C31 = 109.0(1), C1−P1−H54 = 109.9, C21−P1−H54 = 105.4, C31−P1−H54 = 104.9; N1−Re1−C1−P1 = −71.8(2), N1−Re1−C1−C11 = 160.5(2), P2−Re1−C1−P1 = −165.5(1), P2−Re1−C1−C11 = 66.9(2), P2−Re1−C1−H82 = −53.8, N1−Re1−C1−H82 = 39.9, H54−P1−C1−H82 = −168.5, H54−P1−C1−Re1 = −52.7, P1−C1−Re1−N1 = −71.8(2), P1−C1−Re1−P2 = −165.5(1), Cp(centroid)−Re1−C1−H82 = 179.7.

Equilibration of the diastereomers of **8** has never been observed under any conditions, even after prolonged periods at 60 °C in THF. It is also worth emphasizing that when the more stable diastereomers ($S_{Re}S_C$,$R_{Re}R_C$)- and ($S_{Re}S_C$)-**7** are sought (Scheme 2), it is not critical which Re=CHPh isomer of **6** is employed, as long as reaction mixtures are kept at least 2 days at room temperature.

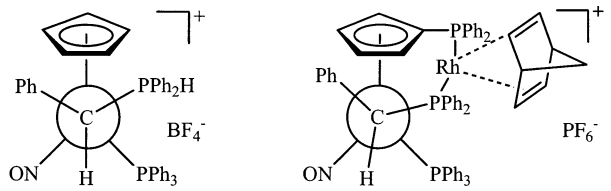
3. Diphosphine and Chelate Complex Synthesis. The conversion of ($S_{Re}S_C$)- and ($S_{Re}R_C$)-**8** to analogous (diphenylphosphido)cyclopentadienyl complexes was attempted, using methodology similar to that employed for **1** and **2**.[6] As shown in Schemes 2 and 3, reactions with *t*-BuLi (THF, −60 to −10 °C) gave deep red solutions typical of lithiocyclopentadienyl complexes that were characterized by ^{31}P NMR previously.[6a] Additions of PPh_2Cl and workups gave the target di-

(20) Isomerizations were followed to at least 3 half-lives (2 days (15 °C) to 30 min (55 °C); each run with 9−15 data points). The k_{obsd} values were obtained by exponential curve fitting to the integrals of the C_5H_5 and ReCH ^{1}H NMR signals of ($S_{Re}R_C$)-**7** vs time (average of four rate constants from two runs). Data (k_{obsd} (10^5 s^{-1})/$t_{1/2}$ (min)/T (°C)): 142 ± 2/8/55; 79 ± 2/15/50; 54 ± 2/22/45; 35 ± 1/33/40; 18 ± 1/65/35; 12 ± 1/100/30; 3.0 ± 0.1/390/20; 2.2 ± 0.1/520/15. A plot of ln (k/T) vs 1/T gave the following values: $\Delta H^{\ddagger}$ = 19.4 kcal mol^{-1}, 81.0 kJ mol^{-1}; $\Delta S^{\ddagger}$ = −12.8 eu, −53.5 J mol^{-1} K^{-1}; $\Delta G^{\ddagger}$(298 K) = 23.2 kcal mol^{-1}, 96.9 kJ mol^{-1}.

Table 2. Summary of $^{31}P\{^1H\}$ NMR Data[a]

complex	$RePPh_3$	$Re(CHX)_nPPh_2Y$	$C_5H_4PPh_2Y'$
($S_{Re}S_C$)-**7**[b,c]	19.2 (d) $^3J(P,P) = 17$	34.4 (d) $^3J(P,P) = 17$	
($S_{Re}S_C$)-**8**[c,d]	18.9 (br s) $w_{1/2} = 6$	21.8 (d) $^3J(P,P) = 3$	
($S_{Re}S_C$)-**9**[c,d]	18.6 (d) $^3J(P,P) = 6$	22.0 (br s) $w_{1/2} = 6$	−18.6 (d) $^3J(P,P) = 6$
($S_{Re}S_C$)-**10**[b,c,e]	14.7 (dd) $^3J(P,P) = 9$ $^3J(P,P) = 6$	63.0 (ddd) $^1J(P,Rh) = 156$ $^2J(P,P) = 24$ $^3J(P,P) = 9$	21.7 (ddd) $^1J(P,Rh) = 165$ $^2J(P,P) = 24$ $^3J(P,P) = 6$
($S_{Re}R_C$)-**7**[b,c,f]	13.8 (br s) $w_{1/2} = 8$	29.6 (br s) $w_{1/2} = 8$	
($S_{Re}R_C$)-**8**[c,d]	14.8 (d) $^3J(P,P) = 5$	23.4 (d) $^3J(P,P) = 5$	
($S_{Re}R_C$)-**9**[c,d]	16.4 (d) $^3J(P,P) = 6$	23.1 (d) $^3J(P,P) = 6$	−18.2 (br s) $w_{1/2} = 6$
($S_{Re}R_C$)-**10**[b,c,e]	15.0 (dd) $^3J(P,P) = 11$ $^3J(P,P) = 7$	57.1 (ddd) $^1J(P,Rh) = 154$ $^2J(P,P) = 30$ $^3J(P,P) = 11$	25.2 (ddd) $^1J(P,Rh) = 165$ $^2J(P,P) = 30$ $^3J(P,P) = 7$
(*S*)-**2**[c,d]	26.3 (d) $^3J(P,P) = 8$	6.9 (dd) $^3J(P,P) = 3$ $^3J(P,P) = 8$	−17.7 (d) $^3J(P,P) = 3$
(*S*)-**4**[b,c,e]	20.2 (dd) $^3J(P,P) = 18$ $^3J(P,P) = 4$	50.5 (ddd) $^1J(P,Rh) = 148$ $^2J(P,P) = 34$ $^3J(P,P) = 18$	23.9 (ddd) $^1J(P,Rh) = 166$ $^2J(P,P) = 34$ $^3J(P,P) = 4$

[a] At room temperature unless noted. δ values are given in ppm and J and $w_{1/2}$ values in Hz. Data in the first and last entries are taken from racemic samples. Nonracemic **4** shows slight differences.[6a] [b] In $CDCl_3$. [c] 162 MHz. [d] In C_6D_6. [e] PF_6^- at −143.9 (sep, $J(P,F) = 712$). [f] At −20 °C.



VIb **VIIb**

Figure 2. Alternative conformations for some of the compounds in Scheme 3.

phosphines (η^5-$C_5H_4PPh_2$)Re(NO)(PPh_3)(CH(Ph)PPh_2) (($S_{Re}S_C$)- and ($S_{Re}R_C$)-**9**) as orange solids in 89−84% yields. These were much more air sensitive than the monophosphines ($S_{Re}S_C$)- and ($S_{Re}R_C$)-**8**.

The formation of chelate complexes was studied next. We had been somewhat concerned that the increased bulk of ($S_{Re}S_C$)- and ($S_{Re}R_C$)-**9** might prove problematic. However, as shown in Schemes 2 and 3, reactions with $[Rh(NBD)_2]^+PF_6^-$ gave the desired compounds [(η^5-$C_5H_4PPh_2$)Re(NO)(PPh_3)μ-CH(Ph)PPh_2)Rh(NBD)]$^+PF_6^-$ (($S_{Re}S_C$)- and ($S_{Re}R_C$)-**10**) as air-stable orange-brown powders in 75−87% yields. This rhodium source proved superior to the $[Rh(NBD)Cl]_2/AgPF_6$ system used earlier, particularly with regard to workup and purification.[6] None of the nonracemic compounds in this study are crystalline, consistent with many past investigations where racemic rhenium complexes proved easier to crystallize.

