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Syntheses and structures of chiral rhenium-containing phosphonium salts and phosphines with $ReCH_2\ddot{P}Ar_2$ or $ReCH(R)\ddot{P}Ar_2$ linkages; enantioselective catalysis of intramolecular Morita–Baylis–Hillman and Rauhut–Currier reactions†

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Easily accessed (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**2**) is treated with Ph_3C^+ PF_6^- (–78 °C) to generate the methylidene cation [(η^5-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+$ and then secondary phosphines PAr_2H (Ar = **a**, Ph; **b**, *p*-tol; **c**, *p*-$C_6H_4OCH_3$; **d**, *p*-$C_6H_4N(CH_3)_2$; **e**, 2-biphen; **f**, α-naph) to give the phosphonium salts [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PAr_2H)]$^+$ PF_6^- ([**1a–f**-H]$^+$ PF_6^-, 87–94%). Additions of *t*-BuOK yield the phosphines **1a–f** (64–91%). Analogous procedures starting with (*S*)-**2** give enantiopure (*S*)-**1a–d** in comparable yields. The ethyl complex (*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3) is similarly treated with Ph_3C^+ PF_6^- to generate the ethylidene cation (*S*)-(*sc*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(=$CHCH_3$)]$^+$ and then PPh_2H to give enantiopure and diastereopure ($S_{Re}S_C$)-[(η^5-C_5H_5)Re(NO)(PPh_3)($CH(CH_3)PPh_2H$)]$^+$ PF_6^- (51%). Addition of *t*-BuOK yields the corresponding $ReCH(CH_3)PPh_2$ adduct. The crystal structures of [**1c**,**d**-1 PF_6^-] are determined and analyzed. Most of the $ReCH_2PAr_2$ species catalyze intramolecular Morita–Baylis–Hillman reactions of $R(CO)CH{=}CH(CH_2)_nCH_2CHO$ (*n*/R = 1/Ph, 1/S-i-Pr, 2/*p*-tol 2/Me) in C_6H_6 or C_6H_5Cl (20 °C) to give $R(CO)\overline{CH{=}CH(CH_2)_nCH_2}CHOH$ (99–86%, 74–38% ee with (*S*)-**1a**) or Rauhut–Currier reactions of $R(CO)CH{=}CHCH_2CH_2CH{=}CH(CO)R$ (R = Ph, S-i-Pr) to give $R(CO)C{=}\overline{CHCH_2CH_2CHCH_2}(CO)R$ (87–82%, 56–42% ee with (*S*)-**1a**).

Introduction

There are now an immense number of phosphine catalyzed organic reactions,[1,2] and many enantioselective transformations have been developed with enantiopure chiral phosphines.[3] Two examples, both intramolecular, are illustrated in Scheme 1: a Morita–Baylis–Hillman reaction (top), and a vinylogous version known as the Rauhut–Currier reaction (bottom).[1,4] At the time our work commenced, the former had been studied by Murphy,[5] Koo,[6] and a few others.[7] Murphy found the phosphine PBu_3 (20 mol%) to be a moderately effective catalyst with two substrates (up to four turnovers), but inferior to other types of Lewis bases. Under Koo's conditions, stoichiometric quantities of PPh_3 were required. Then Miller developed a phosphorus-free chiral pipecolinic acid/*N*-methylimidazole cocatalyst system for effecting closely related cyclizations.[8] This afforded an average ee value of 73% (high/low 80%/51%, five substrates).[9]

We have sought to synthesize and study the catalytic properties of enantiopure phosphines in which a "chiral-at-metal" fragment serves as the sole stereogenic center, in particular the sixteen-valence electron pyramidal rhenium moiety (η^5-C_5H_5)Re(NO)(PPh_3).[10–12] The phosphorus donor group may be directly bound to rhenium ($Re\ddot{P}R_2$ or $Re\ddot{P}Ar_2$), separated by a methylene or similar spacer ($ReCH_2\ddot{P}R_2$ or $ReCH_2\ddot{P}Ar_2$), or attached to the cyclopentadienyl ligand (η^5-$C_5H_4\ddot{P}R_2$ or η^5-$C_5H_4\ddot{P}Ar_2$).[10] As will be described later, analogous species that are furthermore "chiral-at-phosphorus" are easily accessed.[13] At the time our work began, there was only a single example of an enantiopure phosphine being applied to an intramolecular Morita–Baylis–Hillman reaction ((*S*)-CAMP, 18 mol%, 75% GLC yield), and the enantioselectivity was poor (14% ee).[7a]

In a preliminary communication, we established the viability of catalyzing the reactions in Scheme 1 with chiral

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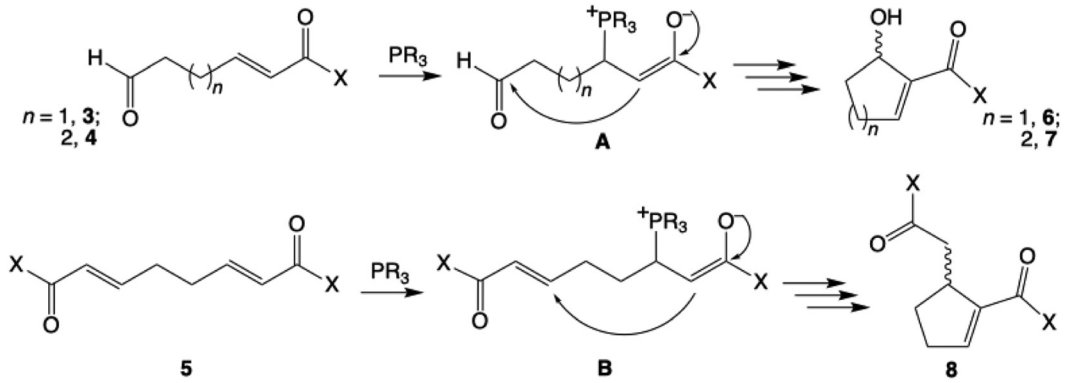
†Electronic supplementary information (ESI) available: General procedures, syntheses of secondary phosphines and organic substrates and products, additional NMR data, and ee determinations. CCDC 2423133([**1c**-H]$^+$ PF_6^-) and 2423134 ([**1d**-H]$^+$ PF_6^-). For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d5dt01102g



Scheme 1 Intramolecular Morita–Bayliss–Hillman (top) or Rauhut–Currier reactions (bottom); **A**, **B**: key stereocenter generating steps.

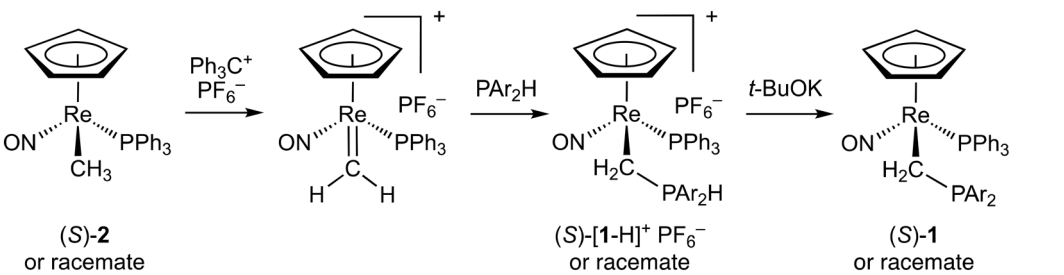
rhenium-containing phosphines.[12] However, data were provided for only two catalysts, racemic or enantiopure (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PAr_2) with Ar = Ph (**1a**) or *p*-$C_6H_4OCH_3$ (**1c**).[10,14] Furthermore, the publisher required that the full set of ESI† be replaced by two footnotes describing representative protocols. This introduced a number of gaps in the documentation. In subsequent efforts, several related catalysts were synthesized and evaluated, some of which exhibited improved performance characteristics. Accordingly, this full paper combines all of these themes into a cohesive, comprehensive narrative.[9]

