Synthesis and Reactivity of 1,2- and 1,3-Diphosphanes that Contain Four Chiral Rhenium Fragments: Architecturally Novel Tetrametallo-DMPE and -DMPP Species that are Unprivileged Ligands for Enantioselective Catalysis

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Keywords: Rhenium / Chiral diphosphane / Phosphane oxide / Rhodium / Hydrogenation / Hydrosilylation

Reactions of enantiopure (*S*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+$ PF_6^- [(*S*)-**2**] and $PH_2CH_2(CH_2)_nCH_2PH_2$ (0.5 equiv.) give ($S_{Re}S_{Re}$)-[(η^5-C_5H_5)Re(NO)(PPh_3){$CH_2PH_2CH_2(CH_2)_n$-$CH_2PH_2CH_2$}(Ph_3P)(ON)Re(η^5-C_5H_5)]$^{2+}$ $2PF_6^-$ [*n* = 0/1, ($S_{Re}S_{Re}$)-**3/4**; 65–62/77–58 %]. Reaction of racemic **2** (BF_4^- salt) and $PH_2(CH_2)_2PH_2$ (0.5 equiv.) gives the *meso* and *rac* diastereomers of **3** (BF_4^- salts) in 28 % and 38 % yields after crystallization. Treatments of ($S_{Re}S_{Re}$)-**3/4** with *t*BuOK and then (*S*)-**2** give the tetrarhenium complexes ($S_{Re}S_{Re}S_{Re}S_{Re}$)[{(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2)}$_2${$PHCH_2(CH_2)_n$-CH_2PH}{(CH_2)(Ph_3P)(ON)Re(η^5-C_5H_5)}$_2$]$^{2+}$ $2PF_6^-$ [*n* = 0/1, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7/8**; 89–88/98–87 %]. The crystal structure of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** is determined and its conformation analyzed. Reactions of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7/8** and *t*BuOK give air-sensitive diphosphanes ($S_{Re}S_{Re}S_{Re}S_{Re}$)-{(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2)}$_2${$PCH_2(CH_2)_nCH_2P$}{(CH_2)(Ph_3P)(ON)Re(η^5-C_5H_5)}$_2$ [*n* = 0/1, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9/10**; 92/62 %]. Additions of (a) PhIO give the corresponding dioxides (72/62 %), and (b) [$Rh(NBD)_2$]$^+$ PF_6^- give the corresponding chelates [(P–P)Rh(NBD)]$^+$ PF_6^- (75/82 %) (NBD = norbornadiene). These catalyze hydrogenations of protected dehydroamino acids and hydrosilylations of propiophenone with only modest enantioselectivities. Similar results are obtained when ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9/10** are applied in rhodium-catalyzed conjugate additions of aryl boronic acids, or palladium-catalyzed allylic alkylations.

Introduction

For some time, we have been interested in incorporating metal fragments into donor ligands that can be used in metal-catalyzed reactions – in other words, bimetallic catalysts in which one metal remains a "spectator" with respect to bond-breaking and bond-making.[1–4] This has in part been inspired by the immensely useful ferrocene-containing ligands, many of which are chiral and regularly applied in a variety of enantioselective catalytic transformations.[5] It would seem logical that other chiral metal fragments could also possess suitable – and perhaps superior – architectures for asymmetric induction. Furthermore, as described in several recent papers,[1,4b,6] eighteen-valence-electron complexes that feature a donor atom in the α or β position (e. g., L_nMPR_2: or $L_nMCH_2PR_2$:) are much more basic and nucleophilic than organic analogs that lack the metal (:PR_3). This is largely due to repulsive interactions involving the lone pair and occupied metal-based orbitals.[7] Hence, there are also opportunities for unusual electronic effects that may aid bond activation.

In previous papers, we have exploited these steric and electronic phenomena in reactions that result in new stereocenters,[2] and those that do not.[4] Other groups are also making important contributions to the design and application of non-ferrocenyl metal-containing ligands in catalysis.[8] We have often but not exclusively[4b] used the easily resolved[9] chiral rhenium fragment [(η^5-C_5H_5)Re(NO)(PPh_3)]$^+$ (**I**). Two types of bidentate ligands have been prepared, as illustrated by the diphosphanes **II** and diamine **IIIa** in Figure 1. In the first, the rhenium is part of the chelate backbone. In the second, two rhenium fragments are positioned exocyclic to the chelate backbone. The former gives rhodium complexes that catalyze hydrogenations and hydrosilylations with good to excellent enantioselectivities.[2a,2b,2e] The latter also gives metal complexes,[3] but these were not extensively investigated as catalysts, in part because the nitrogen atoms are configurationally labile stereocenters that can lead to multiple diastereomers upon chelation.

This situation – which can be desirable for some purposes but undesirable for others – is easily circumvented, as shown in ligand **IV**. Now four rhenium fragments are present, arrayed such that the donor atoms are no longer stereocenters. Accordingly, in this paper we describe (1) an

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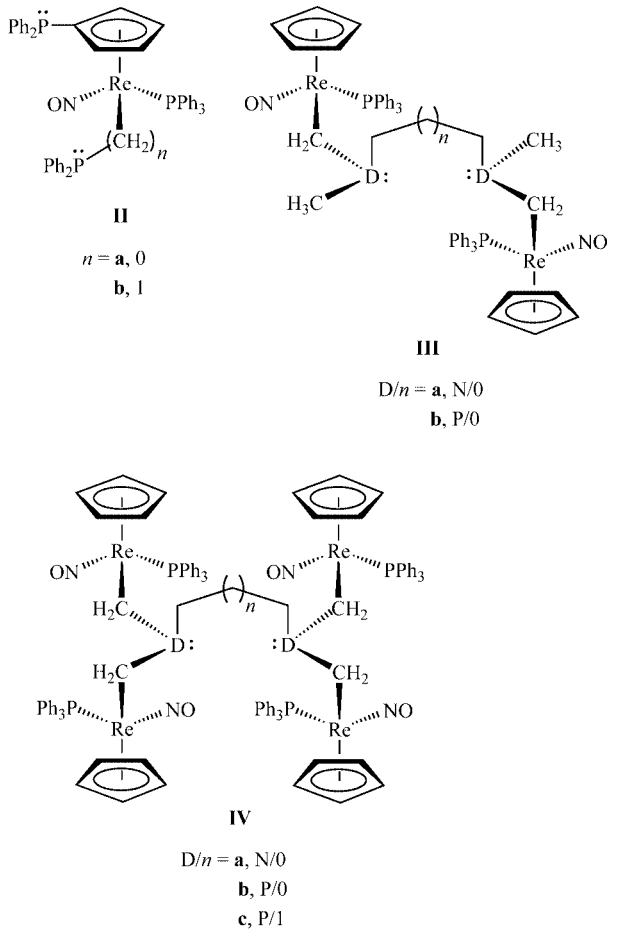


Figure 1. Evolution of families of chiral chelating ligands based upon the chiral rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**).

efficient and convenient route to diphosphanes of the type **IVb**,**c**, (2) the structural characterization of a diprotonated derivative, (3) the formation of dioxide and rhodium derivatives, and (4) exploratory catalytic reactions. These ligands can be regarded as derivatives of 1,2-bis(dimethylphosphanyl)ethane (DMPE) and 1,3-bis(dimethylphosphanyl)-propane (DMPP), the prototypical electron-rich 1,2- and 1,3-diphosphanes in coordination chemistry.[10]

Results

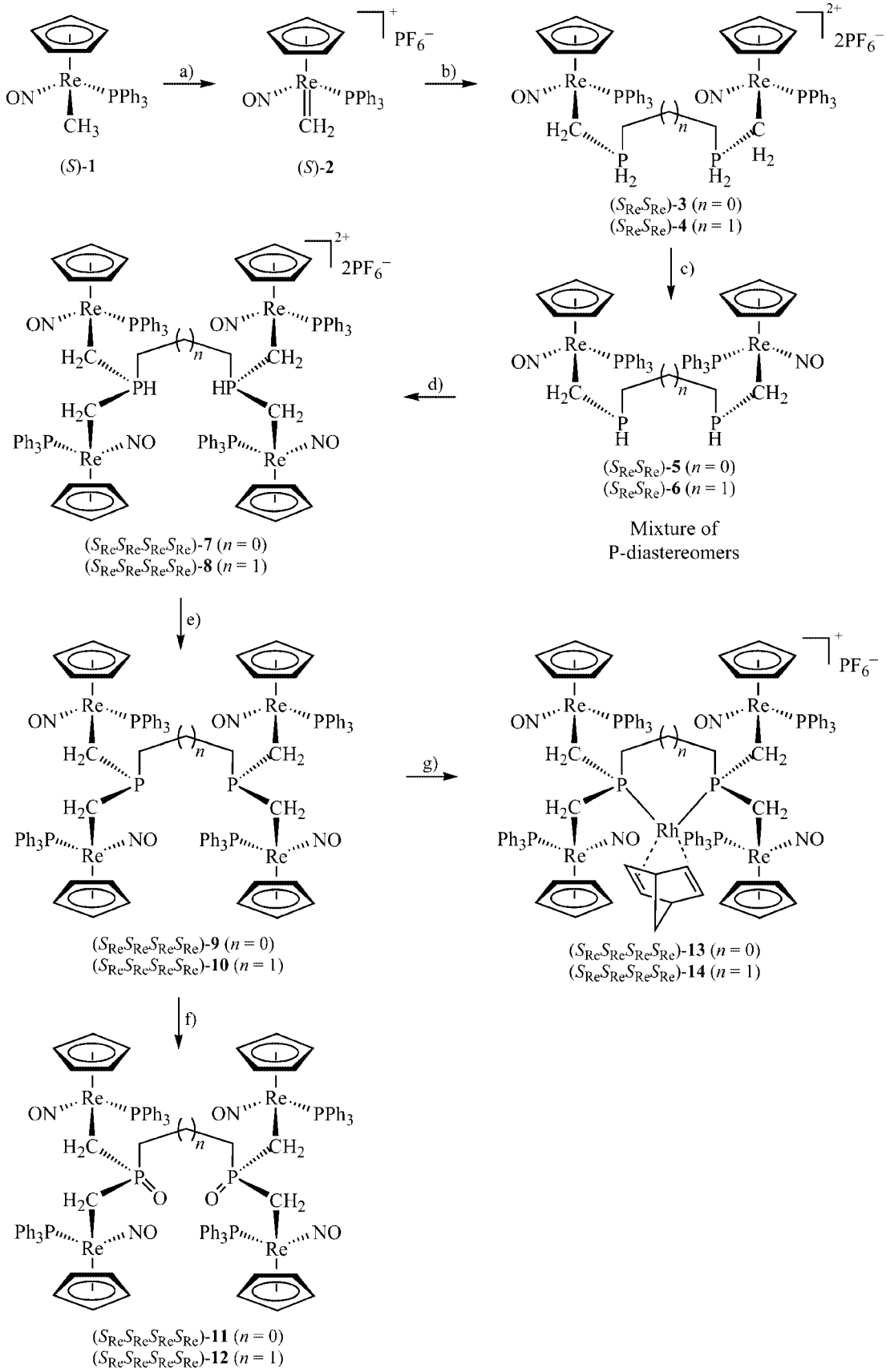
1. Dirhenium Complexes: The diprimary diphosphanes $PH_2CH_2(CH_2)_nCH_2PH_2$ (n = 0, 1) were purchased or prepared from the corresponding dibromides by published Arbuzov/reduction sequences.[11] As shown in Scheme 1, the enantiopure methyl complex (*S*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ [(*S*)-**1**][12,13] and trityl salt Ph_3C^+ PF_6^- were reacted in CH_2Cl_2 at –60 °C to generate the methylidene complex (*S*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH_2)]^+$ PF_6^- [(*S*)-**2**].[14] Then a half-equivalent of $PH_2CH_2(CH_2)_nCH_2PH_2$ was added. Workups gave the diphosphonium salts $(S_{Re}S_{Re})$-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{CH_2PH_2CH_2(CH_2)_n\text{-}CH_2PH_2CH_2\}(Ph_3P)(ON)Re(\eta^5\text{-}C_5H_5)]^{2+}$ $2PF_6^-$ [n = 0/1, $(S_{Re}S_{Re})$-**3/4**][13] as yellow needles or powders in 65–62% and 77–58% yields. Both products were thermally stable and tolerated several hours in air. They were soluble in most polar organic solvents (CH_2Cl_2, DMF, ethanol, THF, dioxane) and insoluble in aliphatic or aromatic hydrocarbons.