The structures of **9** and **10** followed readily from their physical properties. Mass spectra of the latter showed intense molecular ions (100%), and ^{31}P NMR spectra were particularly informative (Table 2). For example, both diastereomers of **9** gave smaller phosphorus−phosphorus couplings that were not always resolved (≤6 Hz). However, the chelates **10** showed larger phosphorus−phosphorus couplings that were in all cases resolved, as well as large rhodium−phosphorus couplings. The ^{31}P chemical shifts and coupling constants of **10** were similar to those of the $ReCH_2P$ analogue **4** (Scheme 1). However, the ReCHPh*P* signals of **8** and **9** showed greater deviations from $ReCH_2P$ analogues ($\Delta\delta$ 14−15). Other NMR properties are discussed below. The signs of the optical rotations of **7**−**10** were controlled by the configuration at rhenium (i.e., identical for $S_{Re}S_C$ and $S_{Re}R_C$ diastereomers), but chelates **10** were reversed from the others. An analogous reversal was found with **2** and **4**.[6a]

4. Other Experiments. The chelate complex **4** has only a rhenium stereocenter. With regard to enantioselective catalysis, we anticipated that one of the new chelates, ($S_{Re}S_C$)- or ($S_{Re}R_C$)-**10**, might function as a "matched" diastereomer and the other as a "mismatched" diastereomer. In other words, the carbon stereocenter might be expected to reinforce the product enantiomer favored by rhenium in one diastereomer and exert an opposite influence in the other. In this context, it would also be informative to study the analogous chelate with *two* phenyl substituents, which would contain only a rhenium stereocenter.

The logical starting material would be the diphenylmethylidene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(=CPh_2)]$^+$-BF_4^- (**11**). Although a variety of diphenylmethylidene complexes are known,[21] a viable synthetic route to this species has yet to be found. In view of the many successful syntheses of alkylidene complexes involving diazoalkanes,[21,22] a similar approach was briefly investigated. Accordingly, the substitution-labile chlorobenzene complex shown in Scheme 4 was generated[23] and treated with diphenyldiazomethane, $NNCPh_2$.[24] However, workup gave a hemisolvate of the diphenyldiazomethane complex [(η^5-C_5H_5)Re(NO)(PPh_3)($NNCPh_2$)]$^+$-BF_4^- (**12**) as deep brown prisms in 68% yield. Complex **12** exhibited a strong UV absorption at 331 nm but only a tail into the visible region.

Diphenyldiazomethane complexes are well-known.[22,25,26] However, to our knowledge there are no

(21) Representative =CPh_2 complexes of 16-valence-electron (η^5-C_5H_5)M(L)(L′) fragments: (a) Herrmann, W. A.; Hubbard, J. L.; Bernal, I.; Korp, J. D.; Haymore, B. L.; Hillhouse, G. L. *Inorg. Chem.* **1984**, *23*, 2978. (b) Braun, T.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1995**, *117*, 7291. (c) Baratta, W.; Herrmann, W. A.; Kratzer, R. M.; Pierluigi, R. *Organometallics* **2000**, *19*, 3664. (d) Bleuel, E.; Gevert, O.; Laubender, M.; Werner, H. *Organometallics* **2000**, *19*, 3109.

(22) Relevant reviews: (a) Putala, M.; Lemenovskii, D. A. *Russ. Chem. Rev. (Engl. Transl.)* **1994**, *63*, 197. (b) Mizobe, Y.; Ishii, Y.; Hidai, M. *Coord. Chem. Rev.* **1995**, *139*, 281. (c) Sutton, D. *Chem. Rev.* **1993**, *93*, 995.

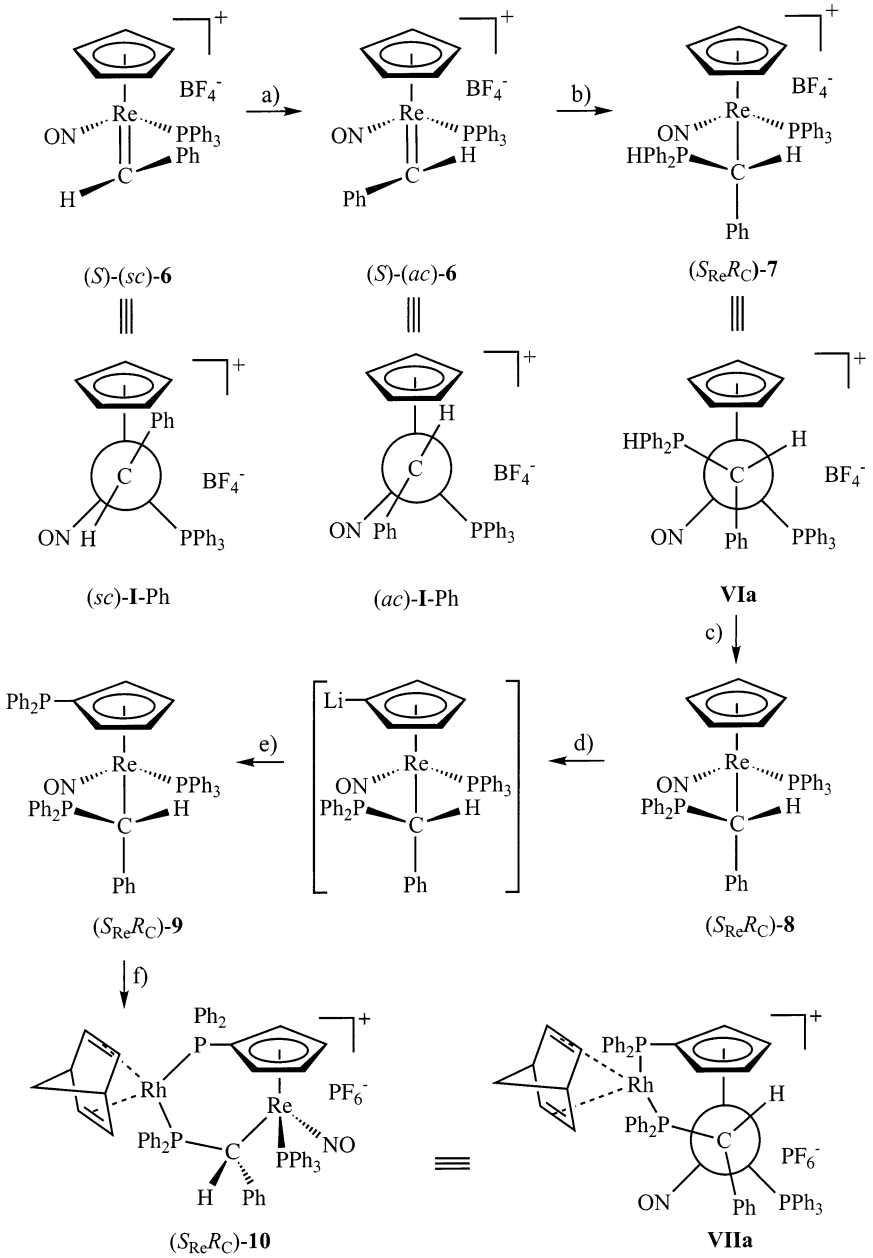
(23) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.

(24) Smith, L. I.; Howard, K. L. *Organic Syntheses*; Wiley: New York, 1955; Collect Vol. III, p 351.

(25) Some structurally characterized $NNCPh_2$ adducts of 16-valence-electron metal fragments: (a) Kool, L. B.; Rausch, M. D.; Alt, H. G.; Herberhold, M.; Hill, A. F.; Thewalt, U.; Wolf, B. *J. Chem. Soc., Chem. Commun.* **1986**, 408. (b) Lemenovskii, D. A.; Putala, M.; Nikonov, G. I.; Kazennova, N. B.; Yufit, D. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1993**, *454*, 123. (c) Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Butler, W. M.; Hay, M. S. *Organometallics* **1986**, *5*, 2283.

(26) Other relevant $NNCPh_2$ complexes: (a) Werner, H.; Schneider, M. E.; Bosch, M.; Wolf, J.; Teuben, J. H.; Meetsma, A.; Troyanov, S. I. *Chem. Eur. J.* **2000**, *6*, 3052. (b) Gerlach, C. P.; Arnold, J. *Organometallics* **1997**, *16*, 5148. (c) Chisholm, M. H.; Heppert, J. A.; Huffman, J. C.; Ontiveros, C. D. *Organometallics* **1989**, *8*, 976. (d) Vigalok, A.; Milstein, D. *Organometallics* **2000**, *19*, 2061.