Results

Chiral-at-rhenium catalysts

The starting material in Scheme 2, methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (**2**), can be prepared from $Re_2(CO)_{10}$ in six steps in 44% overall yield (racemic)[15] or nine steps in 36% overall yield (enantiopure).[15] The racemate and the hydride abstracting reagent Ph_3C^+ PF_6^- were combined at −78 °C. The electrophilic methylidene complex[16] [(η^5-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+$ PF_6^- formed *in situ* and was subsequently treated with a symmetrically substituted secondary phosphine PAr_2H (Ar = Ph (**a**), *p*-tol (**b**), *p*-$C_6H_4OCH_3$ (**c**), *p*-$C_6H_4N(CH_3)_2$ (**d**), 2-biphenyl (**e**), α-naphthyl (**f**)). The phosphines **a**,**b** are commercially available, and **c**,**d**,**f** have been previously reported.[17,18] However, **e** is a new compound, and its preparation is described in the ESI.†

Workups gave the protonated rhenium-containing phosphines [(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2PAr_2H)]$^+$ PF_6^- ([**1a–f**-H]$^+$ PF_6^-) as air-stable orange to red powders in 87–95% yields. The parent $ReCH_2PPh_2H$ species [**1a**-H]$^+$ PF_6^-, enantiopure salts thereof, and phosphines derived therefrom have been described earlier.[10,14] The other complexes were new, and were characterized by NMR (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}) and IR spectroscopy, elemental analysis, and mass spectrometry, as



*This synthesis is from reference 14;

**This synthesis is from reference 10 and involves the BF_4^- salt;

others: this work

racemic series, Ar =
a, Ph, 94%*
b, *p*-tol, 94%
c, *p*-C6H4OCH3, 88%
d, *p*-C6H4N(CH3)2, 93%
e, 2-biphenyl, 95%
f, α-naphthyl, 87%

enantiopure series, Ar =
a, Ph, 98%**
b, *p*-tol, 86%
c, *p*-$C_6H_4OCH_3$, 95%
d, *p*-$C_6H_4N(CH_3)_2$, 90%

racemic series, Ar =
a, Ph, 94%*
b, *p*-tol, 80%
c, *p*-$C_6H_4OCH_3$, 77%
d, *p*-$C_6H_4N(CH_3)_2$, 85%
e, 2-biphenyl, 91%
f, α-naphthyl, 64%

enantiopure series, Ar =
a, Ph, 89%**
b, *p*-tol, 88%
c, *p*-$C_6H_4OCH_3$, 87%
d, *p*-$C_6H_4N(CH_3)_2$, 90%

Scheme 2 Preparation of rhenium-containing phosphonium salts and phosphines.

summarized in the Experimental section. Since the PAr_2 groups are diastereotopic, two sets of ^1H and $^{13}C\{^1H\}$ NMR signals were seen, including those of the *para* substituents in [**1b–d**-H]$^+$ PF_6^-.

As shown in Scheme 2, the phosphonium salts [**1**-H]$^+$ PF_6^- were deprotonated with *t*-BuOK under heterogeneous conditions in benzene. The red suspensions were filtered (Celite), and additions of pentane precipitated the target rhenium-containing phosphines **1a–f** as orange to red solids in 91–64% yields. These were slightly air sensitive and characterized analogously to [**1**-H]$^+$ PF_6^-. The ^1H and $^{13}C\{^1H\}$ spectra again showed separate signals for the diastereotopic PAr_2 groups, consistent with the appreciable pyramidal inversion barriers of most triorganophosphines.[19] The $^{31}P\{^1H\}$ NMR data for all compounds are summarized in Table s1 (ESI).†

The new enantiopure complexes (*S*)-[**1b–d**-H]$^+$ PF_6^- and (*S*)-**1b–d** were synthesized analogously to the racemates, although due to their generally higher solubilities, some workups were slightly modified. Additions of carbon, nitrogen, phosphorus and sulfur nucleophiles to the methylidene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+$ PF_6^- have been shown to proceed with retention at rhenium.[20,21] Since racemic **1e,f** proved to be poor catalysts (*vide infra*), enantiopure analogs were not sought.

Chiral-at-rhenium-and-carbon catalysts

The phosphorus donor atoms in **1a–f** are separated from the stereogenic rhenium by a CH_2 spacer. Complexes that lack the CH_2 spacer – *i.e.*, feature a direct $RePR_2$ linkage – have not been effective in any phosphine-catalyzed reaction examined to date. These are exceptionally nucleophilic systems[22] that appear to have a number of facile deactivation pathways. Therefore, we sought to replace the CH_2 spacer by a CHR spacer, thereby introducing a stereocenter proximal to the reactive site of the catalyst.

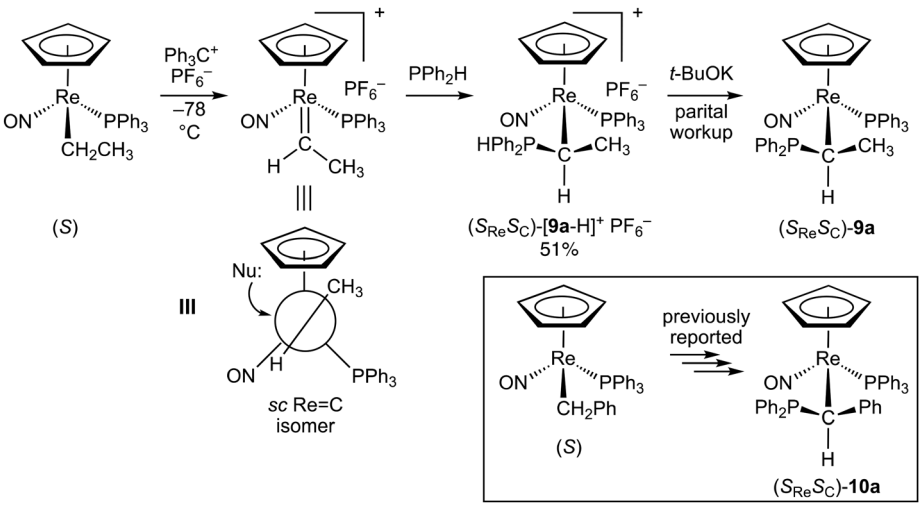
As shown in Scheme 3, the enantiopure rhenium ethyl complex (*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2CH_3)[23] and Ph_3C^+ PF_6^- were combined in CH_2Cl_2 at −78 °C. A hydride moiety was regiospecifically (α ≫ β) and diastereoselectively (pro-*R* ≫ pro-*S*) abstracted to give the ethylidene complex (*S*)-(*sc*)-[(η^5-C_5H_5)Re(NO)(PPh_3)(=$CHCH_3$)]$^+$ PF_6^-. This species is generated in the Re=C conformation **III**,[23] and PPh_2H was added at low temperature to preclude isomerization. Workup gave the phosphonium salt ($S_{Re}S_C$)-[(η^5-C_5H_5)Re(NO)(PPh_3)(CH(CH_3)PPh_2H)]$^+$ PF_6^- (($S_{Re}S_C$)-[**9a**-H]$^+$ PF_6^-) as a pale yellow powder in 51% yield, which was characterized as the other new complexes. The carbon configuration was assigned by analogy to addition products of ethylidene and benzylidene complexes that have been crystallographically characterized.[24]

The ($S_{Re}S_C$)-[**9a**-H]$^+$ PF_6^- was subsequently treated with *t*-BuOK in benzene. An abbreviated workup (filtration/precipitation) gave crude ($S_{Re}S_C$)-**9a**, which was employed without further purification or characterization for catalysis. The analogous benzylidene-derived complex ($S_{Re}S_C$)-**10a** (Scheme 3), which has been previously reported and fully characterized,[24] was similarly synthesized.