Complexes $(S_{Re}S_{Re})$-**3/4** and all other new compounds below were characterized by IR and NMR (^1H, ^{13}C, ^{31}P) spectroscopy, mass spectrometry, and microanalysis, as summarized in the experimental section. The two rhenium moieties gave a single set of NMR signals. The ^1H NMR spectra showed two doublets of multiplets for the diastereotopic PHH′ protons, each with distinct ^1J(H,P) values. The ^{13}C NMR spectra exhibited P*C*H_2C signals (18.9/24.0 ppm) that were coupled to both protonated phosphorus atoms; that in $(S_{Re}S_{Re})$-**4** was particularly well-resolved [dd, ^1J(C,P) = 39, ^3J(C,P) = 15 Hz]. A number of chemical shift trends were evident, as analyzed elsewhere.[10a]

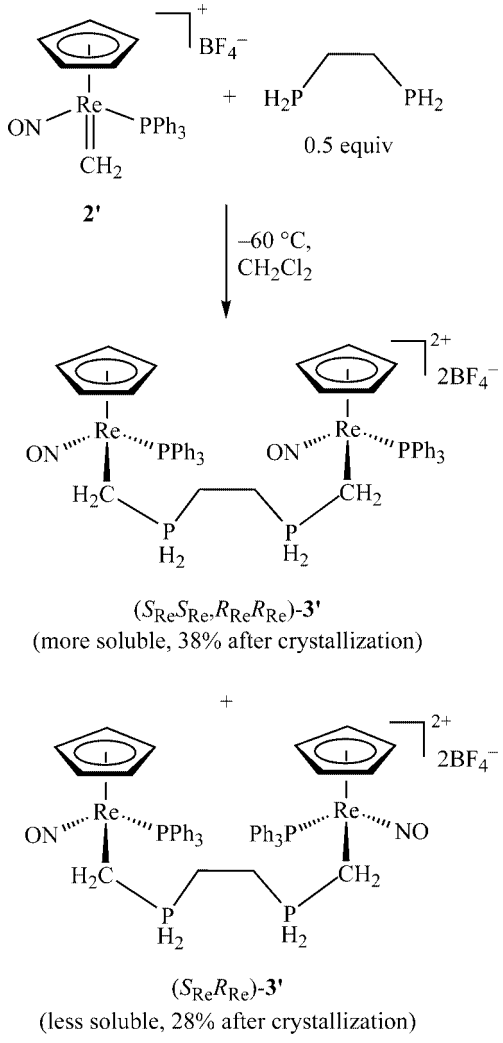
As shown in Scheme 2, a similar sequence was conducted with $PH_2(CH_2)_2PH_2$ and the *tetrafluoroborate* salt of the *racemic* methylidene complex, $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\text{-}(=CH_2)]^+$ BF_4^- (**2′**). The less soluble *meso* diastereomer $(S_{Re}R_{Re})$-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)\{CH_2PH_2(CH_2)_2PH_2\text{-}CH_2\}(Ph_3P)(ON)Re(\eta^5\text{-}C_5H_5)]^{2+}$ $2BF_4^-$ [$(S_{Re}R_{Re})$-**3′**] precipitated from the reaction mixture and was isolated in 28% yield. This material was insoluble in all common solvents except DMSO. The *rac* diastereomer $(S_{Re}S_{Re},R_{Re}R_{Re})$-**3′** was isolated from the supernatant in 38% yield. The configurational assignments followed from the close similarity of the NMR and IR data for the latter diastereomer (especially the ^{13}C ReCH_2 signals) with those of non-racemic $(S_{Re}S_{Re})$-**3**.

As shown in Scheme 1, $(S_{Re}S_{Re})$-**3/4** were treated with *t*BuOK in THF. This gave bright orange solutions of the disecondary diphosphanes $(S_{Re}R_{Re})$-$(\eta^5\text{-}C_5H_5)Re(NO)\text{-}(PPh_3)\{CH_2PHCH_2(CH_2)_nCH_2PHCH_2\}(Ph_3P)(ON)Re(\eta^5\text{-}C_5H_5)$ [n = 0/1, $(S_{Re}S_{Re})$-**5/6**]. Since two phosphorus stereocenters are generated, ^{31}P NMR spectra of $(S_{Re}S_{Re})$-**5** were recorded in situ. In the absence of special kinetic or thermodynamic phenomena,[15] three diastereomers would be expected: $S_{Re}S_PS_PS_{Re}$, $S_{Re}R_PR_PS_{Re}$, and $S_{Re}S_PR_PS_{Re}$ (identical with $S_{Re}R_PS_PS_{Re}$). The last should exhibit two *P*CH_2 signals; the others, which have a C_2 axis, should give only one. The ^{31}P NMR spectrum showed four signals {δ [^1J(P,H)]: –29.6 (189), –32.3 (189), –36.1 (201), –36.4 (201) ppm} in an area ratio of 21:21:40:18. If it is assumed that the two peaks of equal intensity arise from $(S_{Re}S_PR_PS_{Re})$-**5**, a 42:40:18 mixture of diastereomers is obtained. Given this poor selectivity, no attempts were made to deconvolute the other NMR signals, and the mixtures were used directly for subsequent chemistry. The phosphorus inversion barriers are believed to be high, as supported by data for related compounds below.

2. Tetrarhenium Complexes: Following an extraction/filtration step, crude $(S_{Re}S_{Re})$-**5/6** were added to a cold solution of enantiopure (*S*)-**2** in CH_2Cl_2. As shown in Scheme 1, workups gave the ditertiary diphosphonium salts $(S_{Re}S_{Re}S_{Re}S_{Re})$-$[\{(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)\}_2\text{-}\{PHCH_2(CH_2)_nCH_2PH\}\{(CH_2)(Ph_3P)(ON)Re(\eta^5\text{-}C_5H_5)\}_2]^{2+}$



Scheme 1. Syntheses of tetrarhenium complexes; a) Ph_3C^+ PF_6^-, CH_2Cl_2, –60 °C; b) $PH_2CH_2(CH_2)_nCH_2PH_2$ (n = 0, 1), CH_2Cl_2, –60 to 25 °C; c) *t*BuOK, THF or CH_2Cl_2, 25 °C; d) (*S*)-**2**, CH_2Cl_2, –60 to 25 °C; e) *t*BuOK, THF, 25 °C; f) air or PhIO, CH_2Cl_2 or THF, 25 °C; g) $[Rh(NBD)_2]^+$ PF_6^-, THF, 25 °C.



Scheme 2. Syntheses of the racemic and *meso* diphosphonium salt **3′**.

$2PF_6^-$ [n = 0/1, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7/8**].[13] These lack the phosphorus stereocenters of the precursors. The former was isolated as red prisms in 89–88% yields, and the latter as a yellow-orange powder in 98–87% yields. Both could be stored for months under ambient conditions, and were characterized analogously to the dirhenium analogs. They were soluble in CH_2Cl_2, acetone, THF, and 1,2-difluorobenzene, and insoluble in alcohols, ether, benzene, and alkanes.

The two L_nReCH_2 groups on each phosphorus atom of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7/8** are diastereotopic, and related to those on the other phosphorus atom by a C_2 axis. Thus, two sets of NMR signals were observed. For example, ^{13}C NMR spectra showed two signals for the Re*C*H_2P*C*H_2Re carbons, and ^1H NMR spectra four multiplets for the ReC*HH′*PC*H′′H′′′*Re protons. As illustrated with ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** in Figure 2 (top), ^{31}P NMR spectra exhibited two PPh_3 signals. For all tetrarhenium complexes, the ^{31}P NMR coupling patterns are best approximated by non-first-order AA′BB′ CC′ spin systems, with CC′ representing the phosphorus atoms of the $PCH_2(CH_2)_nCH_2P$ moiety. The apparent triplets of the PPh_3 groups of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** could be duplicated in simulations, and the broad singlet of the PCH_2 group is interpreted as an unresolved triplet. Various chemical shift trends are analyzed elsewhere.[10a]

Complexes ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7/8** were reacted with *t*BuOK under rigorous oxygen-free conditions. Workups gave the title ditertiary diphosphanes ($S_{Re}S_{Re}S_{Re}S_{Re}$)-{(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2)}$_2${$PCH_2(CH_2)_nCH_2P$}{(CH_2)-(Ph_3P)(ON)Re(η^5-C_5H_5)}$_2$ [n = 0/1, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9/10**][13] as highly air sensitive, analytically pure red powders in 92% and 62% yields. Solutions could be kept for several hours at room temperature under argon. In contrast, the related monorhenium monophosphanes (η^5-C_5H_5)Re-(NO)(PPh_3)(CH_2PR_2) are stable in air for several hours, with even solutions showing only minor decomposition.[4a] Complexes ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9/10** were characterized similarly to the others described above. The diastereotopic L_nReCH_2 groups gave separate NMR signals, as exemplified by the ^{31}P NMR spectrum of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9** in Figure 2. Mass spectra showed only oxidation products.

In principle, the diastereotopic L_nReCH_2 groups can be exchanged via a phosphorus inversion/bond rotation sequence. Inversion barriers for tertiary organophosphanes are typically 28–36 kcal mol^{-1} (120–150 kJ·mol^{-1}).[16] Thus, NMR spectra of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9** were recorded at elevated temperatures. However, no coalescence phenomena were observed in [D_8]toluene at 110 °C, conditions under which the complex has a half-life of ca. 10 min. From the frequency differences of the diastereotopic cyclopentadienyl (^1H, ^{13}C) and PPh_3 (^{31}P) groups, lower limits of 19.0–20.4 kcal mol^{-1} (79.4–85.5 kJ·mol^{-1}) could be calculated for the phosphorus inversion barrier ($\Delta G^{\ddagger}_{383\ K}$). This is much higher than the 14–16 kcal mol^{-1} typically found for analogous pyramidal metal phosphido complexes, L_nMPR_2.[17,18]

3. Derivatives of Tetrarhenium Diphosphanes and other Reactions: As shown in Scheme 1, when ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9** was worked up in air, the diphosphane dioxide ($S_{Re}S_{Re}S_{Re}S_{Re}$)-{(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2)}$_2$-{$PO(CH_2)_2PO$}{$(CH_2)(Ph_3P)(ON)$Re(η^5-C_5H_5)}$_2$ [($S_{Re}S_{Re}S_{Re}S_{Re}$)-**11**] was isolated in 95% yield. Alternatively, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7/8** were sequentially treated with *t*BuOK and the oxygen atom donor PhIO. Workups gave ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**11/12** in 72% and 62% yields, with the latter containing small amounts of Ph_3PO. Both complexes were yellow-orange powders that could be stored under ambient conditions for months without decomposition. As shown in Figure 2, the ^{31}P NMR signal of the PO group of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**11** was 53 ppm downfield of the corresponding signal in ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9**, and coupled to the phosphorus atoms of the PPh_3 groups [^3J(P,P) = 17 Hz].

Next, the preparation of rhodium chelate complexes of the tetrarhenium diphosphanes was investigated. Thus, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7/8** were sequentially treated with *t*BuOK and $[Rh(NBD)_2]^+$ PF_6^- under rigorous inert atmosphere conditions (NBD = norbornadiene). As shown in Scheme 1, workups gave the target complexes ($S_{Re}S_{Re}S_{Re}S_{Re}$)-[({(η^5-