Scheme 3. Series of Reactions Involving the Thermodynamically Less Stable Diastereomer of 7[a]



[a] Legend: (a) CH_2Cl_2, −60 to 25 °C, 48 h; (b) PPh_2H, −60 °C; (c) *t*-BuOK, CH_2Cl_2, −60 °C; (d) *t*-BuLi, THF, −60 to −10 °C; (e) PPh_2Cl, THF, −60 to 25 °C; (f) $[Rh(NBD)_2]^+PF_6^-$, THF, 25 °C.

adducts of 16-valence-electron fragments of the type (η^5-C_5H_5)M(L)(L′).[27] Although the formulation of **12** was supported by its mass spectrum, there were no strong, distinguishing IR or NMR absorptions. Accordingly, the crystal structure was solved, as summarized in Table 1 and the Experimental Section. The structure of the cation of **12** is presented in Figure 3 and analyzed below. Extensive attempts to effect the conversion of **12** to the target complex **11** were unsuccessful. Some of these gave other types of products, several of which have been characterized and will be described elsewhere.[28]

Discussion

1. Syntheses and Electronic Properties. The preceding syntheses double the number of chiral, rhenium-containing diphosphines and rhodium chelate complexes belonging to the family represented in Scheme 1. Despite the large number of formulas in Schemes 2 and 3, note that benzyl complexes **5** can be converted to **8** in single-flask operations, as detailed for ($S_{Re}R_C$)-**8** (58%). The overall yields of diphosphines **9** from commercially available $Re_2(CO)_{10}$ ($S_{Re}S_C$, 20%; $S_{Re}R_C$, 18%) are slightly lower than those of (*R*)-**1** and (*S*)-**2** (30% and 32%),[6a] mainly due to the extra step needed to introduce the ReCHPh phenyl group. These yields are comparable to those for the conversion of ferrocene to many chiral, nonracemic diphosphines.[6a] However, it should be emphasized that reaction monitoring by ^{31}P NMR is desirable, particularly for larger scale syntheses of ($S_{Re}R_C$)-**8**. Although the rhenium-containing diphos-

(27) Such $NNCR_2$ complexes are known for R ≠ Ph. For a structurally characterized example see: Herrmann, W. A.; Kriechbaum, G.; Ziegler, M. L.; Wülknitz, P. *Chem. Ber.* **1981**, *114*, 276.

(28) Kromm, K. Ph.D. Thesis, Universität Erlangen-Nürnberg, in preparation.

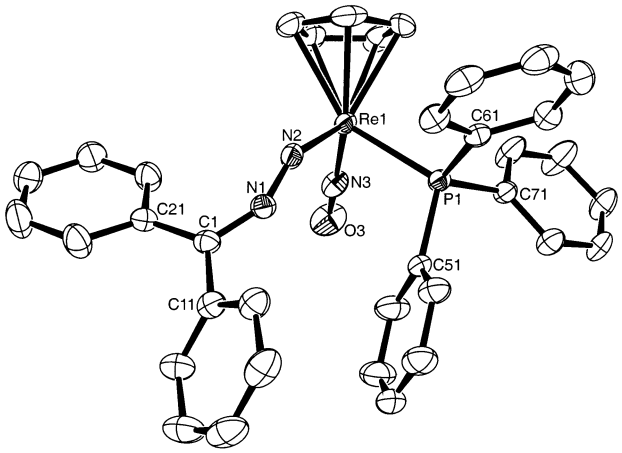
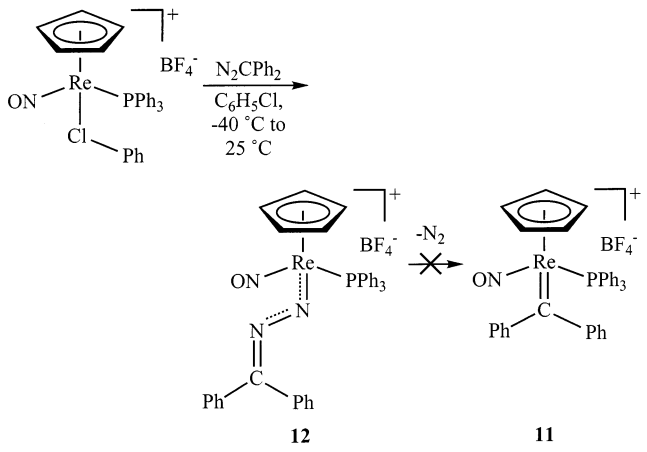


Figure 3. Molecular structure of the cation of **12**. Key interatomic distances (Å), bond angles (deg), and torsion angles (deg): Re1−N2 = 1.914(3), Re1−N3 = 1.761(3), Re1−P1 = 2.402(9), N3−O3 = 1.187(4), N1−N2 = 1.206(4), C1−N1 = 1.292(4), C1−C11 = 1.485(4), C1−C21 = 1.482(4), Re1−Cp(centroid) = 1.979; O3−N3−Re1 = 175.3(3), N3−Re1−P1 = 91.1(1), N3−Re1−N2 = 101.8(1), P1−Re1−N2 = 88.0(1), N1−N2−Re1 = 144.8(2), C1−N1−N2 = 150.8(3), N1−C1−C11 = 116.9(3), N1−C1−C21 = 118.9(3), C11−C1−C21 = 124.3(3); N1−N2−Re1−N3 = 16.8(4), C1−N1−N2−Re1 = −106.1(6), N1−N2−Re1−P1 = −73.9(4), N2−N1−C1−C11 = −167.4(5), N2−N1−C1−C21 = 11.7(7).

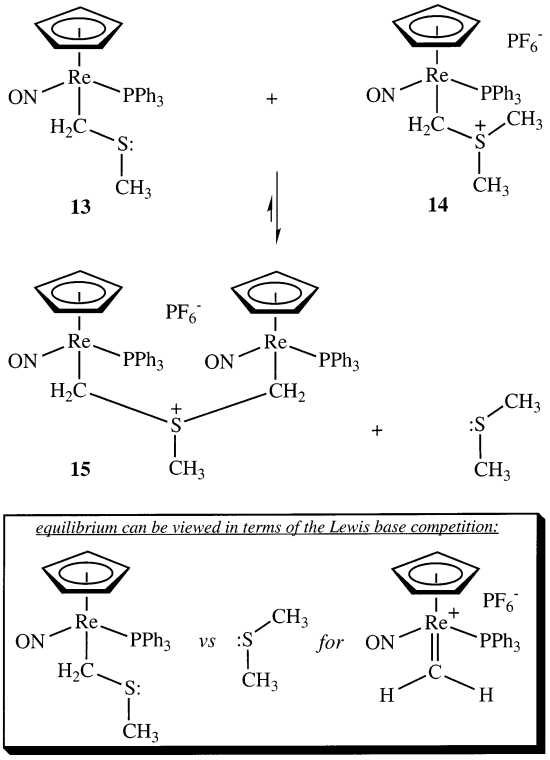
Scheme 4. Other Reactions



phines are oxygen sensitive, their rhodium chelate complexes can be kept in air for months.

The monophosphines **8** and diphosphines **1**, **2**, and **9** share an electronic attribute that often leads to superior catalyst performance: "electron rich" donor atoms.[11] For example, we have shown that phosphido and amido complexes of the formula (η^5-C_5H_5)Re(NO)(PPh$_3$)(ER$_2$) possess much greater basicities and nucleophilicities than the corresponding ER$_3$ compounds and analyzed various contributing factors.[29,30] Although data are not yet available for complexes with Re-CHXPR$_2$ linkages, similar sulfur species have been probed, as illustrated in Scheme 5.[31] This equilibrium, which lies within detection limits completely on the side

Scheme 5. Thermodynamic Competition of Two Sulfur Lewis Bases for a Lewis Acid



of dirhenium complex **15**, shows that (η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_2$SCH$_3$) (**13**) has a much greater Lewis basicity toward the methylidene complex [(η^5-C_5H_5)Re(NO)(PPh$_3$)(=CH$_2$)]$^+$PF$_6^-$ than the organic counterpart S(CH$_3$)$_2$. We believe that analogous trends apply to the η^5-$C_5H_4PPh_2$ groups, and experiments to address this point are in progress.