Crystallography

In the course of the preceding studies, the phosphonium salts [**1c,d**-H]$^+$ PF_6^- crystallized. X-ray data were collected as summarized in Table 1 and the Experimental section. Key metrical parameters are supplied in Table 2, together with previously reported data for a benzene monosolvate of a related deprotonation product, (*S*)-**1a**.[10] Views of the cations are presented in Fig. 1. Both feature the typical octahedral coordination geometries of d^6 piano-stool type complexes, as reflected by the *ca.* 90° L–Re–L bond angles between the non-cyclopentadienyl ligands.

Both cations also exhibit similar conformations, as can be gauged by the torsion angles in Table 2. In particular, the Newman-type projections (Fig. 1, right) show that the CH_2–P (C1–P2) linkages are directed into the most spacious interstice between the cyclopentadienyl and nitrosyl ligands.[25] This is reflected by the P1–Re–C1–P2 and N1–Re–C1–P2 torsion angles (131.9–123.1° and 40.2–29.7°, respectively). Turning to the con-



Scheme 3 Preparation of the diastereopure rhenium-containing phosphine ($S_{Re}S_C$)-**9a**.

Table 1 Crystallographic data for $[\mathbf{1c}\text{-H}]^+\ PF_6^-$ and $[\mathbf{1d}\text{-H}]^+\ PF_6^-$

	$[\mathbf{1c}\text{-H}]^+\ PF_6^-$	$[\mathbf{1d}\text{-H}]^+\ PF_6^-$
Empirical formula	$C_{38}H_{37}F_6NO_3P_3Re$	$C_{40}H_{43}F_6N_3OP_3Re$
Formula weight	948.80	974.88
Temperature [K]	173(2)	173(2)
Diffractometer	Nonius KappaCCD	Nonius KappaCCD
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/*c*	P21/*n*
a [Å]	12.7618(3)	11.84610(1)
b [Å]	15.3419(5)	16.04480(1)
c [Å]	19.2417(5)	21.0727(2)
α [°]	90	90
β [°]	97.260(2)	91.033(1)
γ [°]	90	90
Volume [Å^3]	3737.13(18)	4004.60(6)
Z	4	4
ρ_{calc} [Mg m^{-3}]	1.686	1.617
μ [mm^{-1}]	3.448	3.218
F(000)	1880	1944
Crystal size [mm]	0.20 × 0.15 × 0.01	0.20 × 0.15 × 0.15
Θ range [°]	2.43 to 27.46	1.96 to 27.47
Index ranges	$-16 \le h \le 16$, $-19 \le k \le 19$, $-24 \le l \le 24$	$-15 \le h \le 15$, $-20 \le k \le 20$, $-27 \le l \le 27$
Reflections collected	15 172	17 867
Independent reflections	8539 [*R*(int) = 0.0470]	9171 [*R*(int) = 0.0157]
Reflections [$I > 2\sigma(I)$]	5978	7969
Max. and min. transmission	0.9663 and 0.5455	0.6439 and 0.5654
Data/restraints/parameters	8539/0/470	9171/0/491
Goodness-of-fit on F^2	1.008	1.043
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0384, wR^2 = 0.0814	R_1 = 0.0228, wR^2 = 0.0579
R indices (all data)	R_1 = 0.0714, wR^2 = 0.0920	R_1 = 0.0290, wR^2 = 0.0606
Largest diff. peak/hole [e Å^{-3}]	1.221 and −1.001	1.128 and −1.062

Table 2 Key distances [Å] and angles [°] in $[\mathbf{1c,d}\text{-H}]^+\ PF_6^-$ and (*S*)-**1a**·C_6H_6 [a]

	$[\mathbf{1c}\text{-H}]^+\ PF_6^-$	$[\mathbf{1d}\text{-H}]^+\ PF_6^-$	(*S*)-**1a**·C_6H_6 [b]
Re–N(1)	1.745(4)	1.760(2)	1.773(7)
Re–P(1)	2.3531(13)	2.3487(6)	2.352(2)
Re–C(1)	2.192(5)	2.197(2)	2.170(8)
C(1)–P(2)	1.757(5)	1.770(3)	1.845(8)
Re–Cp(centroid)	1.953	1.942	1.949
N(1)–Re–P(1)	92.33(14)	93.53(7)	92.5(2)
Re–N(1)–O(1)	173.7(4)	170.8(2)	174.5(6)
N(1)–Re–C(1)	99.81(18)	100.87(10)	97.2(3)
P(1)–Re–C(1)	86.38(14)	88.78(7)	87.6(2)
Re–C(1)–P(2)	111.5(3)	109.75(13)	112.1(4)
P(1)–Re–C(1)–P(2)	131.9(2)	123.08(12)	159.9
N(1)–Re–C(1)–P(2)	40.2(3)	29.71(14)	67.6
Re–C(1)–P(2)–H or LP	50.0	59.3	49.1
Re–C(1)–P(2)–C(50)	176.1(2)	172.22(11)	176.9
Re–C(1)–P(2)–C(60)	60.9(3)	59.13(15)	78.8

[a] Some atom labels used in this table, Fig. 1, and elsewhere in the main text have been changed from those in the CIF files to facilitate comparisons. [b] Data for this complex from ref. 10.

formations about the CH_2–P bonds, the large rhenium substituents on C1 are *anti* to one P–C_{ipso} group (torsion angles 176.1–172.2°) and *gauche* to the other (60.9–59.1°) as well as the smaller P–H moiety (50.0–59.3°). In general, (*S*)-**1a** exhibits similar torsion angles, the major difference being a 28–38° rotation about the Re–CH_2 linkage. Hence, the structures of $[\mathbf{1}\text{-H}]^+\ PF_6^-$ do not significantly change upon deprotonation.

Catalysis

Next, the rhenium-containing phosphines in Schemes 2 and 3 were applied as catalysts to the reactions in Schemes 1 and 4. The substrates were easily prepared from succinaldehyde or glutaraldehyde and either one (**3j**,**k**, **4l**,**m**) or two (**5j**,**k**) equivalents of the appropriate phosphorus ylide X(C═O)CHPPh_3. Two were new compounds when this work was carried out (**3k**, **4l**), and characterization is supplied in the ESI.†

In the prototype for one series of reactions, a 0.0100 M benzene solution of racemic catalyst **1a** was added dropwise to an equal volume of a 0.100 M benzene solution of **3j**. This corresponds to a 10 mol% catalyst loading and 0.0050 M and 0.050 M catalyst and substrate concentrations, parameters that were kept constant throughout this work. After 1.5 h at 20 °C, a chromatographic workup gave the known carbocycle 2-benzoylcyclopent-2-en-1-ol (**6j**; Scheme 4)[5] in 91% yield as a spectroscopically pure oil. NMR monitoring *versus* an internal standard (CH_2ClCH_2Cl, 3.73 δ/ppm; used throughout this work) showed a nearly quantitative conversion, with significant amounts of catalyst remaining.

An analogous but slightly slower reaction of the thioester **3k** (6 h) gave the corresponding carbocycle **6k** in 99% yield. This new compound was fully characterized as described in the Experimental section. The substrates **4l**,**m** gave still slower cyclizations, but after 3 d, chromatography afforded the six-membered ring products **7l**,**m** (Scheme 4) in 91–86% yields. However, preliminary experiments with related esters, which would be less electrophilic, gave much slower reactions and lower product yields.