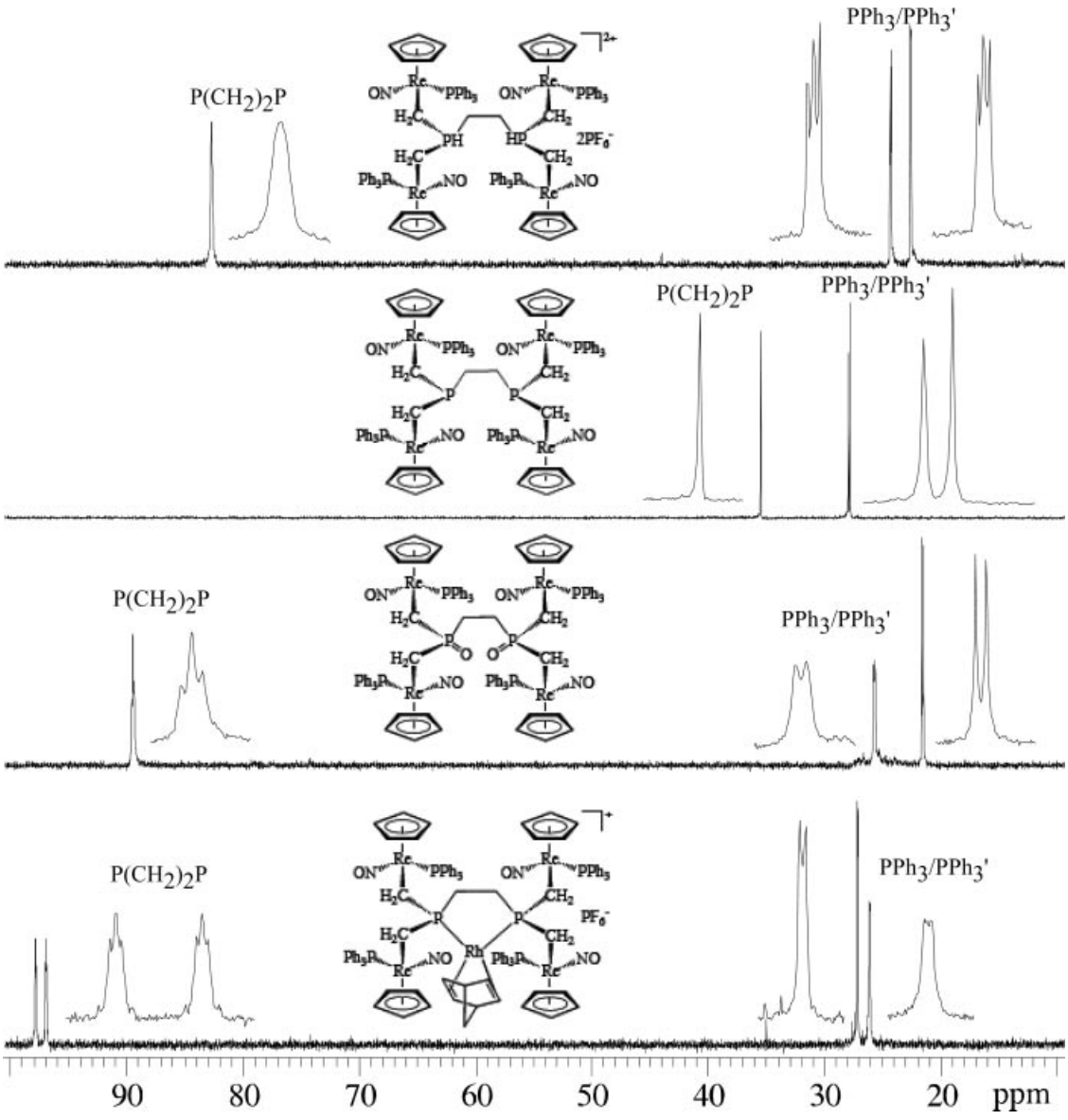
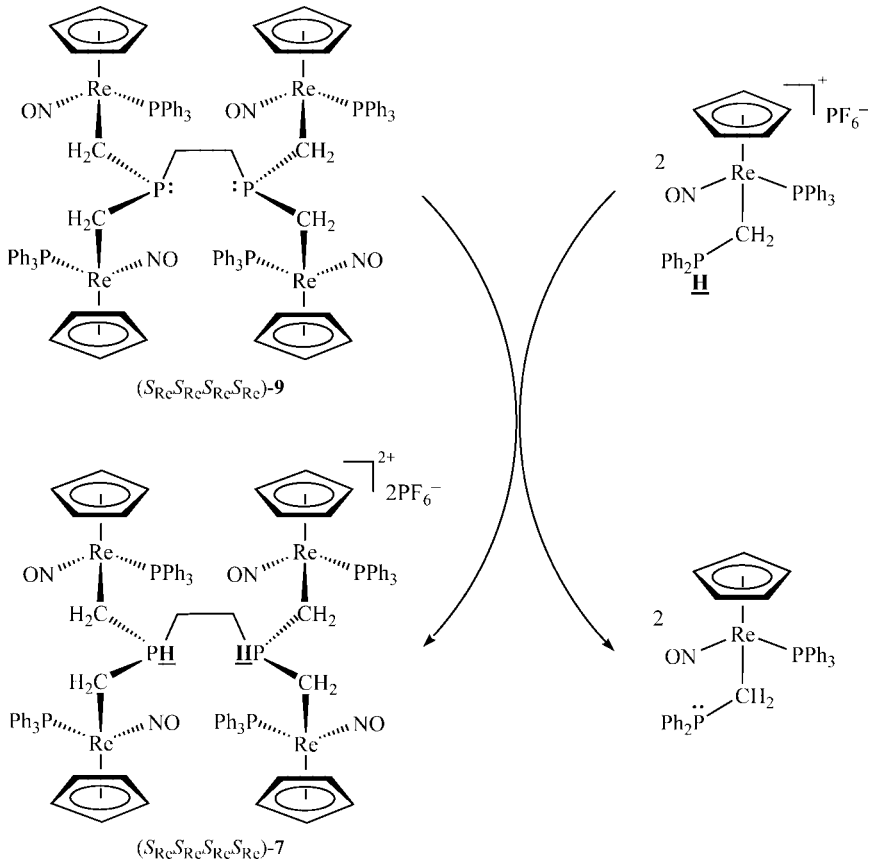


Figure 2. $^{31}P\{^{1}H\}$ NMR spectra of tetrarhenium complexes ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**, -**9**, -**11**, and -**13** (from top to bottom).

C_5H_5)Re(NO)(PPh_3)$(CH_2)\}_2\{PCH_2(CH_2)_nCH_2P\}\{(CH_2)$-$(Ph_3P)(ON)Re(\eta^5$-$C_5H_5)\}_2)Rh(NBD)]^+$ PF_6^- [n = 0/1, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13/14**] as analytically pure red-brown powders in 75% and 82% yields. The mass spectra exhibited molecular ions with the correct isotope distributions. The ^1H and ^{13}C NMR spectra showed diagnostic signals for the NBD ligand. As illustrated in Figure 2, ^{31}P spectra displayed rhodium couplings [^1J(P,Rh) = 150–142 Hz] that confirmed the P–Rh–P chelate. Chemical shift trends, including ^{31}P NMR ring size effects, are analyzed elsewhere.[10a]

Finally, we sought to probe the Brønsted basicities of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9/10** with respect to related monorhenium complexes. Thus, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**, the monorhenium phosphonium salt $[(\eta^5$-$C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2H)]^+$ PF_6^-,[4a] and *t*BuOK were combined in a 1:2:2 mol ratio in an NMR tube. After 1 h, all of the ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** remained. However, the monorhenium complex had been completely converted into the conjugate base (η^5-C_5H_5)Re-(NO)(PPh_3)(CH_2PPh_2). These data strongly suggest that the second L_nReCH_2 moiety on each phosphorus atom in ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9/10** further enhances the Brønsted basicity, and the equilibrium sketched in Scheme 3 can be formulated.

4. Catalysis: The tetrarhenium diphosphanes **9/10** were evaluated as ligands in several metal catalyzed transformations. Reactions previously examined with rhodium chelates of the monorhenium diphosphanes **II** (Figure 1)[2a,2b,2e] were studied first. Thus, the protected dehydroamino acids **15a**–**c** shown in Equation (1) of Scheme 4 were hydrogenated in the presence of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13** or -**14** that had been generated in situ from ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** or -**8**, *t*BuOK, and $[Rh(NBD)_2]^+$ PF_6^-. Reactions were complete over the course of 1–2 days at 75 °C under 8 bar of H_2. However, rhodium adducts of **II** were active at room temperature and under 1 bar of H_2. Furthermore, the enantioselectivities were poor, with the DMPP-type complex ($S_{Re}S_{Re}S_{Re}S_{Re}$)-



Scheme 3. Relative Brønsted basicities.

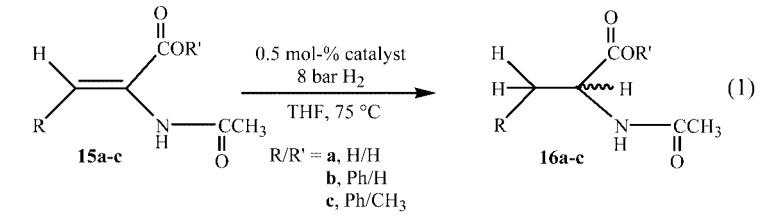
14 slightly better than the DMPE-type complex ($S_{Re}S_{Re}$-$S_{Re}S_{Re}$)-**13** (33–30% vs. 12% *ee*).

As shown in Equation (2) of Scheme 4, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13** was next evaluated as a catalyst for the hydrosilylation of propiophenone (**17**). Reactions with Ph_2SiH_2 were monitored by NMR, and required 6–14 days to reach 85–75% conversions. The silyl ether **18** was deprotected to the alcohol, which was racemic by chiral GC analysis. Under similar conditions, rhodium adducts of **II** gave complete reactions within 12 h, and *ee* values of 62–38%.[2e] Interestingly, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13** that had been isolated was less active than that generated in situ. Parallel experiments with Mes_2SiH_2 gave analogous results. This suggests that some of the activity associated with the catalysts generated in situ may arise from by-products, as opposed to ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13/14**.

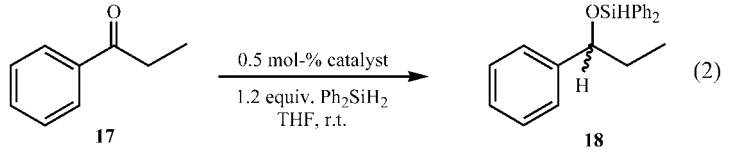
Equation (3) of Scheme 4 shows another type of rhodium-catalyzed reaction, the conjugate addition of an arylboronic acid to an enone.[19] These are commonly carried out in dioxane/water mixtures at 100 °C with catalysts generated in situ from Rh(acac)($H_2C{=}CH_2$)$_2$ and a chelating diphosphorus donor ligand. We first verified earlier reports that (*S*)-BINAP is an effective ligand for the addition of phenylboronic acid to 2-cyclohexen-1-one (**19**).[20] GC and HPLC analysis indicated the formation of 3-phenylcyclohexanone (**20**) in >99% yield and >99% *ee*. However, under analogous conditions, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9** and ($R_{Re}R_{Re}R_{Re}R_{Re}$)-**10** (generated in situ) gave **20** in only 8–7% yields (48–41% conversions) and 38–2% *ee*. The ligand (*R*)-**IIb** (Figure 1) was therefore tested, and afforded **20** in 30% yield (65% conversion) and 40% *ee*.

Many chiral chelating ligands have proven effective in palladium-catalyzed enantioselective allylic alkylations.[21] As shown in Equation (4) of Scheme 4, the condensation of dimethyl malonate with the allylic acetate **21** was probed using a standard set of conditions. Control experiments with racemic BINAP and (*S*)-BINAP gave the substitution product **22** in 61–47% yields (unoptimized) after flash chromatography. Analysis of the latter by chiral HPLC indicated a 94% *ee*. Analogous reactions with ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9** and ($R_{Re}R_{Re}R_{Re}R_{Re}$)-**10** gave **22** in 47–37% yields but *ee* values of only 2%. The ligand (*R*)-**IIb** afforded a 16% *ee*. Hence, the title ligands give disappointing *ee* values in all reactions assayed, as further detailed elsewhere.[10b] They can therefore be regarded as *un*privileged ligands,[22] and possible factors are analyzed below.

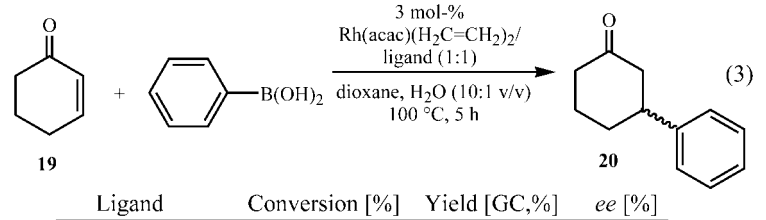
5. Structural Data: The crystal structure of a CH_2Cl_2 disolvate of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** was determined as summarized in Table 2 and the experimental section. The unit cell was tetragonal, with four molecules of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** and belonging to the space group $P4_22_12$. Key metrical parameters are summarized in Table 1. The structure of the dication is depicted in Figure 3, together with *one* of the two PF_6^- anions. The dication features a C_2 axis at the midpoint of the C3/C3A bond and perpendicular to the idealized P–C3–C3A–P plane. This exchanges pairs of atoms such as



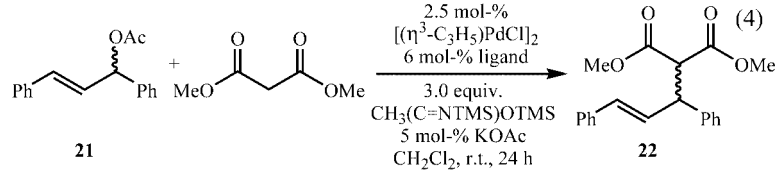
Catalyst	Starting material	Conversion [%]	*ee* [%]
($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13** (in situ)	**15b,c**	92-90	12
($S_{Re}S_{Re}S_{Re}S_{Re}$)-**14** (in situ)	**15a-c**	>99-94	33-30



Catalyst	Conversion [%]	*ee* [%]
($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13** (in situ)	86	0
($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13** (isolated)	32	0



Ligand	Conversion [%]	Yield [GC,%]	*ee* [%]
(*S*)-BINAP	100	>99	>99(*S*)
($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9**	41	7	2(*S*)
($R_{Re}R_{Re}R_{Re}R_{Re}$)-**10**	48	8	38(*R*)
(*R*)-**IIb**	65	30	40(*R*)



Ligand	Yield [isolated,%]	*ee* [%]
rac-BINAP	61	0
(*S*)-BINAP	47	94(*R*)
($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9**	37	2(*S*)
($R_{Re}R_{Re}R_{Re}R_{Re}$)-**10**	47	2(*R*)
(*R*)-**IIb**	45	16(*R*)

Scheme 4. Summary of catalytic reactions.

Re1/Re1A, Re2/Re2A, P3/P3A, and C3/C3A. Three of the fluorine atoms of the PF_6^- ion in Figure 3 are disordered (F33, F34, F35), but only the average positions are shown.