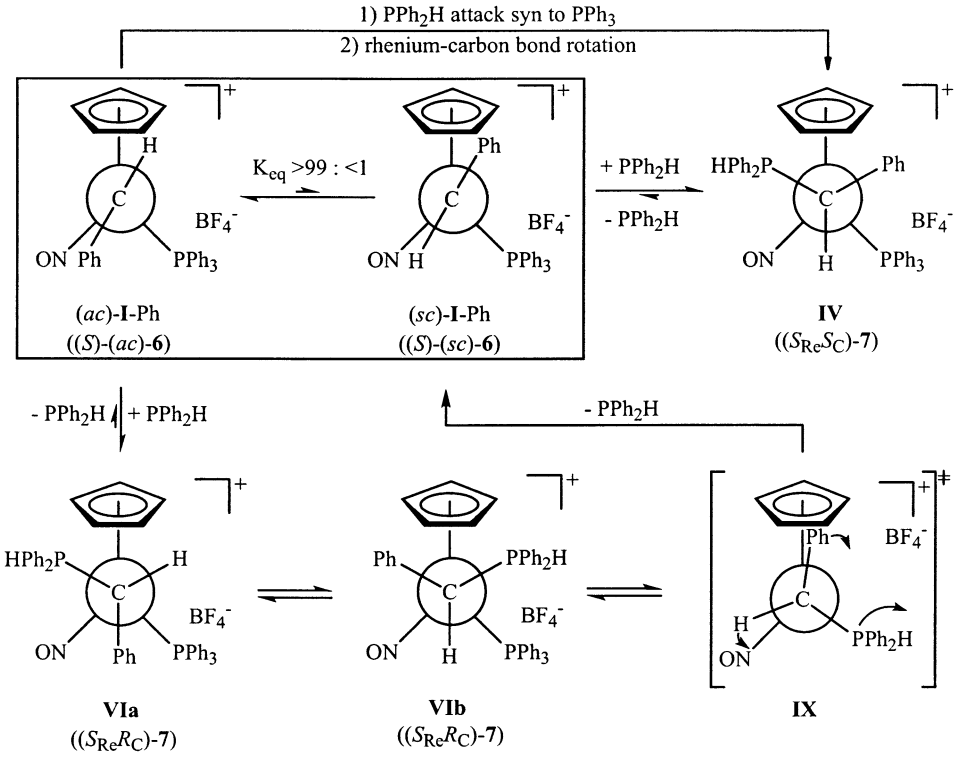
2. Structures of 7−10. The crystal structure of ($S_{Re}S_C$,$R_{Re}R_C$)-**7** (Figure 1) exhibits bond lengths and angles about rhenium that are similar to those of many related compounds, one example of which is the ReCH$_2$-SRR′ system **15** (Scheme 5).[31] As noted above, the rhenium−carbon bond conformation matches the bulkiest groups on carbon with the most spacious interstices on rhenium (**IV**, Scheme 2) and should dominate in solution. In contrast, the opposite $S_{Re}R_C$ series of diastereomers must adopt rhenium−carbon conformations with some type of mismatch, providing a driving force for epimerization. The conformation of ($S_{Re}R_C$)-**7** in **VIa** (Scheme 3) exchanges the optimum sites of the phenyl and hydrogen groups, while that in **VIb** (Figure 2) exchanges those of the phenyl and PPh$_2$ groups.

The conformations of such rhenium complexes in solution are easily probed by NMR. For example, the coupling constants associated with the Ph$_3$*P*Re*CH* linkages (^3J(H,P)) show Karplus-like dependences upon the torsion angle (zero at 90°, maximum at 0/180°).[17] The relatively low value of ($S_{Re}S_C$,$R_{Re}R_C$)-**7** (4 Hz) is in accord with **IV** and the crystallographic P−Re−C−H torsion angle (−52.7°, Figure 1). That of ($S_{Re}R_C$)-**7** (2 Hz) is similar but is not very diagnostic with respect to conformations **VIa** and **VIb**. The diastereomers of an analogous PMe$_3$ addition product, [(η^5-C_5H_5)Re(NO)-

(29) Buhro, W. E.; Zwick, B. D.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 2427.
(30) (a) Dewey, M. A.; Knight, D. A.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1992**, *125*, 815. (b) See also: Fulton, J. R.; Sklenak, S.; Bouwkamp, M. W.; Bergmann, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 4722.

(31) McCormick, F. B.; Gleason, W. B.; Zhao, X.; Heah, P. C.; Gladysz, J. A. *Organometallics* **1986**, *5*, 1778.

Scheme 6. Mechanisms for the Isomerization of ($S_{Re}R_C$)-7 to ($S_{Re}S_C$)-7



$(PPh_3)(CH(Ph)PMe_3)]^+PF_6^-$, exhibit comparable couplings (4.6 and 1.4 Hz).[12] More informative are the ^3J(P,P) values of ($S_{Re}S_C$,$R_{Re}R_C$)-**7** and ($S_{Re}R_C$)-**7**, where a Karplus-like conformational dependence would also be expected. The former is large, 17 Hz, whereas the latter is unresolved and less than 8 Hz. This would be consistent with the rhenium−carbon conformation **IV** for ($S_{Re}S_C$,$R_{Re}R_C$)-**7** (crystallographic P−Re−C−P torsion angle −165.5°) and the dominant but not necessarily exclusive conformation **VIb** for ($S_{Re}R_C$)-**7**.

Interestingly, the ^{1}H NMR chemical shifts of the ReCH protons of ($S_{Re}S_C$)-**7**−**10** fall into the narrow range of δ 4.55−4.70, while those of ($S_{Re}R_C$)-**7**−**9** fall into the narrow range of δ 5.23−5.38. We view this as additional evidence for distinct conformational environments for the ReCH protons. Curiously, when ($S_{Re}R_C$)-**9** is converted to the chelate ($S_{Re}R_C$)-**10**, the chemical shift changes dramatically, from δ 5.29 to 4.26. This suggests a conformational transition. We have considered two general structures for ($S_{Re}R_C$)-**10**, **VIIa** (Scheme 3) and **VIIb** (Figure 2). The latter directs a small hydrogen substituent into the most crowded rhenium interstice. However, the three bulky phosphorus moieties are then forced quite close to each other. Given the chemical shift trends, we suggest that **VIIa** better represents the conformation. The chelate ring of the unsubstituted $ReCH_2P$ analogue **4** adopts a chair conformation,[6a] and the ReCHPh phenyl group in **VIIa** would be accommodated in an equatorial position.

3. Epimerization of 7. The structural and conformational driving forces for this process can be further generalized as follows. Consider any addition to the less stable Re=CHR isomer of the generic alkylidene complex (*sc*)-**I**-R (Scheme 1). When the nucleophile is larger than the =CH*R* group, the most stable diastereomer will be generated in the most stable rhenium−carbon conformation. The opposite Re=CHR isomer, (*ac*)-**I**-R, must give the least stable diastereomer. When the nucleophile is smaller than the =CH*R* group, the diastereomer stability order will be reversed. The former limit clearly applies to the additions of PPh_2H in Schemes 2 and 3 and related additions of P(*p*-tol)$_3$ and PMe_3 described earlier.[12,15] With tertiary phosphines, adducts of (*ac*)-**I**-R cannot be "trapped" by proton removal. The adduct with P(*p*-tol)$_3$ (R = Me) epimerizes at room temperature,[15] whereas that of the more basic phosphine PMe_3 (R = Ph) does not.[12]

Although the purpose of this project was not to study the epimerization mechanism, certain observations are relevant. Three possible pathways are depicted in Scheme 6, all of which are consistent with the observed first-order rate law.[20] One involves the microscopic reverse of PPh_2H addition to give (*S*)-(*ac*)-**6**, followed by Re=CHPh isomerization to (*S*)-(*sc*)-**6** and addition of PPh_2H as in Scheme 2. The activation parameters for the isomerization of (*sc*)-**6** to (*ac*)-**6** have been determined in CD_2Cl_2 ($\Delta H^‡$ = 20.9 kcal mol^{-1}, $\Delta S^‡$ = −3.8 eu, $\Delta G^‡$(298 K) = 22.0 kcal mol^{-1}) and allow the reverse barrier to be estimated as ≥24.7 kcal mol^{-1} ($\Delta G^‡$(298 K)),[12] close to that of the epimerization in $CDCl_3$ (23.2 kcal mol^{-1}).[12] Regardless of whether the first or second step of this pathway was rate determining, a positive $\Delta S^‡$ value would be expected, whereas our data give a slightly negative value (−12.8 eu).[20]

A second possibility would involve analogous PPh_2H dissociation, followed by readdition to the opposite Re=CHPh face of (*S*)-(*ac*)-**6**. Additions to (*sc*)-**6** commonly exhibit diastereoselectivities of ca. 95:5, but those for additions to (*ac*)-**6** are higher (≥99:1).[12] Nonetheless, this pathway, with the second step rate determining, would give a less positive and perhaps negative $\Delta S^‡$ value. A third possibility would involve PPh_2H dissociation from an alternative rhenium−carbon bond conformation, as shown in transition state **IX**. Although

sterically congested, there would be anchimeric assistance from the HOMO of the rhenium fragment shown in **II** (Scheme 1). This mechanism represents nucleophilic catalysis of Re=CHPh isomerization. However, a positive $\Delta S^{\ddagger}$ would again be expected, except in the unlikely event that the conversion of **VIa** to **VIb** were rate determining. Hence, we provisionally favor the second mechanism, which requires a lack of fidelity in the direction of nucleophile addition.