The preceding reactions were repeated on 0.010–0.020 g scales using the enantiopure catalyst (*S*)-**1a**. As summarized in Scheme 4, the Morita–Baylis–Hillman products **6j**,**k** and **7m** were obtained with quite high enantioselectivities (74–62% ee, or er 87 : 13 to 81 : 19), as analyzed by HPLC. The enantiomeric purity of **7l** was somewhat lower (38% ee, or er 69 : 31). NMR analyses indicated yields comparable to those with racemic **1a**. The Rauhut–Currier products **8j**,**k** were isolated in 87% and 82% yields, and 42% ee (er 71 : 29) and 52% ee (er 76 : 24), respectively. These reactions required 5–6 h and 100–120 h, respectively, to go to completion (NMR monitoring).

Other solvents were screened. In chlorobenzene, the reactions of **3j**,**k** were slower, but those of **4l**,**m** were comparable. With **8j**, the enantioselectivity increased from 42% ee (er 71 : 29) to 56% ee (er 78 : 22). However, with the other substrates, values decreased *versus* benzene (62–38% ee; avg. 50% *vs.* 56% in benzene). Since chlorobenzene has a lower freezing point, the reaction of (*S*)-**1a** and **3j** was repeated at −25 °C. Surprisingly, byproducts formed that were not evident in the

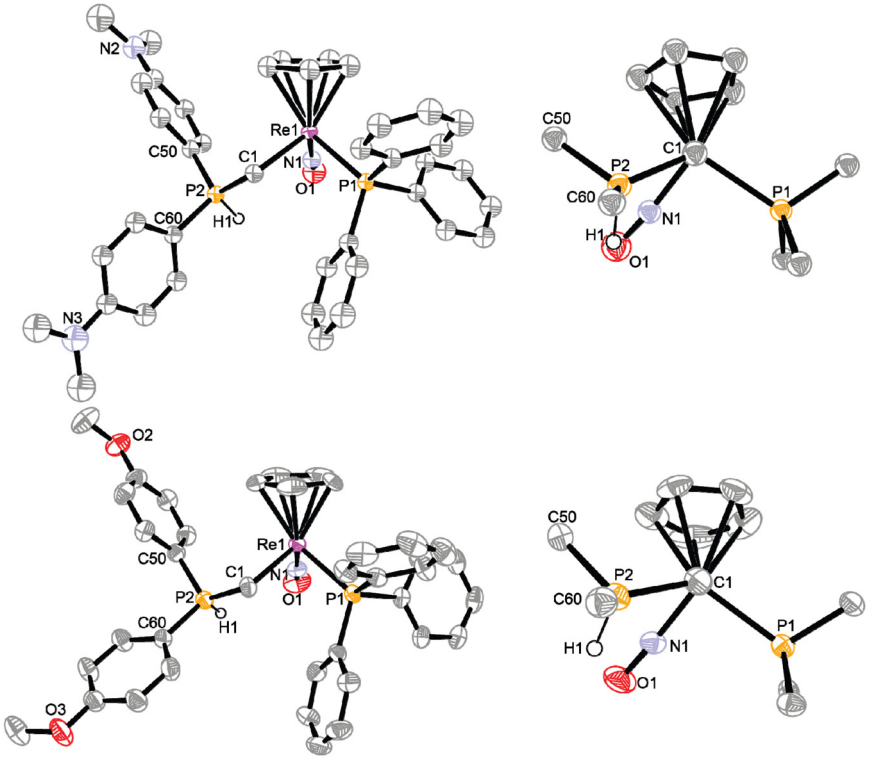


Fig. 1 Structures of the cations of [**1c**-H]$^+$ PF_6^- (bottom) and [**1d**-H]$^+$ PF_6^- (top) with thermal ellipsoids at the 50% probability level. Some of the atom labels have been changed from those in the CIF files to facilitate comparisons.

room temperature reactions. Rates and conversions were much lower in acetonitrile (*e.g.*, *ca.* 45% conversion of **3j** to **6j**, racemic **1a**, 160 h). Many of these trends and generalizations are illustrated graphically, often with additional data, elsewhere.[26]

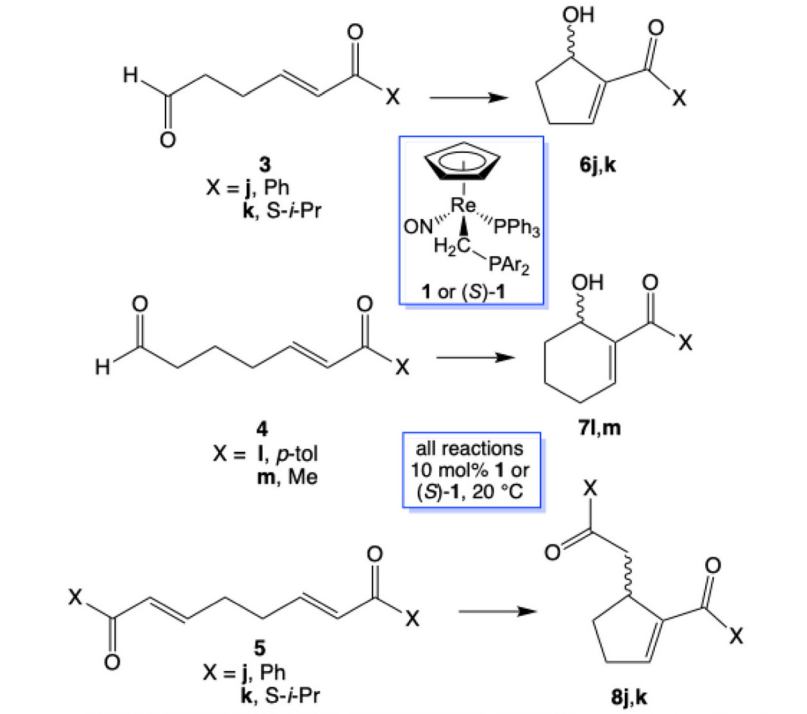
Donor groups in *para* positions (*e.g.*, Me, MeO, Me_2N) normally increase the basicities of aryl phosphines.[27,28] This should accelerate the formation of the intermediates **A** and **B** in Scheme 1. Accordingly, the racemic and enantiopure catalysts **1b–d** were similarly studied. Indeed, racemic **1b** gave faster cyclizations with all six substrates. With (*S*)-**1b**, enantioselectivities averaged marginally higher than those with (*S*)-**1a** (57% *vs.* 56% in benzene), with superior results with **6j**,**k**. However, a few product yields appeared lower as compared to **1a** or (*S*)-**1a**. Disappointingly, **1c**, with still more electron donating *p*-methoxy substituents, gave lower product yields (Scheme 4), and byproducts were evident by NMR. When (*S*)-**1c** was used, enantioselectivities nosedived to 41–0% ee. Such low ee values suggest that an achiral catalyst may be generated. The complexes **1d** and (*S*)-**1d** gave still poorer results.

The bis(2-biphenyl)phosphine adduct **1e** gave no reactions with all substrates examined. The bis(α-naphthyl) catalyst **1f** gave very slow reactions with **3j**,**k** (90% conversion to **6j** over 168 h) and essentially none with the other substrates. Perhaps these aryl substituents are simply too bulky for efficient catalysis. The phosphido complex (η^5-C_5H_5)Re(NO)(PPh_3)(PPh_2)[4a] is the most basic of all the types of rhenium-containing phosphines surveyed in the introduction.[4a] It was rapidly consumed under conditions of Scheme 4, and no catalysis occurred. NMR data strongly suggest the formation of phosphine oxides in some reactions, particularly with the poorer catalysts.

The Re,C stereogenic phosphine (S_{Re},S_C)-**9a** (Scheme 3) proved to be another slow catalyst, giving a *ca.* 86% conversion of **3j** to **6j** over the course of 168 h. It was much less effective with other substrates, and the related species (S_{Re},S_C)-**10a** gave only 10% conversion to **6j** over 120 h. Along the same lines, the previously reported diphosphine (S_{Re},S_C)-**11a** (Scheme 5)[24] gave no reaction with **3j** and other substrates. The diphosphine (S_{Re})-**12a** (Scheme 5),[10] which lacks a carbon stereocenter, did slowly convert **3j** to **6j** (27%, 72 h; 41%, 168–240 h), but the ee value was only 3%.