The most striking feature of the dication is the grouping of the bulky PPh_3 ligands in the same hemisphere. An up/down motif that would minimize steric interactions might have been intuitively expected. Consequently, a cavity is defined by the four cyclopentadienyl rings in the opposite hemisphere. This provides a pocket for the disordered PF_6^- anion. The P30–F34 bond is directed towards the PCH_2CH_2P bridge, and forms F–H–P hydrogen bonds with both PH groups (2.55 Å from the average position for F34 to the calculated hydrogen positions). The non-disordered fluorine atoms F31 and F31A form very slightly longer F–H–P hydrogen bonds with H3 and H3A, respectively.

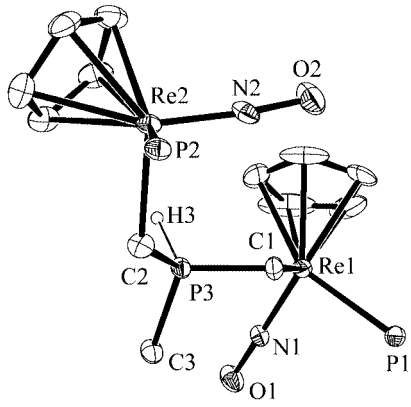
The structures of many related molecules with $ReCH_2X$ linkages have been studied in solution and the solid state.[3,14,23–26] The Re–CH_2 and CH_2–X conformations often have an important bearing upon diastereomer equilibria and reaction stereoselectivity. Thus, Newman-type pro-

Table 1. Key distances [Å] and angles [°] of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**·$(CH_2Cl_2)_2$.

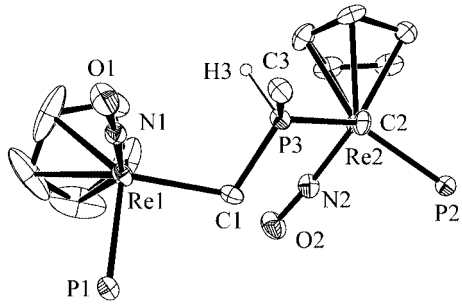
Re1–C1	2.195(8)
Re1–N1	1.744(6)
Re1–P1	2.352(2)
C1–P3	1.777(7)
N1–O1	1.208(7)
Re1–Cp1(centr)	1.964
Re2–C2	2.183(7)
Re2–N2	1.747(6)
Re2–P2	2.347(2)
C2–P3	1.764(7)
N2–O2	1.219(8)
Re2–Cp2(centr)	1.969
H3–F34/H3A–F34	2.55[a]
H3–F31A/H3A–F31	2.64
Re1–N1–O1	174.5(6)
N1–Re1–P1	90.8(2)
N1–Re1–C1	101.6(3)
C1–Re1–P1	88.2(2)
Re1–C1–P3	111.2(4)
Re2–N2–O2	173.6(6)
N2–Re2–P2	92.0(2)
N2–Re2–C2	100.0(3)
C2–Re2–P2	86.4(2)
Re2–C2–P3	111.6(4)
C1–P3–C2	116.6(4)
C1–P3–C3	106.8(4)
C2–P3–C3	111.5(4)
P3–C3–C3A	112.9(6)
N1–Re1–C1–P3	–54.8(4)
P1–Re1–C1–P3	–145.2(4)
N2–Re2–C2–P3	–56.1(5)
P2–Re2–C2–P3	–147.5(4)
Re1–C1–P3–C2	–165.5(4)
Re1–C1–P3–C3	69.1(5)
Re2–C2–P3–C1	74.0(5)
Re2–C2–P3–C3	–162.0(4)
C1–P3–C3–C3A	159.8(3)
C2–P3–C3–C3A	31.3(4)
P3–C3–C3A–P3A	157.0(4)

[a] Average involving two disordered positions of F34.

jections down the C1–Re1 and C2–Re2 bonds of the dication are depicted in Figure 4. In accord with all previous findings,[3,14,23–25] the X group (P3) is *roughly anti* to the bulky PPh_3 ligand, as quantified by the Ph_3P–Re–CH_2–P



V



VI

Figure 4. Partial views of the dication of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** down the C1–Re1 (**V**) and C2–Re2 (**VI**) bonds.

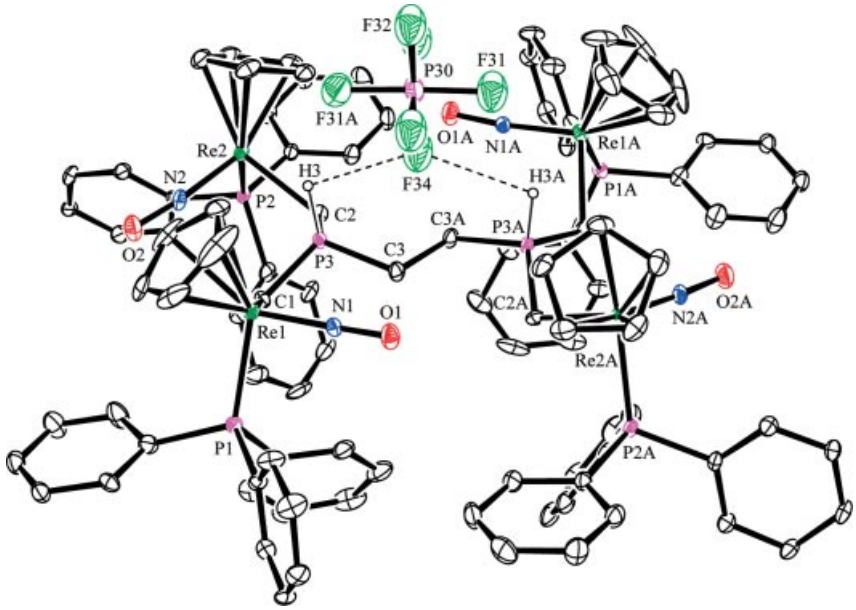


Figure 3. Molecular structure of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**·$(CH_2Cl_2)_2$ with solvate molecules and one PF_6^- anion omitted.

torsion angles (**V**, –145.2°; **VI**, –147.5°). This places the X group between the smaller cyclopentadienyl and nitrosyl ligands, which is the least congested interstice on rhenium.

Complexes are also known in which the X group bears three sterically differentiated substituents (L/M/S). Typically, the largest group (L) exhibits a torsion angle near 180°, such that the Re–CH_2 and X–L bonds are *anti*.[3,23–25] This is evident in the partial structure **V**, where there is a large CH_2Re substituent and a Re1–C1–P3–C2 torsion angle of –165.5. The overall result is a "*W*"-shaped five-atom Ph_3P–*Re*–CH_2–*P*–CH_2Re conformation. However, the situation in **VI** is different. Now the medium CH_2CH_2 group occupies the terminus of the "*W*"-segment (P2–Re2–C2–P3–C3). The large CH_2Re substituent is roughly gauche to the Re2–C2 bond, as reflected by a Re2–C2–P3–C1 torsion angle of 74.0°. Possible implications are analyzed below.

In efforts to better understand the modest enantioselectivities in Scheme 4, crystal structures of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13/14** were sought. All attempts to grow suitable single crystals were unsuccessful. Racemates are often easier to crystallize than enantiopure compounds. However, as easily seen from Scheme 2, the use of racemic rhenium building blocks would give intractable mixtures of diastereomers. Thus, the enantiomers ($S_{Re}S_{Re}S_{Re}S_{Re}$)- and ($R_{Re}R_{Re}R_{Re}R_{Re}$)-**7** were independently synthesized, mixed in a 1:1 ratio, and treated with *t*BuOK and then $[Rh(NBD)_2]^+$ PF_6^-. However, no crystals of racemic **13** could be obtained, even after adding a 10-fold excess of the BAr_F^- anion.

Discussion

1. Design Elements: Scheme 1 establishes the ready availability of a novel new class of diphosphane ligands that contain four symmetrically-disposed chiral-at-rhenium substituents and are based upon 1,ω-bis(dimethylphosphanyl)-alkane carbon skeletons. This methodology can likely be extrapolated to many types of derivatives, such as pentamethylcyclopentadienyl analogs or species with still longer methylene bridges. The overall yields of the ditertiary diphosphonium salts ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7/8** from commercially available $Re_2(CO)_{10}$ (25%/22%) are similar to those of **II-a**,**b**,[2b] which compares well with most of the widely applied chiral ferrocene-based ligands.[5] Since ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7/8** can be stored for indefinite periods, they represent convenient depots for the very air sensitive title diphosphanes ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9/10**.

The title diphosphanes can also be viewed in the evolutionary context of Figure 5. The structure **VII** embodies the essential features of DIOP, the classic chiral diphosphane introduced by Kagan in 1971.[27] The stereocenters can be moved closer to the phosphorus atoms as in **VIII**, a well-known example of which is CHIRAPHOS.[28] In **IX**, the phosphorus atoms become stereocenters, as exemplified by DIPAMP, another very early chiral diphosphane.[29] In later efforts, stereocenters were introduced exocyclic to the chelate backbone. Structure **X** corresponds to the DuPHOS ligand family,[30] in which the phosphorus atoms are no longer stereogenic. Motif **XI** can be viewed as a hybrid with both phosphorus and exocyclic stereocenters, and corresponds to **IIIb** in Figure 1. Finally, **XII** represents our new family of chiral diphosphanes.

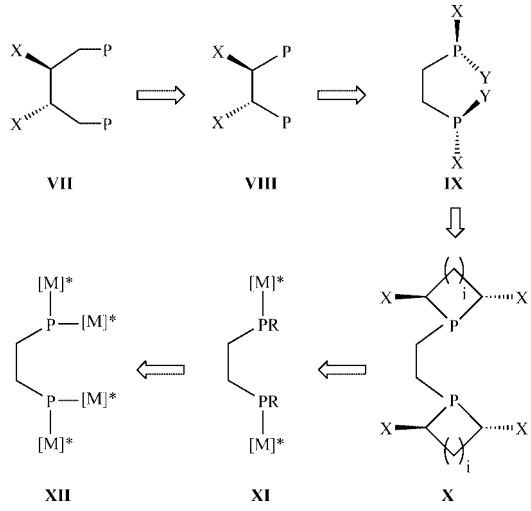


Figure 5. Motifs for chiral chelating diphosphanes. [M]* = "chiral-at-metal" group.

Surprisingly, we have not been able to locate any reports of diphosphanes with analogous arrays of four homochiral substituents. The most readily envisioned cases would involve substituents derived from the chiral pool. Unlike most chiral pool compounds, both enantiomers of the chiral rhenium building blocks are equally available. Therefore, both enantiomers of our ligands are easily accessed. There are also possibilities for other diastereomers, all of which are depicted schematically in Figure 6 using standard formalisms for systems with constitutionally equal stereocenters.[31] The shaded and unshaded circles in formulae **i**–**vii** denote mirror images of the chiral fragments. There are six chiral stereoisomers (**i**–**iii** with enantiomers a/b) and four *meso*-stereoisomers (**iv**–**vii**). Of the latter, **iv** and **v** possess a center of inversion (*i*) and two mirror planes, whereas **vi** and **vii** have only one mirror plane.

In seven of the ten isomers, at least one phosphorus atom is pseudoasymmetric.[32] These are designated with P_r and P_s chirality descriptors in Figure 6.[31] The many consequences of pseudoasymmetric atoms have been analyzed in detail. One requirement is that the configurations, here at phosphorus, remain invariant upon reflection through a mirror plane (e. g., **iia** vs. **iib**; **iiia** vs. **iiib**). Those in *meso* **iv**–**vi** are stereogenic but achirotopic since they lie on a local symmetry plane and permuting two rhenium fragments generates another *meso* form. Formula **ia** corresponds to the isomers synthesized in Scheme 1, ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9/10**. For illustration purposes, **v** would correspond to the structure shown in Figure 6.