4. Diphenyldiazomethane Complex 12. Although the diphenylmethylidene complex **11** sought in Scheme 4 could not be obtained, various aspects of this chemistry merit note. First, there are several other diphenyldiazomethane complexes that resist conversion to diphenylmethylidene complexes,[26] even in cases where closely related NNCRR′ species give carbene adducts.[26d] Second, one other diazoalkane complex of a 16-valence-electron (η^5-C_5H_5)M(L)(L′) fragment has been structurally characterized, (η^5-C_5H_5)Mn(CO)$_2$(NNC(CO$_2$Me)$_2$) (**16**).[27] The nitrogen−nitrogen and nitrogen−carbon bond lengths in **16** are similar to those in **12** (1.165(7) vs 1.206(4) Å; 1.351(8) vs 1.292(4) Å) but suggest somewhat more nitrogen−nitrogen multiple-bond character in **16** and nitrogen−carbon double-bond character in **12**. The MNN linkage is more bent in **12** than in **16** (144.8(2)° vs 176.9(4)°), but the NNC angles are comparable (150.8(3) vs 150.5(4)°). The model compound Ph$_2$C=N−N=CPh$_2$ exhibits N−N and N=C bond lengths of 1.404 and 1.286 Å.[32]

The bonding in MNNCR$_2$ complexes has been analyzed in detail.[22] We believe the above data are best accommodated by the resonance formulation Re−N=N=CPh$_2$, which is one of the most commonly invoked in coordinatively saturated adducts. The more linear MNN linkage in **16** may reflect somewhat greater MN≡N character. Alternatively, the more bent linkage in **12** may reflect some Re=N−N=CPh$_2$ character, resulting from the greater π basicity of the rhenium fragment and the HOMO in **II**. Such weak back-bonding interactions are conformation-determining in related complexes (e.g., σ-aldehyde and ketone adducts).[33] Accordingly, the ON−Re−N−N and P−Re−N−N torsion angles (16.8(4) and −73.9(4)°) indicate a rhenium−nitrogen conformation analogous to the Re=CHR conformation of (*ac*)-**I**-R in Scheme 1. Also, the rhenium−nitrogen bond in **12** (1.914(3) Å) is much shorter than that in the phenylamido complex (η^5-C_5H_5)Re(NO)(PPh$_3$)(NHPh) (2.076(6) Å)[34] and related cationic amine (sp^3 donor nitrogen, 2.193(4) Å),[35] imine (sp^2 donor nitrogen, 2.112(3)−2.097(3) Å),[36] and nitrile complexes (sp donor nitrogen, 2.089(8) Å).[37]

5. Conclusion. This study has enlarged an existing family of chelating diphosphines with rhenium stereocenters in their backbones (Scheme 1) by developing efficient routes to a new subfamily with carbon stereocenters in their backbones. This effort is part of an ongoing trend toward architecturally novel chiral chelate ligands that contain some type of spectator transition metal,[2−8] exclusive of the extensively employed ferrocene platform.[1] These often confer unique steric and electronic properties. In the course of this work, an unexpected epimerization process and a diphenyldiazomethane complex have also been characterized. Applications of rhodium chelate complexes of the new diphosphines in catalytic enantioselective organic syntheses are described in the following paper.[10]

Experimental Section

General Data. Most general procedures, chemical purifications, and instruments were identical with those in two recent full papers.[6,7] IR spectra were measured on an ASI React-IR spectrometer. NMR spectra were referenced to the residual solvent signal (^{1}H, ^{13}C) or H_3PO_4 (internal capillary, ^{31}P). All cold baths below 0 °C represent manually regulated solvent/liquid N_2 slurries.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH(Ph)PPh$_2$H)]$^+$BF$_4^-$ (7). A. $S_{Re}S_C$,$R_{Re}R_C$. A Schlenk flask was charged with racemic **5** (0.1234 g, 0.1934 mmol)[12] and CH_2Cl_2 (10 mL) and cooled to −60 °C. Then $Ph_3C^+BF_4^-$ (0.0706 g, 0.214 mmol) was added with stirring. After 1 h, $HPPh_2$ (0.0432 g, 0.232 mmol) was added by syringe.[38] The yellow-brown solution turned orange-red. After 0.5 h, the cold bath was removed. After 2 h, the mixture was concentrated to ca. 5 mL by oil pump vacuum and added dropwise to vigorously stirred hexanes (40 mL, HPLC grade). After 0.5 h, the beige powder was collected by filtration, washed with pentane (5 × 2 mL), and dried (10^{-3} mbar, 5 h) to give ($S_{Re}S_C$,$R_{Re}R_C$)-**7** (0.1438 g, 0.1586 mmol, 83%). The ^{1}H and ^{31}P NMR spectra were identical to those from proedure B.

B. $S_{Re}S_C$,$R_{Re}R_C$. Racemic **5** (0.3036 g, 0.4780 mmol), CH_2Cl_2 (20 mL), and $Ph_3C^+BF_4^-$ (0.190 g, 0.576 mmol) were combined as in procedure A. After 1 h, the cold bath was removed. After 24 h, the mixture was cooled to −40 °C and $HPPh_2$ (0.178 g, 0.956 mmol) was added by syringe.[38] The yellow solution turned orange-red. After 0.5 h, the cold bath was removed. After 48 h, the mixture was concentrated to ca. 10 mL by oil pump vacuum and layered with hexane (ca. 50 mL). After 1 week, the red-orange prisms were collected by filtration, washed with hexane (2 × 1 mL), and dried (10^{-3} mbar, 1 h) to give ($S_{Re}S_C$,$R_{Re}R_C$)-**7** (0.3267 g, 0.3603 mmol, 75%). A crystal from this sample was used for the structure determination below.

Mp: 185 °C. Anal. Calcd for $C_{42}H_{37}BF_4NOP_2Re$ (906.7): C, 55.64; H, 4.11; N, 1.54. Found: C, 55.89; H, 4.22; N, 1.35. IR (powder film, cm^{-1}): $\tilde{\nu}$ 1664 (s, NO), 1050 (s, BF). MS (FAB, 3-NBA; *m*/*z* (%)): 820 (16) [M]$^+$, 634 (100) [M − HPPh$_2$]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (dd, ^3J(H,H) = 15 Hz, ^1J(H,P) = 512 Hz, PH), 8.03−7.05 (m, 6C$_6$H$_5$), 5.37 (s, C$_5$H$_5$), 4.55 (ddd, ^2J(H,P) = 16 Hz, ^3J(H,P) = 4 Hz, ^3J(H,H) = 16 Hz, ReCH). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): δ 6C$_6$H$_5$ at 133.5 (d, J(C,P) = 11 Hz), 133.1 (d, J(C,P) = 11 Hz), 132.5 (s), 132.1 (s), 131.3 (d, J(C,P) = 9 Hz), 130.8 (s), 129.9 (s), 129.8 (d, J(C,P) = 11 Hz), 129.4 (d, J(C,P) = 13 Hz), 129.2 (s), 128.7 (d, J(C,P) = 11 Hz); 92.4 (s, C$_5$H$_5$), −5.3 (d, ^1J(C,P) = 26 Hz, ReCH). ^{31}P{^{1}H} NMR: see Table 2.

C. $S_{Re}S_C$. Enantiomerically pure (*S*)-**5** (3.174 g, 5.000 mmol), CH_2Cl_2 (100 mL), $Ph_3C^+BF_4^-$ (1.816 g, 5.500 mmol), and $HPPh_2$ (1.024 g, 5.500 mmol) were combined in a procedure analogous to that in procedure A. A similar reaction and workup (with 400 mL of stirred hexanes) gave unsolvated ($S_{Re}S_C$)-**7** (4.140 g, 4.566 mmol, 91%).

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(38) Measured gravimetrically (difference in mass between loaded and discharged syringe).