Discussion

A variety of racemic and enantiopure rhenium-containing phosphine catalysts has been described above. Those in Scheme 2 are easily accessed in two steps from the methyl complexes **2** or (*S*)-**2**, and if desired the second step can be carried out *in situ*. Thus, had a "privileged catalyst" been discovered during this work, it could well have been practical economically. However, in line with observations of other researchers, the optimum catalysts and conditions for intra-



reaction	data for **1a** and (*S*)-**1a** %yield[a] (isol/NMR C_6H_6)	ee % (C_6H_6)	ee % (C_6H_5Cl)	data for **1b** and (*S*)-**1b** %yield[a] (NMR C_6H_6/C_6H_5Cl)	ee % (C_6H_6)	data for **1c** and (*S*)-**1c** %yield[a] (NMR C_6H_6)	ee % (C_6H_6)
3j→6j	91 / 95	62	45	99 / 95	**74**	54	00
3k→6k	99 / 91	74	62	99 / 70	**78**[b]	90	41
4l→7l	91 / 99[c]	**38**	38	85 / 80	31[b]	75	26
4m→7m	86 / 90	**70**	47	85 / 65[d]	59[b]	70	−11
5j→8j	87 / 92[c]	42	**56**	75 / –	51	20	–
5k→8k	82 / 98	**52**	–	95 / –	49	73	–
	average 56% ee	average 50% ee			average 57% ee		

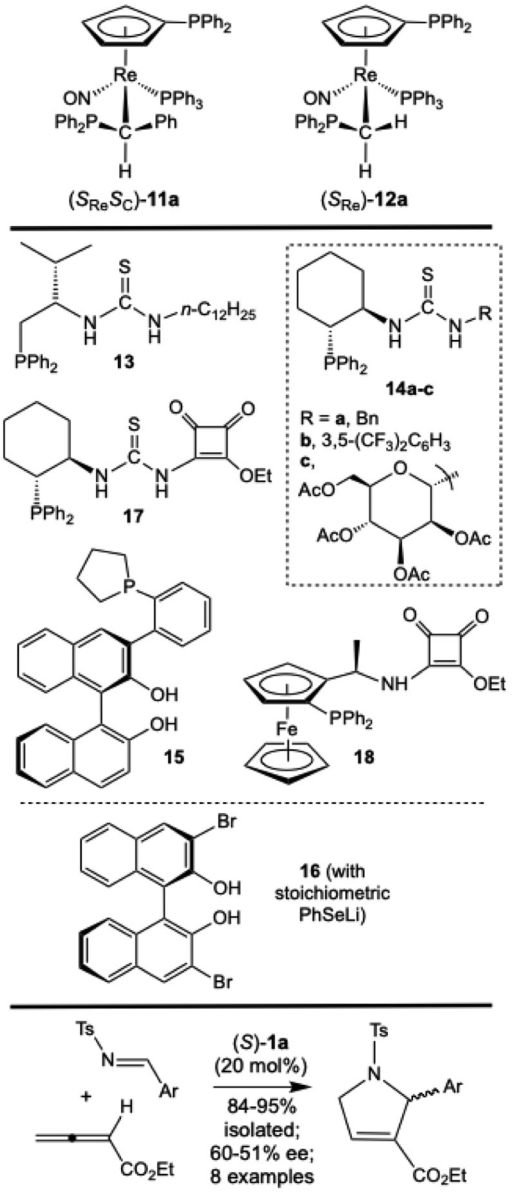
[a]for racemic catalyst. [b]ee in C_6H_5Cl: 40% (**6k**), 26% (**7l**), 10% (**7m**). [c]NMR yield in C_6H_5Cl: 93% (**7l**), 87% (**8j**). [d]starting material incompletely consumed.

Scheme 4 Catalysis of intramolecular Morita–Baylis–Hillman and Rauhut–Currier reactions by chiral rhenium-containing phosphines **1a–c**.

molecular Morita–Baylis–Hillman and Rauhut–Currier reactions can vary greatly from substrate to substrate.[4–6]

Nonetheless, there are discernable trends in our data. The substrates are more rapidly consumed as the donor strengths of the PAr_2 groups in **1** increase (**1a** < **1b** < **1c** < **1d**). However, with methoxy- and dimethylamino-substituted **1c**,**d**, product yields also greatly decrease, reflecting some combination of side-reactions and catalyst deactivation. Similarly, when phenyl is replaced by the much bulkier aryl groups 2-biphenyl and α-naphthyl (**1e**,**f**), little or very slow turnover is seen, perhaps for steric reasons. Related catalysts with an added $ReCH(R)PPh_2$ stereocenter (Scheme 3) or cyclopentadienyl-based PPh_2 group (Scheme 5), are essentially ineffective, for reasons that can only be speculated about.

Since our communication, several other chiral phosphorus-containing catalysts have been developed for intramolecular Morita–Baylis–Hillman or Rauhut–Currier reactions.[4] Those that have been applied to substrates used in this study are illustrated in Scheme 5 (middle).[29–32] Under highly optimized conditions in CH_2Cl_2, the thiourea-containing phosphine **13** effects the Rauhut–Currier cyclization of **5j** to **8k** in 80–88% isolated yields and ≥99% ee at 20 mol% loadings.[29a] The related catalyst **14a** was comparably effective at 10 mol% loadings.[29b] The binapthol-containing phosphine **15** gave **8k** in



Scheme 5 Other complexes used in this study (top) and additional relevant catalysts and reactions (middle, bottom).

only 44–38% isolated yields and 82–94% ee at 20 mol% loadings, although it was much more effective for cyclizations producing six-membered rings.[30] A reviewer has suggested that the non-phosphorus-containing catalyst system **16**, which has been applied to **5j**, also be highlighted.[32d]

The thiourea **14b**, which features an electronegative aryl NH substituent, effected the Morita–Baylis–Hillman cyclization of **4l** to **7l** in 79% isolated yield and 78% ee at 10 mol% loadings.[29c] The catalyst **17**, in which a squaramide unit has been introduced on nitrogen, gave **7l** in 94% isolated yield and 92% ee at 3 mol% loadings.[29d] A variant of **14a**,**b** with a mannose-derived NH substituent, **14c**, catalyzed the conversion of **3a** to **6k** in 93% isolated yield and 97% ee at only 2 mol% loadings.[29e] The ferrocene and squaramide-containing phosphine **18** catalyzed the same cyclization in 68% isolated yield and 88% ee at 20 mol% loadings (CH_2Cl_2, 7 d).[31] All of these catalysts are bifunctional, with extensively employed hydrogen bond donors or acceptors. Protic solvents or additives are often used in phosphine catalyzed reactions,[4,5,7b] but when the reactions in Scheme 4 were doped with *t*-BuOH, CF_3CH_2OH, or binaphthol, poorer results were always obtained.

In another study, we found that the fluorous aliphatic phosphine $P[(CH_2)_3(CF_2)_7CF_3]_3$ is a good achiral catalyst for the conversion of substrates **3j**,**k**, **4l**, and **5k** to **6j**,**k**, **7l**, and **8k**, respectively.[33] The basicity of the phosphorus atom can be modulated by varying the lengths of the methylene spacers and perfluoroalkyl segments, and three methylene groups proved to be the "sweet spot" in these cases. Probably the most obvious way to optimize the catalysts in Schemes 2 and 3 is to introduce chirality at the phosphorus donor atom. Another approach would be to mimic the bifunctionality of catalysts **13**–**18** (Scheme 5) in the rhenium coordination sphere.