Practical syntheses of these other diastereomers will require some serendipity, but should be possible. Consider the diastereomers ($S_{Re}S_{Re}$,$R_{Re}R_{Re}$)-**3′** and ($S_{Re}R_{Re}$)-**3′** in Scheme 2, which are easily separated. Subsequent reaction of the diphosphane corresponding to ($S_{Re}R_{Re}$)-**3′** with

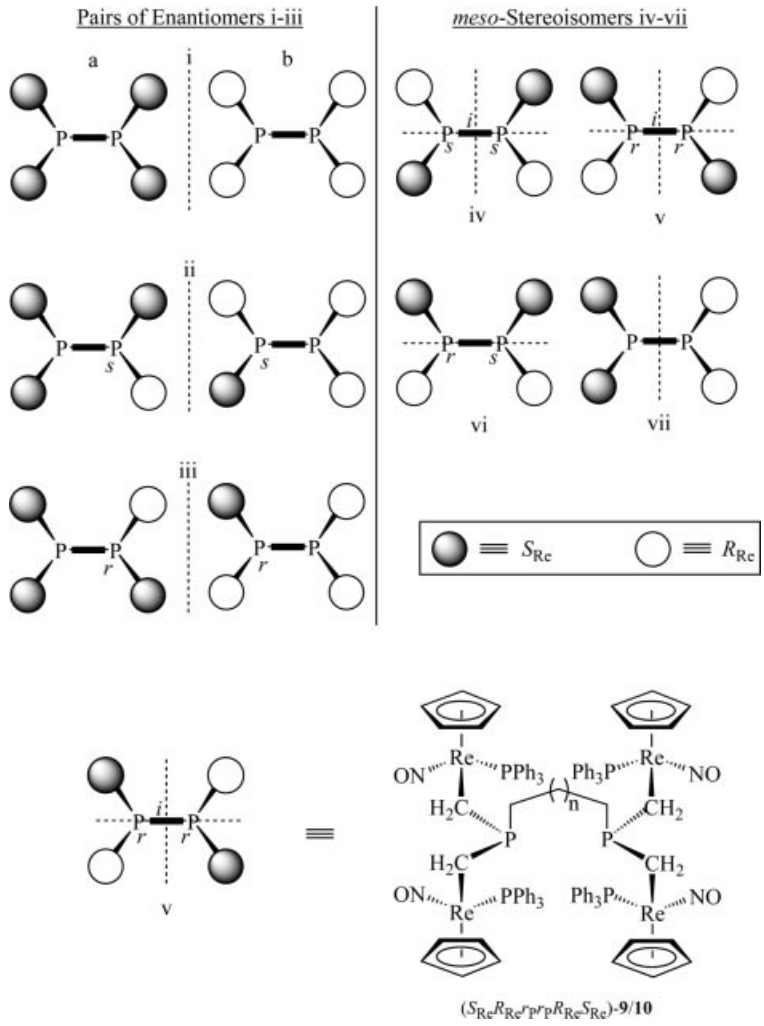
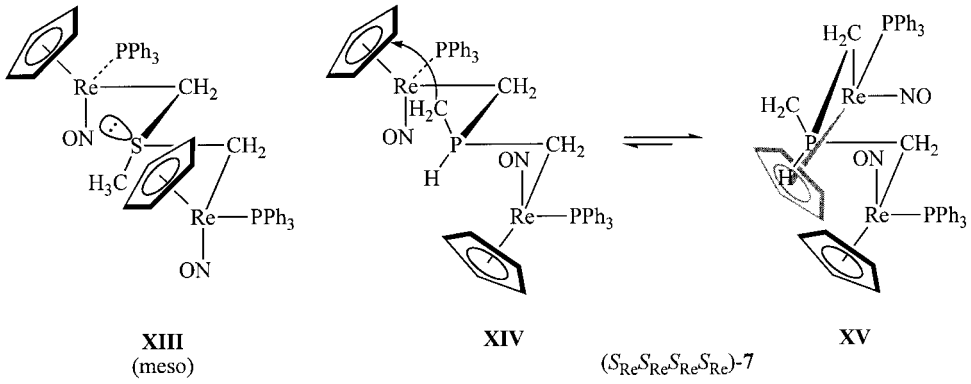


Figure 6. Possible stereoisomers of tetrarhenium diphosphanes. The descriptors *r* and *s* denote pseudoasymmetric phosphorus atoms, and *i* a center of inversion.

enantiopure rhenium methylidene complex **2** would yield only two non-racemic diastereomers, one of the type **ii** and the other of the type **iii**. This likely represents a tractable separation, and would allow all chiral stereoisomers to be secured. On the other hand, an analogous sequence with ($S_{Re}S_{Re}$,$R_{Re}R_{Re}$)-**3′** would be less useful, resulting in the known diastereomer **i**, and as many as three *meso* diastereomers (**iv**–**vi**).

2. Structure and Catalysis: The congested nature of the tetrarhenium systems is obvious in the crystal structure of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** (Figure 3). Despite this, the diphosphane ligands ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9/10** and $[Rh(NBD)_2]^+$ PF_6^- react to form the stable rhodium chelates ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13/14**. Bulky ligands and/or sterically restricted binding pockets can be favorable for asymmetric catalysis. However, the rates and *ee* values for enantioselective hydrogenations and hydrosilylations (Scheme 4) are much lower than those with analogous rhodium chelates of the diphosphanes **IIa**,**b** (Figure 1). One possible explanation is that the ligands in ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13/14** are simply too voluminous to allow effective catalysis. The residual activities might be due in part to achiral rhodium-containing decomposition products, which would be consistent with the modest *ee* values. One probe would be to test related complexes with only two chiral rhenium fragments, such as could be derived from **IIIb** (Figure 1). However, as noted above, multiple diastereomers are possible due to the phosphorus stereocenters.

The performances of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9** and ($R_{Re}R_{Re}R_{Re}R_{Re}$)-**10** in rhodium-catalyzed conjugate additions of aryl boronic acids and palladium-catalyzed allylic alkylations are also disappointing (Scheme 4). In both reactions, catalysts are commonly generated in situ, and there is the question whether analogous species are formed from ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9** and ($R_{Re}R_{Re}R_{Re}R_{Re}$)-**10**. The aqueous conditions associated with the former reaction are a possible complicating factor. The diphosphane **IIb**, which we view as sterically less congested, also gives *ee* values distinctly lower than those of benchmark ligands. This leads us to believe that both classes of ligands are simply not



XIII (meso) **XIV** **XV** ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**

Figure 7. Conformations of compounds with Ph_3P–Re–CH_2–X–CH_2–Re–PPh_3 linkages.

competitive with existing systems. However, we note in passing that a DIOP derivative has been prepared with four P-ferrocenyl substituents.[33] The rhodium chelate catalyzes the hydrogenation of itaconic acid with reasonable enantioselectivities (40% *ee*).

The conformational features of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** highlighted in Figure 4 can be compared to those in related complexes. The crystal structure of the *meso* sulfonium salt ($S_{Re}R_{Re}$)-[{(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2)}$_2$(SCH_3)]$^+$ I^- has been determined, and the conformation of the cation is depicted in **XIII** in Figure 7.[23] The seven-atom P–Re–CH_2–S–CH_2–Re–P linkage adopts an extended "*VVV*"-shape, with *anti* relationships between the bulkiest groups (*Ph*$_3$*P*–Re vs. CH_2–*S* and *Re*–CH_2 vs. S–*C*H_2*Re*). The sulfur atom is a pseudoasymmetric, and can assume a "matched" configuration such that the small lone pair is *syn* to both larger cyclopentadienyl ligands, and the medium CH_3 substituent is *syn* to both smaller nitrosyl ligands.

Since the rhenium atoms in ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** have the same configuration, a conformation analogous to that in **XIII** is not possible. The conformation **XIV** would maintain *anti* relationships between the bulkiest groups (*Ph*$_3$*P*–Re vs. CH_2–*P* and *Re*–CH_2 vs. P–*C*H_2*Re*) and a "*VVV*" shape. However, now the medium *C*H_2CH_2 substituent on phosphorus is forced into a *syn* relationship with one of the larger cyclopentadienyl ligands. This unavoidable "mismatch" raises the steric energy, and the alternative conformation **XV** is found in the crystal instead. Here, the ReCH_2–P bond has been rotated to bring the *Re*–CH_2 group *anti* to the P–*C*H_2CH_2 group, as in the partial structure **VI** (Figure 4). We therefore speculate that diastereomers of **7/8** of the types **ii** or **iii** (Figure 6), in which the type of "matched" relationship in **XIII** can be maintained on one of the two phosphorus atoms, may afford less congested and therefore superior catalysts.

Despite the inauspicious beginning in Scheme 4, we continue to believe that the tetrarhenium complexes in Scheme 1 should have useful applications in enantioselective catalysis, especially for reactions that involve fundamentally different mechanisms. For example, chiral phosphane oxides, diphosphane dioxides, and related species are very useful nucleophilic catalysts for enantioselective condensations of appropriate allylsilanes with carbonyl compounds.[34] High *ee* values can be obtained, and ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**11/12** represent attractive candidates for such chemistry. Furthermore, we have recently found that the rhenium-containing monophosphane (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2) effects enantioselective Baylis–Hillman reactions.[35] Thus, this general class of complexes has a promising future in catalysis, as will be detailed in future reports from this laboratory.

3. Conclusion

The types of chelating ligands available that contain the chiral rhenium fragment **I** have been significantly augmented by the new 1,2- and 1,3-diphosphanes ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9/10**. These electron-rich, DMPE/DMPP derivatives are efficiently synthesized as outlined in Scheme 1, and are readily converted to diphosphane dioxides and rhodium chelate complexes. However, they have not proved to be effective ligands for metal-catalyzed enantioselective reactions in the cases examined to date. This may be due to their considerable bulk, as reflected by the crystal structure of a diprotonated derivative. Nonetheless, metal-containing ligands continue to make a major impact in enantioselective catalysis,[1,5] and additional applications of the compounds reported herein remain under investigation.

Experimental Section

General: Most general procedures, chemical purifications, and instruments were identical with those in a recent full paper.[4a] Further information is provided elsewhere.[10] HPLC was conducted using a ThermoQuest instrument package (pump/autosampler/detector P4000/AS 3000/UV 6000LP). Solvents were freshly dried before use, as detailed in the supporting information; for supporting information see also the footnote on the first page of this article. Purification steps new to this study: 2-cyclohexen-1-one (95+%, Aldrich), vacuum-distilled; H_2O (reaction cosolvent), freeze-pump-thaw degassed (3 cycles); KOAc (Merck), dried 24 h at 120 °C.

[(η^5-C_5H_5)Re(NO)(PPh_3){$CH_2PH_2CH_2(CH_2)_nCH_2PH_2CH_2$}-($Ph_3P$)(ON)Re($\eta^5$-$C_5H_5$)]$^{2+}$ 2X$^-$ (*n*/X = 0/PF_6, 3; 0/BF_4, 3′; 1/PF_6, 4): (**A**) A Schlenk flask was charged with (*S*)-**1** (0.327 g,

0.585 mmol)[9,36,37] and CH_2Cl_2 (15 mL), and was cooled to –60 °C. Then Ph_3C^+ PF_6^- (0.250 g, 0.644 mmol) was added with stirring. After 30 min, $PH_2(CH_2)_2PH_2$ (0.0275 g, 0.293 mmol) was added by syringe to the yellow solution, which turned orange. After 30 min, the cold bath was removed. Some precipitate formed. The suspension was concentrated by oil pump vacuum to ca. 10 mL. After 5 h, the precipitate was collected by filtration and dried by oil pump vacuum. The product was dissolved in a minimum of boiling CH_2Cl_2 and stored at –32 °C. After 24 h, the fine yellow needles were collected by filtration and dried by oil pump vacuum to give ($S_{Re}S_{Re}$)-**3** (0.286 g, 0.191 mmol, 65%). M. p. 160–162 °C (dec). $C_{50}H_{52}F_{12}N_2O_2P_6Re_2$ (1499.2): calcd. C 40.05, H 3.50, N 1.87; found C 40.06, H 3.50, N 1.87. IR (thin film [cm^{-1}]): $\tilde{\nu}$ = 1650 (s, NO), 830 (s, PF). ^1H NMR (400 MHz, CD_3NO_2): PPh_3 at δ = 7.57–7.40 (m, 30 H); 6.63/6.09 [2 dm, ^1J(H,P) = 480/496 Hz, 4 H, PHH′], 5.36 (s, 10 H, C_5H_5), 2.27 (m, 4 H, PCH_2C), 2.03 (m, 2 H, ReC*H*H′), 1.86 (m, 2 H, ReCH*H*′). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_3NO_2): PPh_3 at δ = 135.2 [d, ^1J(C,P) = 53 Hz, *i*], 134.8 [d, ^2J(C,P) = 11 Hz, *o*], 132.5 (s, *p*), 130.3 [d, ^3J(C,P) = 9 Hz, *m*]; 92.2 (s, C_5H_5), 18.9 (m, P*C*H_2C), –43.5 (m, $ReCH_2$). $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_3NO_2): δ = 21.0 [d, ^3J(P,P) = 18 Hz, PPh_3], 1.5 {br. s [t, ^1J(P,H) = 488 Hz without ^1H decoupling], PCH_2}, –143.0 [sept, ^1J(P,F) = 705 Hz, PF_6]. MS (FAB, 3-NBA): *m*/*z* (%) = 1353 (2) $[M + PF_6]^+$, 1207 (6) $[M – H]^+$, 558 (100) $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+$.

(**B**) Complex **1** (0.551 g, 0.987 mmol),[9,36,37] CH_2Cl_2 (20 mL), Ph_3C^+ BF_4^- (0.363 g, 1.10 mmol), and $PH_2(CH_2)_2PH_2$ (0.050 g, 0.53 mmol) were combined in a procedure analogous to **A**. After 30 min, the cold bath was removed. Some precipitate formed. After 2 h, the yellow powder was collected by filtration, washed with CH_3CN (2×5 mL), and dried by oil pump vacuum to give ($S_{Re}R_{Re}$)-**3′** (0.191 g, 0.138 mmol, 28%). The volatiles were removed from the filtrate by oil pump vacuum. The residue was dissolved in a minimum of CH_2Cl_2 and a layer of ether (30 mL) was gently added. After 2 days, the supernatant was decanted and the orange powder dried by oil pump vacuum to give ($S_{Re}S_{Re}$,$R_{Re}R_{Re}$)-**3′** (0.259 g, 0.188 mmol, 38%).