Mp: 183−185 °C. Anal. Calcd for $C_{42}H_{37}BF_4NOP_2Re$ (906.7): C, 55.64; H, 4.11; N, 1.54. Found: C, 55.49; H, 4.55; N, 1.27. $[\alpha]^{26}_{589} = 390 \pm 6°$ ($c = 1.05$ mg mL^{-1}, $CHCl_3$).[39] The NMR spectra (^{1}H, ^{13}C, ^{31}P) were similar to those from procedure B.

D. $S_{Re}S_C$. Complex (*S*)-**5** (0.3327 g, 0.5242 mmol),[16] $Ph_3C^+BF_4^-$ (0.1904 g, 0.5766 mmol), and $HPPh_2$ (0.1171 g, 0.6290 mmol) were reacted in a procedure analogous to that in procedure B. The concentrated CH_2Cl_2 solution was layered with hexane. After 1 week, fine orange needles were collected by filtration, washed with pentane (2 × 3 mL), and dried by oil pump vacuum (10^{-3} mbar, 1 h) to give ($S_{Re}S_C$)-**7**· 0.5CH_2Cl_2 (0.4130 g, 0.4351 mmol, 83%).

Mp: 181−183 °C. Anal. Calcd for $C_{42}H_{37}BF_4NOP_2Re$·0.5CH_2Cl_2 (949.2): C, 53.77; H, 4.04; N, 1.48. Found: C, 53.72; H, 4.17; N, 1.37. $[\alpha]^{26}_{589} = 382 \pm 5°$ ($c = 2.16$ mg mL^{-1}, $CHCl_3$; the value is lower than in procedure C, due to the solvate).[39] The NMR spectra (^{1}H, ^{13}C, ^{31}P) were similar to those from procedure B and showed the CH_2Cl_2 solvate.

E. $R_{Re}S_C$.[18] A Schlenk flask was charged with (*R*)−(*ac*)-**6** (0.0080 g, 0.111 mmol)[12] and CH_2Cl_2 (5 mL) and cooled to −40 °C. Then $HPPh_2$ (0.023 mL, 0.122 mmol) was added by syringe[38] with stirring. After 15 min, the solvent was removed at −20 °C, by oil pump vacuum. The orange solid, ($R_{Re}S_C$)-**7**, was dissolved in cold $CDCl_3$ (0.60 mL). The mixture transferred to a NMR tube that had been cooled to −20 °C, and the tube transferred to a −20 °C NMR probe.

^{1}H NMR (400 MHz, $CDCl_3$, −20 °C): δ 7.72 (dd, ^3J(H,H) = 13 Hz, ^1J(H,P) = 485 Hz, PH), 7.63−7.35 (m, 6C_6H_5), 5.14 (s, C_5H_5), 5.38 (ddd, ^2J(H,P) = 20 Hz, ^3J(H,P) = 2 Hz, ^3J(H,H) = 14 Hz, ReCH). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, −20 °C): δ 6C_6H_5 at 133.9 (d, J(C,P) = 17 Hz), 133.2 (d, J(C,P) = 10 Hz), 132.8 (s), 131.7 (d, J(C,P) = 10 Hz), 131.4 (d, J(C,P) = 10 Hz), 130.6 (s), 129.8 (d, J(C,P) = 14 Hz), 129.4 (d, J(C,P) = 8 Hz), 128.5 (m), 128.2 (d, J(C,P) = 9 Hz), 124.3 (s), 123.6 (s), 122.9 (s), 122.0 (s); 92.2 (s, C_5H_5), −18.1 (d, ^1J(C,P) = 29 Hz, ReCH). ^{31}P{^{1}H} NMR: see Table 2.

(η^5-C_5H_5)Re(NO)(PPh_3)(CH(Ph)PPh_2) (8). A. $S_{Re}S_C$. A Schlenk flask was charged with ($S_{Re}S_C$)-**7** (1.500 g, 1.654 mmol) and THF (80 mL). A *t*-BuOK solution (2.00 mL, 2.0 mmol, 1.0 M in THF) was added with stirring. The solution turned red, and a white precipitate formed. After 0.5 h, volatiles were removed by oil pump vacuum. The residue was extracted with benzene (30 mL). The extracts were filtered through a Celite plug (3 × 3 cm), which was rinsed with benzene. The filtrate was concentrated to 20 mL and layered with pentane (100 mL). After 2 days, the supernatant was decanted. The residue was washed with pentane (5 × 10 mL), and small amounts of amorphous inorganic salts were removed by decantation. The remaining solid was dried under oil pump vacuum (10^{-3} mbar, 2 h) to give ($S_{Re}S_C$)-**8** (0.9950 g, 1.215 mmol, 73%) as a microcrystalline red powder.

Mp: 185 °C dec. Anal. Calcd for $C_{42}H_{36}NOP_2Re$ (818.9): C, 61.60; H, 4.43; N, 1.71. Found: C, 61.47; H, 4.71; N, 1.53. $[\alpha]^{26}_{589} = 344 \pm 7°$ ($c = 1.3$ mg mL^{-1}, THF).[39] IR (powder film, cm^{-1}): $\tilde{\nu}$ 1652 (s, NO). MS (FAB, 3-NBA; *m*/*z* (%)): 820 (22) [MH]$^+$, 634 (100) [M − PPh_2]$^+$, 544 (70) [M − CHPhPPh_2]$^+$. ^{1}H NMR (400 MHz, C_6D_6): δ 6C_6H_5 at 8.16 (dt, J = 2, J = 7 Hz, 2H), 7.45 (m, 3H), 7.01−6.75 (m, 25 H); 4.91 (s, C_5H_5), 4.68 (dd, ^2J(H,P) = 10 Hz, ^3J(H,P) = 3 Hz, ReCH). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ 6C_6H_5 at 159.4 (s), 145.8 (d, J(C,P) = 28 Hz), 142.5 (d, J(C,P) = 12 Hz), 142.4 (s), 136.7 (s), 136.2 (s), 136.0 (s), 135.6 (d, J(C,P) = 24 Hz), 134.1 (s), 132.6 (d, J(C,P) = 19 Hz), 131.7 (s), 131.5 (s), 130.0 (s), 128.8 (s), 128.6 (s), 128.1 (s), 127.1 (s), 122.7 (s); 91.8 (s, C_5H_5), 6.9 (d, ^1J(C,P) = 36 Hz, ReCH);; ^{31}P{^{1}H} NMR: see Table 2.

B. $R_{Re}S_C$.[18] A Schlenk flask was charged with (*R*)-**5** (0.3072 g, 0.4840 mmol)[16] and CH_2Cl_2 (20 mL) and cooled to −60 °C. Then $Ph_3C^+BF_4^-$ (0.1677 g, 0.5079 mmol) was added with stirring. After 0.5 h, the cold bath was removed. After 48 h, the solution was cooled to −60 °C and $HPPh_2$ (0.0946 g, 0.5081 mmol) was added by syringe.[38] The yellow solution turned orange-red, and a precipitate slowly formed. After 0.5 h (−60 °C), a *t*-BuOK solution (1.0 M in THF, 0.580 mL, 0.58 mmol) was added with stirring. After 30 min, the mixture was warmed to 0 °C and the solvent removed by oil pump vacuum. The orange residue was extracted with benzene. The extracts were filtered through a Celite plug (2 × 1 cm), which was rinsed with benzene. The filtrate was concentrated (ca. 10 mL) and layered with pentane (50 mL). After 48 h, the supernatant was decanted and the orange powder washed with pentane (2 × 5 mL) and dried by oil pump vacuum (10^{-3} mbar, 2 h) to give ($R_{Re}S_C$)-**8** (0.2305 g, 0.2815 mmol, 58%).

Mp: 187 °C dec. Anal. Calcd for $C_{42}H_{36}NOP_2Re$ (818.9): C, 61.60; H, 4.43; N, 1.71. Found: C, 61.69; H, 4.63; N, 1.62. $[\alpha]^{26}_{589} = -198 \pm 7°$ ($c = 3.58$ mg mL^{-1}, THF).[39] IR (powder film, cm^{-1}): $\tilde{\nu}$ 1652 (s, NO). MS (FAB, 3-NBA; *m*/*z* (%)): 820 (15) [MH]$^+$, 634 (100) [M − PPh_2]$^+$, 544 (25) [M − CHPhPPh_2]$^+$. ^{1}H NMR (400 MHz, C_6D_6): δ 7.57−6.90 (m, 6C_6H_5), 5.23 (dd, ^2J(H,P) = 8 Hz, ^3J(H,P) = 6 Hz, ReCH), 4.83 (s, C_5H_5). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ 6C_6H_5 at 156.0 (s), 144.6 (d, J(C,P) = 20 Hz), 142.6 (d, J(C,P) = 24 Hz), 136.0 (d, J(C,P) = 51 Hz), 135.7 (s), 135.6 (d, J(C,P) = 27 Hz), 134.4 (d, J(C,P) = 8 Hz), 133.4 (d, J(C,P) = 19 Hz), 129.9 (d, J(C,P) = 24 Hz), 129.2 (s), 122.7 (s); 90.5 (s, C_5H_5), 3.8 (d, ^1J(C,P) = 46 Hz, ReCH); ^{31}P{^{1}H} NMR: see Table 2.