Nonetheless, the phosphines **1** have other types of applications. For example, (*S*)-**1a** is a good catalyst for the enantioselective cycloaddition of allenes and tosylated aryl imines (Scheme 5, bottom),[11] and when combined with $[Pd(allyl)Cl]_2$, for the kinetic resolution of racemic esters of chiral alcohols, such as cyclohex-2-en-1-yl acetate.[13] Alternatively, they may serve as springboards to diphosphines of the types (S_{Re})-**12a** and (S_{Re},S_C)-**11a** (Scheme 5, top).[10,24] Such diphosphines chelate to rhodium, giving excellent catalysts for enantioselective hydrogenations of olefins and hydrosilylations of ketones.[34] This study provides a library of building blocks for further developing this catalyst family.

In conclusion, this investigation has greatly expanded the range of racemic and enantiopure rhenium-containing phosphorus donor ligands. Among these, **1a**,**b** and (*S*)-**1a**,**b** have clearly emerged as the best catalysts for (enantioselective) intramolecular Morita–Baylis–Hillman and Rauhut–Currier reactions. While several researchers have also made significant contributions to catalyst development, including bifunctional phosphorus Lewis bases that sometimes exhibit superior efficacy,[29–31] there is still much room for improvement regarding generality, enantioselectivity, catalyst loading, and other performance factors. Parallel efforts involving rhenium-containing *P*-stereogenic catalysts will be reported in a subsequent paper.[13]

Experimental section

General data

All reactions were conducted under N_2. The Ph_3C^+ PF_6^- (≥95%, Fluka)[35] was stored under argon at −30 °C. Other (mostly routine) details are provided in the ESI.†

$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2P(p\text{-}tol)_2H)]^+$ PF_6^- ($[\mathbf{1b\text{-}H}]^+$ PF_6^-)

A Schlenk flask was charged with racemic $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_3)$ (**2**, 0.244 g, 0.437 mmol)[15] and CH_2Cl_2 (15 mL). The solution was cooled to −78 °C and Ph_3C^+ PF_6^- (0.187 g, 0.481 mmol) added with stirring. After 1 h, $P(p\text{-tol})_2H$ (**b**,

0.112 g, 0.787 mmol) dissolved in CH_2Cl_2 (1 mL) was added. After 20 min, the cold bath was removed. After 1 h, the mixture was concentrated by oil pump vacuum (to *ca.* 2.5 mL) and added dropwise to stirred hexanes (25 mL). An orange powder precipitated, which was collected by filtration and washed with pentane (3 × 5 mL). The powder was dissolved in CH_2Cl_2 (3 mL) and benzene (15 mL). Hexanes (15 mL) were added with stirring and again an orange powder precipitated, which was collected by filtration, washed with hexanes (2 × 5 mL) and pentane (5 × 5 mL), and dried by oil pump vacuum to give [**1b**-H]$^+$ PF_6^- (0.376 g, 0.411 mmol, 94%), mp 179–181 °C, dec. Anal. calcd (%) for $C_{38}H_{37}F_6NOP_3Re$ (917.2): C 49.78, H 4.07, N 1.53; found: C 49.45, H 3.98, N 1.50.

NMR (CD_2Cl_2, δ/ppm): ^{1}H (400 MHz) 7.73–7.65, 7.51–7.43, 7.37–7.30 (3 m, $C_6\underline{H}_5$ and $C_6\underline{H}_4$, 23H), 6.91 (dd, ^1J(H,P) = 484 Hz, ^3J(H,H) = 13.3 Hz, P$\underline{H}$, 1H), 4.87 (s, $C_5\underline{H}_5$, 5H), 2.65–2.54 (m, C$\underline{H}$H′, 1H), 2.50, 2.40 (2 s, C$\underline{H}_3$ and C$\underline{H}_3$′, 2 × 3H), 2.32–2.18 (m, CH$\underline{H}$′, 1H); ^{13}C{^{1}H} (101 MHz) 91.0 (s, $\underline{C}_5H_5$), −34.9 (dd, ^1J(C,P) = 29.8 Hz, ^2J(C,P) = 4.1 Hz, $\underline{C}$HH′); PPh_3 at[36] 134.4 (d, ^1J(C,P) = 54.0 Hz, *i*), 134.0 (d, ^2J(C,P) = 10.6 Hz, *o*), 131.6 (d, ^4J(C,P) = 2.1 Hz, *p*), 129.5 (d, ^3J(C,P) = 10.4 Hz, *m*); P(*p*-tol)(*p*-tol)′ at 146.1 (d, ^4J(C,P) = 2.8 Hz, *p* to P), 145.5 (d, ^4J(C,P) = 2.8 Hz, *p*′ to P), 132.6 (d, ^2J(C,P) = 10.6 Hz, *o* to P), 131.9 (d, ^2J(C,P) = 10.5 Hz, *o*′ to P), 131.2 (d, ^3J(C,P) = 12.9 Hz, *m* to P), 130.9 (d, ^3J(C,P) = 12.2 Hz, *m*′ to P), 121.5 (d, ^1J(C,P) = 71.8 Hz, *i* to P), 119.2 (d, ^1J(C,P) = 88.2 Hz, *i*′ to P), 22.1, 22.0 (2 s, $\underline{C}H_3$ and C$\underline{H}_3$′); ^{31}P{^{1}H} (162 MHz) 28.8 (d, ^3J(P,P) = 10.9 Hz, $\underline{P}$H), 21.7 (d, ^3J(P,P) = 10.9 Hz, $\underline{P}Ph_3$), −144.0 (sept, ^1J(P,F) = 708 Hz, $\underline{P}F_6$).

IR (thin film, cm^{-1}): 1668 (s, ν_{NO}). MS:[37] 772 (90) [**1b**-H]$^+$, 558 (100) [**1b**-P(*p*-tol)$_2$H]$^+$.

(*S*)-[1b-H]$^+$ PF_6^-

A Schlenk flask was charged with (*S*)-**2** (0.250 g, 0.448 mmol)[15] and CH_2Cl_2 (15 mL). The solution was cooled to −78 °C and Ph_3C^+ PF_6^- (0.191 g, 0.493 mmol) added with stirring. After 1 h, **b** (0.115 g, 0.787 mmol) dissolved in CH_2Cl_2 (1 mL) was added. After 20 min, the cold bath was removed. After 1 h, the mixture was concentrated by oil pump vacuum (to *ca.* 2.5 mL) and EtOH (7 mL) added with stirring. A yellow powder precipitated, and the solvent volume was reduced by oil pump vacuum (to *ca.* 6 mL). The mixture was kept at −20 °C. After 2 h, the yellow powder was collected by filtration, washed with EtOH (1 mL) and hexanes (2 × 5 mL), and dried by oil pump vacuum to give (*S*)-[**1b**-H]$^+$ PF_6^- (0.353 g, 0.385 mmol, 86%), mp 179–180 °C, dec. Anal. calcd (%) for $C_{38}H_{37}F_6NOP_3Re$ (917.2): C 49.78, H 4.07, N 1.53; found: C 49.50, H 4.12, N 1.54. $[\alpha]_{26}^{589}$ = 257° ± 2° (*c* = 2.00 mg mL^{-1}, CH_2Cl_2). Spectroscopic data were similar to those of the racemate.

(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2P(*p*-tol)$_2$) (1b)

A Schlenk flask was charged with [**1b**-H]$^+$ PF_6^- (0.161 g, 0.191 mmol) and benzene (20 mL). The suspension was vigorously stirred and *t*-BuOK (0.0321 g, 0.287 mmol) added. After 1 h, the orange suspension was filtered through a plug of Celite. The plug was rinsed with benzene until the filtrate became colorless. The filtrate was concentrated by oil pump vacuum (to *ca.* 2 mL), layered with pentane (15 mL), and kept at 4 °C. After 48 h, the orange crystals were collected by filtration and dried by oil pump vacuum to give **1b** (0.118 g, 0.153 mmol, 80%), Dec. pt. 160–162 °C. Anal. calcd (%) for $C_{38}H_{36}NOP_2Re$ (770.9): C 59.21 H 4.71, N 1.82; found: C 58.98, H 4.98, N 1.81.