Data for ($S_{Re}R_{Re}$)-3′: M. p. 152–154 °C (dec). $C_{50}H_{52}B_2F_8N_2O_2P_4Re_2$ (1382.9): calcd. C 44.43, H 3.79, N 2.03; found C 43.20, H 3.68, N 2.05. IR (thin film [cm^{-1}]): $\tilde{\nu}$ = 1638 (s, NO). ^1H NMR (400 MHz, [D$_6$]DMSO): PPh_3 at δ = 7.50–7.48 (m, 18 H), 7.28–7.24 (m, 12 H); 5.35 (s, 10 H, C_5H_5), 3.95 (br. s, 4 H, PH_2), 2.08 (m, 4 H, PCH_2C), 1.64 (m, 4 H, $ReCH_2$). $^{13}C\{^1H\}$ NMR (100.5 MHz, [D$_6$]DMSO): PPh_3 at δ = 133.8 [d, ^1J(C,P) = 53 Hz, *i*], 133.0 [d, ^2J(C,P) = 11 Hz, *o*], 130.9 (s, *p*), 129.0 [d, ^3J(C,P) = 9 Hz, *m*]; 90.7 (s, C_5H_5), 17.5 (m, P*C*H_2C), –37.1 (m, $ReCH_2$). $^{31}P\{^1H\}$ NMR (161.8 MHz, [D$_6$]DMSO): δ = 21.5 (br. s, PPh_3), 3.4 (br. m, PCH_2), –143.2 [sept, ^1J(P,F) = 705 Hz, PF_6].

Data for ($S_{Re}S_{Re}$,$R_{Re}R_{Re}$)-3′: M. p. 171–174 °C (dec). $C_{50}H_{52}B_2F_8N_2O_2P_4Re_2$ (1382.9): calcd. C 43.43, H 3.79, N 2.03; found C 43.50, H 3.75, N 1.92. IR (thin film [cm^{-1}]): $\tilde{\nu}$ = 1652 (s, NO). ^1H NMR (400 MHz, CD_3CN): PPh_3 at δ = 7.52–7.47 (m, 30 H); 6.60/6.02 [2 dm, ^1J(H,P) = 480/492 Hz, 4 H, PHH′], 5.30 (s, 10 H, C_5H_5), 2.08 (m, 4 H, PCH_2C), 1.80 (m, 2 H, ReC*H*H′), 1.65 (m, 2 H, ReCH*H*′). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_3CN): PPh_3 at δ = 135.1 [d, ^1J(C,P) = 53 Hz, *i*], 134.5 [d, ^2J(C,P) = 9 Hz, *o*], 132.0 (s, *p*), 130.0 [d, ^3J(C,P) = 9 Hz, *m*]; 91.9 (s, C_5H_5), 18.4 (m, P*C*H_2C), –43.5 (m, $ReCH_2$). $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_3CN): δ = 21.0 (br. s, PPh_3), 3.1 (br. s, PCH_2), –143.2 [sept, ^1J(P,F) = 705 Hz, PF_6].

(**C**) Complex (*R*)-**1** (0.871 g, 1.56 mmol),[9,36,37] CH_2Cl_2 (35 mL), Ph_3C^+ PF_6^- (0.666 g, 1.72 mmol), and $PH_2(CH_2)_3PH_2$ (0.0926 g, 0.857 mmol)[11] were combined in a procedure analogous to **A**. A similar workup gave ($R_{Re}R_{Re}$)-**4** as a yellow microcrystalline powder (1.368 g, 0.904 mmol, 58%). M. p. 154–155 °C (dec). $C_{51}H_{54}F_{12}N_2O_2P_6Re_2$ (1513.2): calcd. C 40.48, H 3.60, N 1.85; found C 40.24, H 3.41, N 1.68. IR (thin film [cm^{-1}]): $\tilde{\nu}$ = 1652 (s, NO), 836 (s, PF). ^1H NMR (400 MHz, CD_3NO_2): PPh_3 at δ = 7.57–7.39 (m, 30 H); 6.59/6.04 [2 dm, ^1J(H,P) = 476/468 Hz, 4 H, PHH′], 5.36 (s, 10 H, C_5H_5), 2.25 (m, 6 H, $CH_2CH_2CH_2$), 2.02 (m, 2 H, ReC*H*H′), 1.89 (m, 2 H, ReCH*H*′). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_3NO_2): PPh_3 at δ = 135.4 [d, ^1J(C,P) = 53 Hz, *i*], 134.9 [d, ^2J(C,P) = 9 Hz, *o*], 132.5 (s, *p*), 130.3 [d, ^3J(C,P) = 10 Hz, *m*]; 92.3 (s, C_5H_5), 24.1 [dd, ^1J(C,P) = 39, ^3J(C,P) = 15 Hz, P*C*H_2C], 18.9 (s, C*C*H_2C), –43.3 (m, $ReCH_2$). $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_3NO_2): δ = 21.1 [d, ^3J(P,P) = 16 Hz, PPh_3], 0.1 [d, ^3J(P,P) = 16 Hz, PCH_2], –143.2 [sept, ^1J(P,F) = 706 Hz, PF_6]. MS (FAB, 3-NBA): *m*/*z* (%) = 1367 (10) $[M + PF_6]^+$, 1221 (10) $[M – H]^+$, 558 (100) $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+$.

$[\{(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)\}_2\{PHCH_2(CH_2)_nCH_2PH\}\text{-}\{(CH_2)(Ph_3P)(ON)Re(\eta^5\text{-}C_5H_5)\}_2]^{2+}$ $2PF_6^-$ (n = 0/1, 7/8): (**A**) A Schlenk flask was charged with ($S_{Re}S_{Re}$)-**3** (0.831 g, 0.554 mmol) and THF (50 mL). Then *t*BuOK (1.0 M in THF; 1.39 mL, 1.39 mmol) was added dropwise with stirring. After 30 min, the solvent was removed by oil pump vacuum. The residue was extracted with CH_2Cl_2 (30 mL). The extract was filtered through a Celite plug (2×3 cm, CH_2Cl_2 rinses). A Schlenk tube was charged with (*S*)-**1** (0.650 g, 1.16 mmol)[9,36,37] and CH_2Cl_2 (30 mL), and was cooled to –60 °C. Then Ph_3C^+ PF_6^- (0.497 g, 1.28 mmol) was added with stirring. After 30 min, the Celite filtrate was added via cannula along the wall of the tube, such that it cooled before reaching the solution. The cold bath was then removed. After 3 h, the mixture was filtered through a Celite plug (4×5 cm). The filtrate was concentrated by oil pump vacuum to ca. 15 mL and a layer of ether (ca. 50 mL) was added. After 48 h, the red prisms were isolated by decantation of the supernatant and dried under a N_2 stream to give ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**·$(CH_2Cl_2)_2$ (1.352 g, 0.486 mmol, 88%).[38] M. p. 288 °C (dec). $C_{98}H_{94}F_{12}N_4O_4P_8Re_4\cdot(CH_2Cl_2)_2$ (2782.3): calcd. C 43.17, H 3.55, N 2.01; found C 43.38, H 3.70, N 2.01. IR (thin film [cm^{-1}]): $\tilde{\nu}$ = 2015 (w, PH), 1633 (s, NO), 830 (s, PF). ^1H NMR (400 MHz, CD_3NO_2): PPh_3 at δ = 7.66–7.14 (m, 60 H); 6.35 [dt, ^1J(H,P) = 472, ^3J(P,P) = 13 Hz, 2 H, PH], 5.34 (s, 10 H, C_5H_5), 5.32 (s, 4 H, CH_2Cl_2), 5.21 (s, 10 H, $C_5H'_5$), CH_2 at 2.61, 2.38, 1.98, 1.78, 1.64, 1.52 (6 m, 12 H). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_3NO_2): PPh_3 at δ = 135.8 [d, ^1J(C,P) = 54 Hz, *i*], 134.9 [d, ^2J(C,P) = 10 Hz, *o*], 134.7 [d, ^2J(C,P) = 10 Hz, *o′*], 132.6 (s, *p*), 132.4 (s, *p′*), 130.4 [d, ^3J(C,P) = 10 Hz, *m*], 130.2 [d, ^3J(C,P) = 10 Hz, *m′*]; 92.8 (s, C_5H_5), 92.5 (s, C′$_5H_5$), 53.8 (s, CH_2Cl_2), 21.7 [d, ^1J(C,P) = 34 Hz, P*C*H_2C], –27.4 (m, $ReCH_2$), –31.5 [d, ^1J(C,P) = 34 Hz, ReC′H_2]. $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_3NO_2): δ = 80.0 {br. s [d, ^1J(P,H) = 472 Hz without ^1H decoupling], PCH_2}, 23.3 [apparent t, ^3J(P,P) = 12 Hz, PPh_3], 21.6 [apparent t, ^3J(P,P) = 10 Hz, P′Ph_3], –142.8 [sept, ^1J(P,F) = 705 Hz, PF_6]. MS (FAB, 3-NBA): *m*/*z* (%) = 2467 (12) $[M + PF_6]^+$, 2321 (2) $[M – H]^+$, 558 (100) $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+$.

(**B**) Complex ($R_{Re}R_{Re}$)-**4** (1.311 g, 0.866 mmol), THF (60 mL), *t*BuOK (1.0 M in THF; 2.17 mL, 2.2 mmol), (*R*)-**1** (1.016 g, 1.82 mmol),[9,36,37] CH_2Cl_2 (50 mL), and Ph_3C^+ PF_6^- (0.740 g, 1.91 mmol) were combined in a procedure analogous to **A**. A similar workup in which the product was collected by filtration, washed with ether (2×10 mL), and dried by oil pump vacuum gave ($R_{Re}R_{Re}R_{Re}R_{Re}$)-**8**·$(CH_2Cl_2)_2$ as a yellow-orange powder (1.976 g, 0.752 mmol, 87%).[38] M. p. 242 °C (dec). $C_{99}H_{96}F_{12}N_4O_4P_8Re_4\cdot(CH_2Cl_2)_2$ (2796.3): calcd. C 43.38, H 3.63, N 2.00; found C 42.94, H 3.58, N 1.90. IR (thin film [cm^{-1}]): $\tilde{\nu}$ = 2015 (w, PH), 1633 (s,

NO), 830 (s, PF). ^{1}H NMR (400 MHz, $CDCl_3$): PPh_3 at δ = 7.41–7.20 (m, 60 H); 6.08 [dm, ^1J(H,P) = 460 Hz, 2 H, PH], 5.32 (s, 4 H, CH_2Cl_2), 5.19 (s, 10 H, C_5H_5), 5.15 (s, 10 H, $C_5H'_5$), CH_2 at 2.15–1.91 (m, 8 H), 1.52–1.38 (m, 6 H). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_3NO_2): δ = PPh_3 at 135.1 [d, ^1J(C,P) = 46 Hz, *i*], 134.5 [d, ^1J(C,P) = 47 Hz, *i'*], 134.0 [d, ^2J(C,P) = 10 Hz, *o*], 139 [d, ^2J(C,P) = 11 Hz, *o'*], 131.3 [d, ^4J(C,P) = 2 Hz, *p*], 131.2 [d, ^4J(C,P) = 2 Hz, *p'*], 129.4 [d, ^3J(C,P) = 10 Hz, *m*], 129.2 [d, ^3J(C,P) = 10 Hz, *m'*]; 91.4 (s, C_5H_5), 91.1 (s, C'_5H_5), 53.8 (s, CH_2Cl_2), 28.9 [d, ^1J(C,P) = 14 Hz, P*C*H$_2$C], 28.5 [d, ^2J(C,P) = 9 Hz, C*C*H$_2$C], –27.3 [d, ^1J(C,P) = 21 Hz, ReCH$_2$], –32.6 [d, ^1J(C,P) = 39 Hz, ReC′H$_2$]. $^{31}P\{^1H\}$ NMR (161.8 MHz, CD_3NO_2): δ = 72.1 [apparent t, ^3J(P,P) = 16 Hz, PCH$_2$], 23.3 [d, ^3J(P,P) = 14 Hz, PPh_3], 22.6 [d, ^3J(P,P) = 18 Hz, P′Ph$_3$], –142.3 [sept, ^1J(P,F) = 718 Hz]. MS (FAB, 3-NBA): *m/z* (%) = 2337 (2) $[M - H]^+$, 558 (100) $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+$.