(η^5-$C_5H_4PPh_2$)Re(NO)(PPh_3)(CH(Ph)PPh_2) (9). A. $S_{Re}S_C$. A Schlenk tube was charged with ($S_{Re}S_C$)-**8** (0.304 g, 0.371 mmol) and THF (15 mL) and cooled to −60 °C. A solution of *t*-BuLi (1.75 M in pentane; 0.212 mL, 0.371 mmol) was slowly added against a N_2 flow (the reagent is easily flammable) with stirring. The cold bath was warmed to −10 °C. The orange solution turned red. After 0.5 h, the mixture was cooled to −60 °C and PPh_2Cl (0.098 g, 0.445 mmol)[38] was added via syringe. The bath was warmed to room temperature over the course of 1 h. The mixture was stirred for an additional 2 h at 25 °C, and the solvent was removed by oil pump vacuum. Benzene (10 mL) was added. The mixture was stirred and filtered through a Celite plug (2 × 2 cm), which was rinsed with benzene. Solvent was removed from the filtrate by oil pump vacuum (10^{-3} mbar, 12 h) to give ($S_{Re}S_C$)-**9** (0.331 g, 0.330 mmol, 89%) as a red foam. Attempted precipitations from layered benzene/hexane gave oils.

Mp: 128−130 °C dec. Anal. Calcd for $C_{54}H_{45}NOP_3Re$ (1003.1): C, 64.66; H, 4.52; N, 1.40. Found: C, 64.71; H, 4.64; N, 1.35. $[\alpha]^{26}_{589} = 195 \pm 4°$ ($c = 1.84$ mg mL^{-1}, THF).[39] IR (powder film, cm^{-1}): $\tilde{\nu}$ 1648 (s, NO). MS (FAB, 3-NBA; *m*/*z* (%)): 1003 (45) [M]$^+$, 818 (100) [M − PPh_2]$^+$. ^{1}H NMR (400 MHz, C_6D_6): δ 8C_6H_5 at 8.11−8.05 (m, 3H), 7.46−6.78 (m, 37H); C_5H_4 at 6.08, 5.69, 5.29, 3.39 (4 br s); 4.67 (dd, ^2J(H,P) = 10 Hz, ^3J(H,P) = 3 Hz, ReCH). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ PPh_3 at 136.3 (d, J(C,P) = 12 Hz, o), 130.0 (s, p), 128.5 (d, J(C,P) = 11 Hz, m); 5C_6H_5 at 155.3 (d, J(C,P) = 10 Hz), 145.8 (d, J(C,P) = 29 Hz), 141.5 (d, J(C,P) = 12 Hz), 138.7 (d, J(C,P) = 12 Hz), 136.2 (s), 135.7 (s), 135.3 (d, J(C,P) = 21 Hz), 134.2 (d, J(C,P) = 15 Hz), 134.1 (d, J(C,P) = 13 Hz), 133.8 (d, J(C,P) = 20 Hz), 132.8 (d, J(C,P) = 18 Hz), 128.9 (d, J(C,P) = 18 Hz), 128.8 (d, J(C,P) = 18 Hz), 129.2 (s), 128.6 (s), 127.6 (s), 127.1 (s); C_5H_4 at 106.3 (d, J(C,P) = 20 Hz), 100.0 (dd, J(C,P) = 19 Hz, J(C,P) = 3 Hz), 96.4 (m), 91.1 (d, J(C,P) = 18 Hz), 89.4 (d, J(C,P) = 3 Hz); 7.2 (dd, ^1J(C,P) = 38 Hz, ^2J(C,P) = 4 Hz, ReCH). ^{31}P{^{1}H} NMR: see Table 2.

B. $R_{Re}S_C$.[18] Complex ($R_{Re}S_C$)-**8** (0.3980 g, 0.4860 mmol), THF (15 mL), and *t*-BuLi (1.42 M in pentane; 0.411 mL, 0.583 mmol) were combined as described in procedure A. An identical reaction and workup gave ($R_{Re}S_C$)-**9** (0.4119 g, 0.4106 mmol, 84%) as an orange foam. Attempted precipitations from layered benzene/hexane gave oils.

Mp: 122−125 °C dec. Anal. Calcd for $C_{54}H_{45}NOP_3Re$ (1003.1): C, 64.66; H, 4.52; N, 1.40. Found: C, 64.57; H, 4.82;

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

N, 1.18. $[\alpha]^{26}_{589} = -181 \pm 5°$ (c = 0.97 mg mL^{-1}, THF).[39] IR (powder film, cm^{-1}): $\tilde{\nu}$ 1652 (s, NO). ^{1}H NMR (300.1 MHz, C_6D_6): δ 7.65−6.82 (m, 8C_6H_5), C_5H_4 at 5.54 (br s, 1H), 5.15 (m, 2H), 3.85 (br s, 1H); 5.29 (dd, ^2J(H,P) = 8 Hz, ^3J(H,P) = 6 Hz, ReCH). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6): δ PPh_3 at 136.0 (d, J(C,P) = 10 Hz, o), 130.1 (s, p), 128.8 (d, J(C,P) = 10 Hz, m); 5C_6H_5 at 144.4 (d, J(C,P) = 21 Hz), 142.1 (d, J(C,P) = 23 Hz), 138.7 (d, J(C,P) = 12 Hz), 136.6 (d, J(C,P) = 12 Hz), 135.7 (s), 135.5 (d, J(C,P) = 8 Hz), 135.2 (d, J(C,P) = 8 Hz), 135.0 (s), 134.9 (d, J(C,P) = 7 Hz), 134.8 (s), 134.7 (d, J(C,P) = 7 Hz), 134.6 (s), 134.4 (s), 134.1 (d, J(C,P) = 4 Hz), 133.8 (d, J(C,P) = 4 Hz), 133.5 (s), 133.2 (s), 129.5 (d, J(C,P) = 7 Hz), 129.0 (s); C_5H_4 at 102.4 (d, J(C,P) = 22 Hz), 100.1 (d, J(C,P) = 24 Hz), 95.3 (m), 91.1 (s), 88.0 (d, J(C,P) = 30 Hz); 4.3 (dd, ^1J(C,P) = 47 Hz, ^2J(C,P) = 4 Hz, ReCH). ^{31}P{^{1}H} NMR: see Table 2.

[(η^5-$C_5H_4$$PPh_2$)Re(NO)($PPh_3$)($\mu$-CH(Ph)$PPh_2$)Rh(NBD)]$^+$-$PF_6^-$ (10). A. $S_{Re}S_C$. A Schlenk tube was charged with ($S_{Re}S_C$)-**9** (0.3600 g, 0.3589 mmol) and THF (10 mL), and $[Rh(NBD)_2]^+PF_6^-$ (0.1551 g, 0.3589 mmol)[40] was added with stirring. The orange solution turned deep red. After 0.5 h, pentane (30 mL) was added. The orange-brown powder was collected by filtration, washed with pentane (2 × 10 mL), and dried by oil pump vacuum (10^{-3} mbar, 1 h) to give ($S_{Re}S_C$)-**10** (0.4403 g, 0.3278 mmol, 91%).