NMR (C_6D_6, δ/ppm): ^{1}H (300 MHz) 7.74 (apparent t, ^3J(H,H) = ^3J(H,P) = 7.0 Hz, $C_6\underline{H}_4$, *o* to P, 2H), 7.66 (apparent t, ^3J(H,H) = ^3J(H,P) = 7.0 Hz, $C_6\underline{H}_4$′, *o* to P, 2H), 7.53 (dd, ^3J(H,P) = 11.6 Hz, ^3J(H,H) = 9.6, *o*-$C_6\underline{H}_5$, 6H), 7.12–6.93 (m, *m*-, *p*-$C_6\underline{H}_5$ and $C_6\underline{H}_4$, *m* to P, 13H), 4.55 (s, $C_5\underline{H}_5$, 5H), 2.83 (dd, ^2J(H,H) = 11.6 Hz, J(H,P) = 9.7 Hz, C$\underline{H}$H′, 1H), 2.12, 2.08 (2 s, C$\underline{H}_3$ and C$\underline{H}_3$′, 2 × 3H), 2.15–2.05 (m, CH$\underline{H}$′, 1H); ^{13}C{^{1}H} (76 MHz) 89.9 (s, $\underline{C}_5H_5$), −18.1 (dd, ^1J(C,P) = 37.2 Hz, ^2J(C,P) = 4.7 Hz $\underline{C}$HH′); PPh_3 at 136.6 (d, ^1J(C,P) = 50.8 Hz, *i*), 134.0 (d, ^2J(C,P) = 10.2 Hz, *o*), 130.1 (s, *p*), 128.5 (d, ^3J(C,P) = 10.2 Hz, *m*); P(*p*-tol)(*p*-tol)′ at 144.7 (d, ^1J(C,P) = 20.6 Hz, *i* to P), 143.4 (d, ^1J(C,P) = 19.8 Hz, *i*′ to P), 137.0, 136.6 (2 s, *p* and *p*′ to P), 133.7 (d, ^2J(C,P) = 18.6 Hz, *o* to P), 133.1 (d, ^2J(C,P) = 17.6 Hz, *o*′ to P), 128.9 (d, ^3J(C,P) = 4.9 Hz, *m* to P), 128.9 (d, ^3J(C,P) = 5.8 Hz, *m*′ to P), 21.3, 21.2 (2 s, $\underline{C}H_3$ and C$\underline{H}_3$′); ^{31}P{^{1}H} (121 MHz) 26.8 (d, ^3J(P,P) = 6.7 Hz, $\underline{P}Ph_3$), 5.8 (d, ^3J(P,P) = 6.7 Hz, $\underline{P}$(*p*-tol)$_2$).

IR (thin film, cm^{-1}): 1644 (s, ν_{NO}). MS:[37] 771 (11) [**1b**]$^+$, 558 (100) [**1b**-P(*p*-tol)$_2$]$^+$.

(*S*)-1b

(*S*)-[**1b**-H]$^+$ PF_6^- (0.187 g, 0.204 mmol), *t*-BuOK (0.0343 g, 0.306 mmol), and benzene (20 mL) were combined in a procedure analogous to that given for the racemate. An identical workup gave (*S*)-**1b** as an orange powder (0.138 g, 0.180 mmol, 88%). Dec. pt. 125–130 °C. Spectroscopic data were similar to those of the racemate.

[(η^5-C_5H_5)Re(NO)(PPh_3)(CH_2P(*p*-$C_6H_4OCH_3$)$_2$H)]$^+$ PF_6^- ([**1c**-H]$^+$ PF_6^-)

A Schlenk flask was charged with racemic **2** (0.246 g, 0.441 mmol)[15] and CH_2Cl_2 (15 mL). The solution was cooled to −78 °C and Ph_3C^+ PF_6^- (0.188 g, 0.485 mmol) added with stirring. After 1 h, P(*p*-$C_6H_4OCH_3$)$_2$H (**c**, 0.141 g, 0.573 mmol)[17] dissolved in CH_2Cl_2 (1 mL) was added dropwise. After 20 min, the cold bath was removed. After 1 h, the sample was concentrated by oil pump vacuum (to *ca.* 4 mL). A CH_3OH/EtOH mixture (2.5 mL, 2 : 3 v/v) was added, followed by CH_2Cl_2 until the sample became homogeneous. Hexanes (*ca.* 20 mL) were added with stirring and an orange powder precipitated, which was collected by filtration, washed with hexanes (3 × 3 mL), and dried by oil pump vacuum to give [**1c**-H]$^+$ PF_6^- (0.369 g, 0.389 mmol, 88%), mp 207–208 °C, dec. Anal. calcd (%) for $C_{38}H_{37}F_6NO_3P_3Re$ (949.1): C 48.10, H 3.93, N 1.48; found: C 47.76, H 3.84, N 1.45.

NMR (δ/ppm): ^{1}H (400 MHz, $CDCl_3$) 7.78 (dd, ^3J(H,P) = 13.0, ^3J(H,H) = 8.5 Hz, $C_6\underline{H}_4$, *o* to P, 2H), 7.31–7.49 (m, $C_6\underline{H}_5$ and $C_6\underline{H}_4$′, *o* to P, 17H), 7.12 (d, ^3J(H,H) = 8.8 Hz, $C_6\underline{H}_4$, *m* to P, 2H), 6.96 (d, ^3J(H,H) = 8.5 Hz, $C_6\underline{H}_4$′, *m* to P, 2H), 6.90 (dd, ^1J(H,P) = 478 Hz, ^3J(H,H) = 12.0 Hz, P$\underline{H}$, 1H), 4.90 (s, $C_5\underline{H}_5$,

5H), 3.89, 3.83 (2 s, OCH$_3$ and OCH$_3$′, 2 × 3H), 2.68 (apparent dt, ^2J(H,H) = 19.8 Hz, J(H,P) = ^3J(H,H) = 14.5 Hz, CHH′, 1H), 2.50 (dd, ^2J(H,H) = 19.8 Hz, J(H,P) = 12.2 Hz CHH′, 1H); ^{13}C{^{1}H} (101 MHz, CD_2Cl_2) 90.9 (s, C$_5$H$_5$), −34.0 (dd, ^1J(C,P) = 30.8 Hz, ^2J(C,P) = 4.4 Hz, CHH′); PPh$_3$ at 134.4 (d, ^1J(C,P) = 40.0 Hz, *i*), 134.0 (d, ^2J(C,P) = 10.4 Hz, *o*), 131.6 (d, ^4J(C,P) = 2.4 Hz, *p*), 129.5 (d, ^3J(C,P) = 10.4 Hz, *m*); P(C$_6$H$_4$OCH$_3$)(C$_6$H$_4$OCH$_3$)′ at 164.8 (d, ^4J(C,P) = 2.8 Hz, *p* to P), 164.4 (d, ^4J(C,P) = 2.4 Hz, *p*′ to P), 134.71, 134.70 (2 s, *m* and *m*′ to P), 116.2 (d, ^2J(C,P) = 13.6 Hz, *o* to P), 115.8 (d, ^2J(C,P) = 12.8 Hz, *o*′ to P), 115.5 (d, ^1J(C,P) = 75.9 Hz, *i* to P), 113.0 (d, ^1J(C,P) = 92.7 Hz, *i*′ to P), 56.3, 55.2 (2 s, OCH$_3$ and OCH$_3$′); ^{31}P{^{1}H} (162 MHz, $CDCl_3$) 29.2 (d, ^3J(P,P) = 10.9 Hz, PH), 23.1 (d, ^3J(P,P) = 10.9 Hz, PPh$_3$), −142.9 (sept, ^1J(P,F) = 708 Hz, PF$_6$).