{(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_2$)}$_2${PCH$_2$(CH$_2$)$_n$CH$_2$P}{(CH$_2$)(Ph$_3$P)(ON)Re(η^5-C$_5$H$_5$)}$_2$ (*n* = 0/1, 9/10): (**A**) A glass vial was charged with ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**·$(CH_2Cl_2)_2$ (0.180 g, 0.0647 mmol) and THF (5 mL) in a glove box. Then *t*BuOK (1.0 M in THF; 0.142 mL, 0.14 mmol) was added dropwise with stirring, and the vial sealed with a screw cap. After 30 min, the solvent was removed by oil pump vacuum. [D$_8$]Toluene (2 mL) was added with stirring. After 10 min, the sample was passed through a PTFE syringe filter. An aliquot of the orange filtrate was assayed by NMR (^{1}H, ^{13}C, ^{31}P). The aliquot was readded and the solvent removed by oil pump vacuum to give ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**9** as an orange powder (0.138 g, 0.0595 mmol, 92%). M. p. 178–180 °C (dec). $C_{98}H_{92}N_4O_4P_6Re_4$ (2320.5): calcd. C 50.73, H 4.00, N 2.41; found C 51.12, H 3.88, N 2.25. IR (thin film [cm^{-1}]): $\tilde{\nu}$ = 1610 (s, NO). ^{1}H NMR (400 MHz, [D$_8$]toluene): PPh_3 at δ = 7.61–7.49 (m, 24 H), 6.93–6.91 (m, 36 H); 5.14 (s, 10 H, C_5H_5), 5.09 (s, 10 H, $C_5H'_5$), CH_2 at 2.60–2.50 (m, 8 H), 1.73–1.56 (m, 4 H). $^{13}C\{^1H\}$ NMR (75.5 MHz, [D$_8$]toluene): PPh_3 at δ = 138.5 (d, ^1J(C,P) = 50 Hz, *i*), 134.5 (d, ^2J(C,P) = 10 Hz, *o*), 134.3 (d, ^2J(C,P) = 10 Hz, *o'*), 129.8 (d, ^3J(C,P) = 10 Hz, *m*), 128.5 (s, *p*), 128.4 (s, *p'*); 91.7 (s, C_5H_5), 91.6 (s, C'_5H_5), 31.8 [dd, *J*(C,P) = 14, *J*(C,P) = 7 Hz, P*C*H$_2$C], –8.1 (m, ReCH$_2$), –11.8 (m, ReC′H$_2$). $^{31}P\{^1H\}$ NMR (121.5 MHz, [D$_8$]toluene or [D$_8$]THF): δ = 37.5 or 34.9 (br. s, PCH$_2$), 27.9 or 27.6 (br. s, PPh_3), 27.4 or 27.4 (br. s, P′Ph$_3$).

(**B**) Complex ($R_{Re}R_{Re}R_{Re}R_{Re}$)-**8**·$(CH_2Cl_2)_2$ (0.150 g, 0.0536 mmol), THF (10 mL) and *t*BuOK (1.0 M *in* THF; 0.161 mL, 0.16 mmol) were combined in a procedure analogous to **A**. The toluene filtrate was concentrated to ca. 3 mL and layered with pentane (10 mL). After 3 days, the supernatant was decanted from an orange powder, which was dried by oil pump vacuum to give ($R_{Re}R_{Re}R_{Re}R_{Re}$)-**10** (0.078 g, 0.033 mmol, 62%). M. p. 164–166 °C (dec). $C_{99}H_{94}N_4O_4P_6Re_4$ (2334.5): calcd. C 50.93, H 4.06, N 2.40; found C 50.29, H 4.35, N 2.03. IR (thin film [cm^{-1}]): $\tilde{\nu}$ = 1617 (s, NO). ^{1}H NMR (400 MHz, C_6D_6 or [D$_8$]toluene): PPh_3 at δ = 7.74–7.70 or 7.64–7.61 (m, 10 H), 7.56–7.51 or 7.47–7.40 (m, 12 H), 7.11–7.08 or 7.04–7.02 (m, 12 H), 7.03–6.95 or 6.97–6.89 (m, 26 H); 5.15 or 5.04 (s, 10 H, C_5H_5), 4.92 or 4.84 (s, 10 H, $C_5H'_5$), CH_2 at 2.69–2.61 or 2.57–2.52 (m, 6 H), 1.98–1.69 or 1.80–1.72 (m, 8 H). $^{13}C\{^1H\}$ NMR (100.5 MHz, C_6D_6): PPh_3 at δ = 138.0 [d, ^1J(C,P) = 50 Hz, *i*], 137.4 (d, ^1J(C,P) = 50 Hz, *i'*), 134.4 (d, ^2J(C,P) = 10 Hz, *o*), 134.2 (d, ^2J(C,P) = 11 Hz, *o'*), 129.8 (s, *p*), 131.1 (s, *p'*), 129.7 [d, ^3J(C,P) = 10 Hz, *m*], 129.3 [d, ^3J(C,P) = 10 Hz, *m'*]; 91.5 (s, C_5H_5), 91.1 (s, C'_5H_5), 39.7 [dd, ^1J(C,P) = 22, ^3J(C,P) = 8 Hz, P*C*H$_2$C], 24.6 [t, ^2J(C,P) = 13 Hz, C*C*H$_2$C], –5.6 [dd, ^1J(C,P) = 41, ^2J(C,P) = 5 Hz, ReCH$_2$], –12.9 [dd, ^1J(C,P) = 32, ^2J(C,P) = 5 Hz, ReC′H$_2$]. $^{31}P\{^1H\}$ NMR (161.8 MHz, C_6D_6): δ = 31.4 (s, PCH$_2$), 27.3 (s, PPh_3), 26.8 (s, P′Ph$_3$).

{(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_2$)}$_2${POCH$_2$(CH$_2$)$_n$CH$_2$PO}{(CH$_2$)(Ph$_3$P)(ON)Re(η^5-C$_5$H$_5$)}$_2$ (*n* = 0/1, 11/12): (**A**) A Schlenk tube was charged with ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**·$(CH_2Cl_2)_2$ (0.120 g, 0.0431 mmol) and THF (10 mL). Then *t*BuOK (1.0 M *in* THF; 0.134 mL, 0.13 mmol) was added dropwise with stirring. After 30 min, the solvent was removed by oil pump vacuum. The remaining workup was conducted in air. The residue was extracted with CH_2Cl_2 (20 mL), and the extract filtered through Celite (2×2 cm). The filtrate was concentrated to ca. 5 mL and layered with ether (10 mL). After 2 days, the supernatant was decanted from a yellow powder, which was dried by oil pump vacuum to give ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**11** (0.0963 g, 0.0409 mmol, 95%). M. p. 195–198 °C (dec). $C_{98}H_{92}N_4O_6P_6Re_4$ (2352.5): calcd. C 50.04, H 3.94, N 2.38; found C 49.81, H 3.63, N 2.09. IR (thin film [cm^{-1}]): $\tilde{\nu}$ = 1637 (s, NO), 1181 (m, PO). ^{1}H NMR (400 MHz, [D$_8$]THF): PPh_3 at δ = 7.53–7.22 (m, 60 H); 5.45 (br. s, 10 H, C_5H_5), 5.29 (br. s, 10 H, $C_5H'_5$), CH_2 at 3.12 (br. s, 2 H), 2.64 (m, 2 H), 2.46 (m, 2 H), 2.24 (m, 4 H), 2.05 (m, 2 H). $^{13}C\{^1H\}$ NMR (100.5 MHz, [D$_8$]THF): PPh_3 at δ = 134.8 [d, ^1J(C,P) = 53 Hz, *i*], 134.4 [d, ^2J(C,P) = 11 Hz, *o*], 132.1 (s, *p*), 131.7 (s, *p'*), 129.8 [d, ^3J(C,P) = 11 Hz, *m*], 129.6 [d, ^3J(C,P) = 9 Hz, *m'*]; 92.4 (s, C_5H_5), 91.0 (s, C'_5H_5), 28.7 [d, ^1J(C,P) = 56 Hz, P*C*H$_2$C], –18.3 [d, ^1J(C,P) = 22 Hz, ReCH$_2$], –22.8 [d, ^1J(C,P) = 39 Hz, ReC′H$_2$]. $^{31}P\{^1H\}$ NMR (161.8 MHz, [D$_8$]THF or $CDCl_3$): δ = 88.2 or 80.5 [apparent t, ^3J(P,P) = 17 Hz, or br. s, PO], 25.6 or 28.3 [d, ^3J(P,P) = 16 Hz, or br. s, PPh_3], 21.2 or 26.4 [d, ^3J(P,P) = 18 Hz, or br. s, P′Ph$_3$]. MS (FAB, 3-NBA): *m/z* (%) = 2353 (5) $[M]^+$, 2337 (4) $[M - O]^+$, 558 (100) $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2)]^+$.

(**B**) A Schlenk flask was charged with ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** (0.131 g, 0.0501 mmol) and THF (10 mL). Then *t*BuOK (1.0 M in THF; 0.16 mL, 0.16 mmol) was added dropwise with stirring. After 10 min, PhIO (0.034 g, 0.16 mmol)[39] was added. The mixture turned orange. After 2.5 h, the solvent was removed by rotary evaporation. The residue was extracted with benzene (6×5 mL). The extracts were filtered through Celite (2×4 cm). The orange filtrate was concentrated by rotary evaporation to ca. 2 mL, and hexanes (80 mL) were added with vigorous stirring. The yellow-orange precipitate was collected by filtration, washed with hexanes (5 mL), and dried by oil pump vacuum to give ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**11** (0.085 g, 0.036 mmol, 72%). M. p. 200–203 °C (dec). $C_{98}H_{92}N_4O_6P_6Re_4$ (2352.5): calcd. C 50.04, H 3.94, N 2.38; found C 50.41, H 4.23, N 2.08.

(**C**) Complex ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**8** (0.131 g, 0.0499 mmol), THF (10 mL), *t*BuOK (1.0 M *in* THF; 0.16 mL, 0.16 mmol), and PhIO (0.034 g, 0.16 mmol)[39] were combined in a procedure analogous to **B**. A similar workup (precipitation with 50 mL of hexanes; washing with 2 mL) gave ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**12** (0.074 g, 0.0031 mmol, 62%) that typically contained ca. 5% of Ph_3PO. M. p. 190–192 °C (dec). IR (thin film [cm^{-1}]): $\tilde{\nu}$ = 1629 (s, NO), 1183 (w, PO). ^{1}H NMR (500 MHz, $CDCl_3$): PPh_3 at δ = 7.69–7.06 (m, 60 H); 5.17 (s, 10 H, C_5H_5), 5.09 (s, 10 H, $C_5H'_5$), CH_2 at 2.18, 2.08, 1.78, 1.63, 1.48, 1.11 (6 m, 12 H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$): PPh_3 at δ = 136.5 [d, ^1J(C,P) = 51 Hz, *i*], 136.1 [d, ^1J(C,P) = 52 Hz, *i'*], 133.7 [d, ^2J(C,P) = 12 Hz, *o*], 133.6 [d, ^2J(C,P) = 10 Hz, *o'*], 129.9 (s, *p*), 128.3 [d, ^3J(C,P) = 9 Hz, *m*], 128.3 [d, ^3J(C,P) = 9 Hz, *m'*]; 90.6 (s, C_5H_5), 90.5 (s, C'_5H_5), 35.2 [d, ^1J(C,P) = 12 Hz, P*C*H$_2$C], 34.7 [d, ^2J(C,P) = 13 Hz, C*C*H$_2$C], –13.0 [d, ^1J(C,P) = 57 Hz, ReCH$_2$], –13.5 [d, ^1J(C,P) = 72 Hz, ReC′H$_2$]. $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$): δ = 78.8 [apparent t, ^3J(P,P) = 13 Hz, PO], 26.7 [d, ^3J(P,P) = 15 Hz, PPh_3], 26.5 [d, ^3J(P,P) = 13 Hz, P′Ph$_3$]. MS (FAB, 3-NBA): *m/z* (%) = 2367 (9) $[M]^+$, 544 (100) $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$.