Mp: 200−202 °C dec. Anal. Calcd for $C_{61}H_{53}F_6NOP_4ReRh$ (1343.1) C, 54.55; H, 3.98; N, 1.04. Found: C, 54.35; H, 4.12; N, 0.93. $[\alpha]^{26}_{589} = -159 \pm 6°$ (c = 1.80 mg mL^{-1}, THF).[39] IR (powder film, cm^{-1}): $\tilde{\nu}$ 1671 (s, NO), 834 (s, PF). MS (FAB, 3-NBA; m/z (%)): 1198 (100) [M]$^+$, 1106 (30) [M − NBD]$^+$, 936 (11) [M − PPh_3]$^+$, 818 (25) [M − NBD − Rh − PPh_2]$^+$. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 8C_6H_5 at 8.04−8.02 (m, 2H), 7.69−7.19 (m, 36 H), 6.99−6.81 (m, 2H); C_5H_4 at 5.33, 5.20, 4.78, 4.15 (4 br s); NBD at 4.20 (br m, 4 CH), 3.73 (2 br s, 2 CH), 1.36 (m, CH_2); 4.70 (dd, ^2J(H,P) = 16 Hz, ^3J(H,P) = 3 Hz, ReC*H*). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ PPh_3 at 133.7 (d, J(C,P) = 12 Hz, o), 131.6 (d, J(C,P) = 53 Hz, i), 131.1 (s, p), 128.9 (d, J(C,P) = 11 Hz, m); 5C_6H_5 at 149.5 (s), 136.4 (s), 136.2 (s), 135.6 (d, J(C,P) = 11 Hz), 135.0 (s), 134.6 (s), 133.8 (d, J(C,P) = 12 Hz), 133.2 (s), 132.8 (s), 132.6 (d, J(C,P) = 8 Hz), 131.8 (s), 130.6 (d, J(C,P) = 8 Hz), 129.8 (d, J(C,P) = 10 Hz), 129.7 (d, J(C,P) = 10 Hz), 129.2 (s), 129.0 (d, J(C,P) = 10 Hz), 128.6 (s), 127.8 (d, J(C,P) = 8 Hz); C_5H_4 at 109.0, 102.6, 99.9, 86.3, 82.8 (5 m, C_5H_4); NBD at 91.6, 88.8, 86.3, 69.0, 52.9, 52.7 (6 m), 22.7 (s); 15.3 (br s, ReCH). ^{31}P{^{1}H} NMR: see Table 2.

B. $R_{Re}S_C$.[18] Complex ($R_{Re}S_C$)-**9** (0.2120 g, 0.2113 mmol), THF (20 mL), and $[Rh(NBD)_2]^+PF_6^-$ (0.0913 g, 0.2113 mmol) were combined as described in procedure A. An identical reaction and workup gave ($R_{Re}S_C$)-**10** as an orange-brown powder (0.2480 g, 0.1846 mmol, 87%).

Mp: 190−192 °C dec. Anal. Calcd for $C_{61}H_{53}F_6NOP_4ReRh$ (1343.1): C, 54.55; H, 3.98; N, 1.04. Found: C, 54.38; H, 4.11; N, 1.11. $[\alpha]^{26}_{589} = 72°$ (c = 1.00 mg mL^{-1}, THF).[39] IR (powder film, cm^{-1}): $\tilde{\nu}$ 1676 (s, NO), 834 (s, PF). MS (FAB, 3-NBA; m/z (%)): 1198 (100) [M]$^+$, 1106 (28) [M − NBD]$^+$, 1030 (8) [M − NBD − C_6H_5]$^+$, 936 (20) [M − PPh_3]$^+$, 818 (72) [M − NBD − Rh − PPh_2]$^+$, 633 (51) [M − NBD − Rh − 2 PPh_2]$^+$. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 8C_6H_5 at 7.95−7.82 (m, 5H), 7.62−7.26 (m, 30 H), 6.84−6.78 (m, 5H); C_5H_4 at 4.65, 4.59, 4.49, 4.00 (4 br s); NBD at 4.42 (br m, 4 CH), 3.92/3.86 (2 br s, 2 CH), 1.53/1.44 (d, ^2J(H,H′) = 8.6/8.2 Hz, C*H*H′/CH*H*′); 4.26 (dd, ^2J(H,P) = 15 Hz, ^3J(H,P) = 6 Hz, ReC*H*). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ PPh_3 at 133.7 (d, J(C,P) = 10 Hz, o), 131.7 (d, J(C,P) = 44 Hz, i), 130.7 (s, p), 128.4 (d, J(C,P) = 10 Hz, m); 5C_6H_5 at 136.2 (d, J(C,P) = 36 Hz), 134.9 (d, J(C,P) = 12 Hz), 134.2 (d, J(C,P) = 12 Hz), 133.7 (d, J(C,P) = 36 Hz), 133.2 (s), 133.1 (s), 132.9 (d, J(C,P) = 4 Hz), 132.7 (s), 132.3 (d, J(C,P) = 30 Hz), 132.3 (s), 132.1 (d, J(C,P) = 12 Hz), 131.8 (s), 129.9 (s), 129.5 (d, J(C,P) = 10 Hz), 129.4 (d, J(C,P) = 10 Hz), 129.1 (d, J(C,P) = 16 Hz), 128.7 (s), 128.2 (s), 128.0 (s), 127.4 (d, J(C,P) = 8 Hz), 124.6 (d, J(C,P) = 4 Hz, p); C_5H_4 at 102.1 (m), 101.0 (d, J(C,P) = 14 Hz), 86.6, 83.1, 79.2 (3 m); 99.5, 94.0, 88.4, 83.1, 52.8, 52.4, 22.6 (7 br s, NBD), 14.1 (br s, ReCH). ^{31}P{^{1}H} NMR: see Table 2.

[(η^5-C_5H_5)Re(NO)(PPh_3)(NNCPh_2)]$^+$$BF_4^-$ (12). A Schlenk tube was charged with racemic (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (0.327 g, 0.585 mmol)[41] and C_6H_5Cl (30 mL) and cooled to −40 °C with stirring. Then HBF_4 (7.3 M in Et_2O, 0.104 mL, 0.761 mmol, 1.3 equiv) was added via syringe. After 10 min, a solution of $NNCPh_2$ in pentane (10 mL, ca. 2.5 mmol)[24] was added dropwise. The bath was removed, and the solution was warmed to room temperature with stirring. After 3 h at room temperature, the precipitate was collected on a sinter frit, washed with pentane (3 × 5 mL), dried by oil pump vacuum, and crystallized from CH_2Cl_2/hexane to give **12**·0.5CH_2Cl_2 (0.347 g, 0.400 mmol, 68%) as deep brown prisms.

Mp: 147−150 °C dec. Anal. Calcd for $C_{36}H_{30}BF_4N_3OPRe$·0.5CH_2Cl_2 (867.1): C, 50.56; H, 3.60; N, 4.85. Found: C, 50.84; H, 3.79; N, 4.52. IR (powder film, cm^{-1}): $\tilde{\nu}$ 1710 (s, NO), 1586 (w, NN), 1046 (s, BF). UV−vis (2.00 × 10^{-5} M, CH_2Cl_2; λ (nm)/ϵ (cm^{-1} M^{-1})): 331/30 200. MS (FAB, 3-NBA; m/z (%)): 738 (100) [M]$^+$, 544 (92) [M − NNCPh_2]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5C_6H_5 at 7.53−7.51 (m, 10H), 7.33−7.24 (m, 15H); 6.00 (s, C_5H_5), 5.32 (s, CH_2Cl_2). ^{13}C{^{1}H} (100.4 MHz, $CDCl_3$): δ PPh_3 at 133.1 (d, J(C,P) = 11 Hz, o), 132.6 (d, J(C,P) = 4 Hz, p), 129.9 (d, J(C,P) = 12 Hz, m), 127.8 (d, J(C,P) = 60 Hz, i); 2C_6H_5 at 129.1, 129.0, 127.5 (3 br s); 100.4 (s, C_5H_5), 92.2 (s, CN_2), 53.8 (s, CH_2Cl_2). ^{31}P{^{1}H} NMR (161.7 MHz, $CDCl_3$): δ 15.9 (s, PPh_3).

Crystallography. Data were collected as summarized in Table 1. Cell parameters were obtained from 10 frames using a 10° scan and refined with 25 reflections. Lorentz−polarization and absorption corrections were applied.[42] The space groups were determined from systematic absences and subsequent least-squares refinement. The structures were solved by direct methods. The parameters were refined with all data by full-matrix least squares on F^2 using SHELXL-97.[43] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions using a riding model. Scattering factors were taken from the literature.[44] Data were deposited at the Cambridge Crystallographic Data Centre as supplementary publications with the refcodes 185403 (($S_{Re}S_C$,$R_{Re}R_C$)-**7**) and 185402 (**12**·0.5CH_2Cl_2). Further details are available on request from the CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+44)1223−336−033).

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