[({(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2)}$_2${$PCH_2(CH_2)_nCH_2P$}{(CH_2)-(Ph_3P)(ON)Re(η^5-C_5H_5)}$_2$)Rh(NBD)]$^+$ PF_6^- [*n* = 0/1, 13/14 (see Scheme 1)**]:** (**A**) A glass vial was charged with ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**·(CH_2Cl_2)$_2$ (0.124 g, 0.0447 mmol) and THF (5 mL) in a glove box. Then *t*BuOK (1.0 M *in* THF; 0.107 mL, 0.11 mmol) was added dropwise with stirring. The vial was sealed with a screw cap. After 30 min, the solvent was removed by oil pump vacuum. The orange powder was extracted with toluene (5 mL) in a glove box. The extract was passed through a PTFE syringe filter. Then [Rh(NBD)$_2$]$^+$ PF_6^- (0.0193 g, 0.0447 mmol)[40] was added with stirring. After 1 h, pentane (20 mL) was added dropwise. After 30 min, the precipitate was collected by filtration and dissolved in $CHCl_3$ (5 mL). A layer of pentane was gently added. After 2 days, the supernatant was decanted and the red-brown powder dried by oil pump vacuum to give ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**13**·($CHCl_3$)$_2$ (0.093 g, 0.032 mmol, 75%). M. p. 230–235 °C (dec). $C_{105}H_{100}F_6N_4O_4P_8Re_4Rh$·($CHCl_3$)$_2$ (2899.3): calcd. C 44.33, H 3.55, N 1.93; found C 44.26, H 3.86, N 1.72. IR (thin film [cm^{-1}]): ṽ = 1630 (s, NO), 834 (s, PF). ^{1}H NMR (400 MHz, [D$_8$]THF): PPh_3 at δ = 7.38–7.36 (m, 32 H), 7.29–7.24 (m, 18 H), 7.14–7.11 (m, 10 H); 7.27 (s, 2 H, $CHCl_3$), 5.20 (s, 10 H, C_5H_5), 5.14 (s, 10 H, $C_5H'_5$), NBD at 5.45 (br. s, 4 H, =CH),[41] 3.16 (br. s, 2 H, bridgehead CH),[41] 1.68 (br. s, 2 H, CH_2); CH_2 at 2.48–2.42 (m, 2 H), 2.20–2.01 (m, 10 H). ^{13}C{^{1}H} NMR (100.5 MHz, [D$_8$]THF): PPh_3 at δ = 136.2 [d, ^1J(C,P) = 53 Hz, *i*], 136.0 [d, ^1J(C,P) = 51 Hz, *i'*], 135.1 [d, ^2J(C,P) = 11 Hz, *o*], 134.9 [d, ^2J(C,P) = 10 Hz, *o'*], 131.1 (s, *p*), 130.9 (s, *p'*), 129.5 [d, ^3J(C,P) = 10 Hz, *m*], 129.3 [d, ^3J(C,P) = 10 Hz, *m'*]; 91.3 (s, C_5H_5), 90.0 (s, C'_5H_5), 77.0 (s, $CHCl_3$), NBD at 91.2/91.0 (2 br. s, =CH),[41] 81.6/80.0 (2 m, bridgehead CH),[41] 54.8 (br. s, CH_2); 31.9 (m, P*C*H$_2$C), –16.3 (m, Re*C*H$_2$), –21.5 (m, Re*C'*H$_2$). ^{31}P{^{1}H} NMR (161.8 MHz, [D$_8$]THF): δ = 97.3 [dt, ^1J(P,Rh) = 150, ^3J(P,P) = 9 Hz, P*C*H$_2$], 27.1 [d, ^3J(P,P) = 9 Hz, PPh_3], 26.0 [d, ^3J(P,P) = 9 Hz, P'Ph$_3$], –143.5 [sept, ^1J(P,F) = 709 Hz, PF_6]. MS (FAB, 3-NBA): *m*/*z* (%) = 2516 (8) [M]$^+$, 558 (100) [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2)]$^+$.

(**B**) Complex ($R_{Re}R_{Re}R_{Re}R_{Re}$)-**8**·(CH_2Cl_2)$_2$ (0.120 g, 0.0428 mmol), THF (5 mL), *t*BuOK (1.0 M in THF; 0.094 mL, 0.094 mmol), and [Rh(NBD)$_2$]$^+$ PF_6^- (0.0185 g, 0.0428 mmol)[40] were combined in a procedure analogous to **A**. The crude product was dissolved in THF (5 mL) and pentane (20 mL) was added with stirring. The brown powder was collected by filtration and dried by oil pump vacuum to give ($R_{Re}R_{Re}R_{Re}R_{Re}$)-**14** (0.094 g, 0.035 mmol, 82%). M. p. 223–226 °C (dec). $C_{106}H_{102}F_6N_4O_4P_7Re_4Rh$ (2674.6): calcd. C 47.60, H 3.84, N 2.09; found C 47.19, H 4.09, N 2.05. IR (thin film [cm^{-1}]): ṽ = 1640 (vs, NO), 842 (s, PF). ^{1}H NMR (400 MHz, [D$_8$]THF): PPh_3 at δ = 7.46–7.40 (m, 60 H); 5.28 (s, 10 H, C_5H_5), 4.39 (br. s, 10 H, $C_5H'_5$), NBD at 5.23/5.20 (2 br. s, 4 H, =CH),[41] 3.89/3.75 (2 br. s, 2 H, bridgehead CH),[41] 1.49 (br. s, 2 H, CH_2); CH_2 at 2.65–2.55 (m, 4 H), 1.98–1.92 (m, 2 H), 1.62–1.55 (m, 8 H). ^{13}C{^{1}H} NMR (100.5 MHz, [D$_8$]THF): PPh_3 at δ = 137.2 [d, ^1J(C,P) = 52 Hz, *i*], 136.9 [d, ^1J(C,P) = 50 Hz, *i'*], 134.6 [d, ^2J(C,P) = 12 Hz, *o*], 134.4 [d, ^2J(C,P) = 12 Hz, *o'*], 131.3 (s, *p*), 131.1 (s, *p'*), 129.7 [d, ^3J(C,P) = 10 Hz, *m*], 129.3 [d, ^3J(C,P) = 10 Hz, *m'*]; 91.7 (s, C_5H_5), 91.5 (s, C'_5H_5), NBD at 91.9/91.8 (2 br. s, =CH),[41] 77.7/73.5 (2 m, bridgehead CH),[41] 53.7 (br. s, CH_2); 29.1 [dd, J(C,P) = 16, J(C,P) = 4 Hz, P*C*H$_2$C], 23.5 [t, ^2J(C,P) = 6 Hz, C*C*H$_2$C], –13.2 (m, Re*C*H$_2$), –14.1 (m, Re*C'*H$_2$). ^{31}P{^{1}H} NMR (161.8 MHz, [D$_8$]THF): δ = 53.7 [d, ^1J(P,Rh) = 141 Hz, P*C*H$_2$], 24.3 (br. s, PPh_3), 21.7 (br. s, P'Ph$_3$), –143.5 [sept, ^1J(P,F) = 709 Hz, PF_6]. MS (FAB, 3-NBA): *m*/*z* (%) = 2529 (6) [M]$^+$, 558 (100) [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2)]$^+$.

Relative Brønsted Basicities: A 5-mm NMR tube was charged with ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7** (0.0196 g, 0.0075 mmol), [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2H)]$^+$ PF_6^- (0.0133 g, 0.015 mmol),[4a] and CD_2Cl_2 (0.60 mL) in a glove box. A reference ^{31}P{^{1}H} NMR spectrum was recorded. Then *t*BuOK (1.0 M in THF; 0.015 mL, 0.015 mmol) was added. The orange solution became darker. After 1 h, a ^{31}P{^{1}H} NMR spectrum showed complete conversion of [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2H)]$^+$ PF_6^- to (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PPh_2) and no reaction of ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**.

Hydrogenations: A Fisher–Porter bottle was charged with **7** or **8** (0.012 mmol) and THF (10 mL) in a glove box, and *t*BuOK (1.0 M in THF; 0.028 mL, 0.028 mmol) was added with stirring. After 5 min, [Rh(NBD)$_2$]$^+$ PF_6^- (0.0043 g, 0.010 mmol)[40] was added, giving an orange solution. After 30 min, **15** (2.00 mmol; Scheme 4) and THF (10 mL) were added. The bottle was closed under argon and purged with H_2 (75 psi, 3 ×). The mixture was vigorously stirred under H_2 (120 psi, 8 bar, 75 °C). After 1–2 h, **16** was isolated by a standard workup.[2b,2e] Configurations and enantiomeric purities were determined as described previously.[2b,2e]

Hydrosilylations: A glass vial was charged with **7** or **8** (0.0052 mmol) and THF (5 mL) in a glove box, and *t*BuOK (1.0 M *in* THF; 0.0125 mL, 0.012 mmol) was added with stirring. After 5 min, [Rh(NBD)$_2$]$^+$ PF_6^- (0.0022 g, 0.0050 mmol)[40] was added. After 30 min, **17** (0.184 g, 1.00 mmol; Scheme 4), and Ar_2SiH_2 (1.2 mmol) were added, and the vial sealed with a screw cap. The sample was stirred (24–26 °C, glove box). Aliquots were dissolved in $CDCl_3$ and the ^{1}H NMR signals of **17** integrated against those of **18**.[2e] After 14 days, a saturated solution of K_2CO_3 in methanol was added (1 mL). After 1 h, the solvents were removed by oil pump vacuum and the residue filtered through a silica gel column (4 × 1 cm) using hexanes. This gave crude 1-phenyl-1-propanol, the enantiomeric purity of which was assayed by GC (Lipodex-E).

Conjugate Additions: A Schlenk tube was charged with **7** or **8** (0.0144 mmol) and dioxane (1 mL) in a glove box, and *t*BuOK (1.0 M in THF, 0.03 mL, 0.03 mmol) was added with stirring. After 30 min, Rh(acac)(H_2C=CH_2)$_2$ (0.0031 g, 0.012 mmol)[42] was added, giving a brown mixture. After 30 min, phenylboronic acid (0.244 g, 2.00 mmol) and **19** (0.039 mL, 0.039 g, 0.40 mmol; Scheme 3) were added. After 15 min, H_2O (0.100 mL) was added, giving a brown solution. The sample was stirred under argon at 100 °C. After 5 h, the dark brown solution was cooled to room temperature. Saturated aqueous $NaHCO_3$ (5 mL) was added. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phases were dried ($MgSO_4$). Hexanes (10 mL) were added, and the solution was filtered through a silica gel pad (2 × 3 cm) using hexanes/EtOAc (5:1 v/v, 2 × 5 mL; this removes rhodium complex). Decane (0.039 mL, 0.029 g, 0.20 mmol; internal standard) was added to the filtrate. The yield of **20** was assayed by GC (OPTIMA-5). The solution was filtered through a silica gel column using hexanes/EtOAc (5:1 v/v) and the enantiomeric purity was assayed by HPLC (Chiralcel OD). NMR: See Supporting Information.

Allylic Alkylations: A Schlenk tube was charged with **7** or **8** (0.0180 mmol) and CH_2Cl_2 (1 mL) in a glove box, and *t*BuOK (1.0 M in THF, 0.054 mL, 0.054 mmol) was added with stirring. After 5 min, [Pd(η^3-C_3H_5)Cl]$_2$ (0.0027 g, 0.0074 mmol) was added, followed by a solution of **21** (0.0757 g, 0.300 mmol; Scheme 4)[43] in CH_2Cl_2 (1 mL). A vial was charged with dimethyl malonate (0.103 mL, 0.119 g, 0.901 mmol), CH_3(C=NTMS)OTMS (0.220 mL, 0.183 g, 0.900 mmol), KOAc (0.0015 g, 0.015 mmol), and CH_2Cl_2 (1 mL). This mixture was added dropwise to the Schlenk tube with stirring. After 24 h, ether (15 mL) was added. The mixture was washed with cold, saturated aqueous NH_4Cl (2 × 7.5 mL), dried (Na_2SO_4), and concentrated by rotary evaporation. Flash chromatography on silica gel (1.5 × 17 cm, 3:1 v/v, hex-

anes/EtOAc, R_f = 0.68) gave a slightly yellow oil that when dried by oil pump vacuum afforded **22** as white solid. The enantiomeric purity was analyzed by HPLC (Chiralcel OD). NMR: See Supporting Information.

X-ray Crystallography: Data were collected on ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**·$(CH_2Cl_2)_2$ (see above) as outlined in Table 2. Cell parameters were obtained from 10 frames using a 10° scan and refined with 12270 reflections. Lorentz, polarization and absorption corrections were applied.[44] The space group was determined from systematic absences and subsequent least-squares refinement. The structure was solved by direct methods. The parameters were refined with all data by full-matrix-least-squares on F^2 using SHELXL-97.[45] 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.[46] The asymmetric unit contained a half molecule of the tetrarhenium complex. Three fluorine atoms of one PF_6^- anion (F33, F34, and F35) were disordered about a symmetry axis and were refined with an occupancy ratio of 50:50. The rhenium configuration was established by Flack's *x* parameter [found: –0.018(7); theory for correct and inverted structures: 0 and 1].[47]

Table 2. Crystallographic data for ($S_{Re}S_{Re}S_{Re}S_{Re}$)-**7**·$(CH_2Cl_2)_2$.

Molecular formula	$C_{100}H_{98}Cl_4F_{12}N_4O_4P_8Re_4$
Molecular mass	2782.18
Temp. of collection [°C]	–100(2)
Diffractometer	KappaCCD
Radiation [Å]	Mo-K_α
Crystal system	tetragonal
Space group	$P4_22_12$
Unit cell dimensions:	
a [Å]	20.5410(2)
b [Å]	20.5410(2)
c [Å]	24.5424(3)
V [Å^3]	10355.2(2)
Z	4
$\rho_{calcd.}$ [Mg·m^{-3}]	1.785
μ [mm^{-1}]	4.961
Crystal dimensions, mm	0.30 × 0.30 × 0.25
Θ Range [°]	1.29 ≤ Θ ≤ 27.88
Range/indices (*h*,*k*,*l*)	–27,27; –19,19; –32,32
No. of reflections	24377
No. of unique data	12348
No. of observed data	8896 [$I > 2\sigma(I)$]
No. refined parameters	608
Refinement	least-squares on F^2
R_{int}	0.0598
R indices [$I > 2\sigma(I)$]	R_1 = 0.0380
	wR_2 = 0.0757
R indices (all data)	R_1 = 0.0751
	wR_2 = 0.0952
Goodness of fit	1.007
Largest diff. peak/hole [e·Å^{-3}]	1.451/–0.926

CCDC-265274 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information: Sources and purification of starting materials; independent characterization of enantiomeric complexes, NMR spectroscopic data for known compounds, and polarimetric data.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (DFG; GL 300–4/1) and Johnson Matthey PMC (rhodium and palladium loans) for support.

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Received: March 23, 2005
Published Online: July 4, 2005