IR (thin film, cm^{-1}): 1640 (s, ν_{NO}). MS:[37] 804 (100) [**1b**-H]$^+$, 558 (90) [**1b**-P(*p*-C$_6$H$_4$OCH$_3$)$_2$H]$^+$.

(*S*)-[1c-H]$^+$ PF$_6^-$

Complex (*S*)-**2** (0.399 g, 0.715 mmol),[15] CH_2Cl_2 (20 mL), Ph_3C^+ PF_6^- (0.305 g, 0.787 mmol), **c** (0.211 g, 0.858 mmol),[17] and CH_2Cl_2 (1 mL) were combined in a procedure analogous to that given for the racemate. An identical workup gave (*S*)-[**1c**-H]$^+$ PF$_6^-$ as an orange powder (0.645 g, 0.680 mmol, 95%), mp 204–205 °C, dec. Anal. calcd (%) for $C_{38}H_{37}F_6NO_3P_3Re$ (949.1): C 48.10, H 3.93, N 1.48; found: C 47.98, H 3.67, N 1.45. $[\alpha]_{25}^{589}$ = 248° ± 2° (*c* = 2.00 mg mL^{-1}, CH_2Cl_2). Spectroscopic data were similar to those of the racemate.

(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_2$P(*p*-C$_6$H$_4$OCH$_3$)$_2$) (1c)

A Schlenk flask was charged with [**1c**-H]$^+$ PF$_6^-$ (0.154 g, 0.162 mmol) and benzene (10 mL). The suspension was vigorously stirred and *t*-BuOK (0.0273 g, 0.243 mmol) added. After 1 h, the orange suspension was filtered through a plug of Celite. The plug was rinsed with benzene until the filtrate became colorless. The filtrate was concentrated by oil pump vacuum (to *ca.* 2 mL), layered with pentane (15 mL), and kept at 4 °C. After 48 h, the orange crystals were collected by filtration and dried by oil pump vacuum to give **1c** (0.100 g, 0.125 mmol, 77%), Dec. pt. 162 °C. Anal. calcd (%) for $C_{38}H_{36}NO_3P_2Re$ (802.9): C 56.85, H 4.52, N 1.74; found: C 56.38, H 4.46, N 1.74.

NMR (δ/ppm): ^{1}H (400 MHz, C_6D_6) 7.74 (dd, ^3J(H,H) = 8.6 Hz, ^3J(H,P) = 5.8 Hz, C$_6$H$_4$, *o* to P, 2H), 7.68 (dd, ^3J(H,H) = 8.6, ^3J(H,P) = 5.8 Hz, C$_6$H$_4$′, *o* to P, 2H), 7.56–7.50 (m, *o*-C$_6$H$_5$, 6H), 7.07–7.01, 7.00–6.95 (2 m, *m*-, *p*-C$_6$H$_5$, 9H), 6.91 (d, ^3J(H,H) = 8.6 Hz, C$_6$H$_4$, *m* to P, 2H), 6.79 (d, ^3J(H,H) = 8.6 Hz, C$_6$H$_4$′, *m* to P, 2H), 4.59 (s, C$_5$H$_5$, 5H), 3.30, 3.27 (2 s, OCH$_3$ and OCH$_3$′, 2 × 3H), 2.83 (dd, ^2J(H,H) = 11.9 Hz, J(H,P) = 9.7 Hz, CHH′, 1H), 2.09 (dd, ^2J(H,H) = 11.9 Hz, J(H,P) = 2.5 Hz, CHH′, 1H); ^{13}C{^{1}H} (101 MHz, CD_2Cl_2) 90.3 (s, C$_5$H$_5$), −18.1 (dd, ^1J(C,P) = 35.4 Hz, ^2J(C,P) = 5.2 Hz, CHH′); PPh$_3$ at 136.3 (d, ^1J(C,P) = 51.6 Hz, *i*), 134.1 (d, ^2J(C,P) = 10.7 Hz, *o*), 130.5 (s, *p*), 128.8 (d, ^3J(C,P) = 10.4 Hz, *m*); P(C$_6$H$_4$OCH$_3$)(C$_6$H$_4$OCH$_3$)′ at 159.8, 159.5 (2 s, *p* and *p*′ to P), 138.4 (d, ^1J(C,P) = 18.8 Hz, *i* to P), 137.4 (d, ^1J(C,P) = 18.1 Hz, *i*′ to P), 134.2 (d, ^2J(C,P) = 20.6 Hz, *o* to P), 134.0 (d, ^2J(C,P) = 18.4 Hz, *o*′ to P), 113.7 (d, ^3J(C,P) = 7.0 Hz, *m* to P), 113.6 (d, ^3J(C,P) = 5.9 Hz, *m*′ to P), 55.5, 55.4 (2 s, OCH$_3$ and OCH$_3$′); ^{31}P{^{1}H} (162 MHz, C_6D_6) 27.6 (d, ^3J(P,P) = 6.9 Hz, PPh$_3$), 5.1 (d, ^3J(P,P) = 6.9 Hz, P(C$_6$H$_4$OCH$_3$)$_2$).

IR (thin film, cm^{-1}): 1633 (s, ν_{NO}). MS:[37] 803 (10) [**1c**]$^+$, 558 (100) [**1c**-P(*p*-C$_6$H$_4$OCH$_3$)$_2$H]$^+$.

(*S*)-1c

(*S*)-[**1c**-H]$^+$ PF$_6^-$ (0.225 g, 0.237 mmol), *t*-BuOK (0.0398 g, 0.356 mmol), and benzene (20 mL) were combined in a procedure analogous to that given for the racemate. An identical workup gave (*S*)-**1c** as an orange-red powder (0.166 g, 0.206 mmol, 87%), mp 125–130 °C, dec. Spectroscopic data were similar to those of the racemate.

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_2$P(*p*-C$_6$H$_4$N(CH$_3$)$_2$)$_2$H)]$^+$ PF$_6^-$ ([**1d**-H]$^+$ PF$_6^-$)

A Schlenk flask was charged with racemic **2** (0.212 g, 0.380 mmol)[15] and CH_2Cl_2 (15 mL). The solution was cooled to −78 °C and Ph_3C^+ PF_6^- (0.162 g, 0.418 mmol) added with stirring. After 1 h, P(*p*-C$_6$H$_4$N(CH$_3$))$_2$H (**d**, 0.134 g, 0.494 mmol)[17] dissolved in CH_2Cl_2 (1 mL) was added dropwise. After 20 min, the cold bath was removed. After 1 h, the sample was concentrated by oil pump vacuum (to *ca.* 4 mL). A CH_3OH/EtOH mixture (5.5 mL, 4 : 5 v/v) was added, followed by CH_2Cl_2 until the sample became homogeneous. Then hexanes (*ca.* 20 mL) were added with stirring. The precipitate was washed with EtOH (2 × 1 mL) and hexanes (2 × 3 mL). After drying by oil pump vacuum [**1d**-H]$^+$ PF$_6^-$ was obtained as an orange powder (0.345 g, 0.349 mmol, 93%), mp 230–232 °C, dec. Anal. calcd (%) for $C_{41}H_{45}F_6N_3OP_3Re$ (989.2): C 49.28, H 4.45, N 4.31; found: C 48.91, H 4.39, N 4.22.

NMR (δ/ppm): ^{1}H (400 MHz, $CDCl_3$) 7.61 (dd, ^3J(H,P) = 12.6 Hz, ^3J(H,H) = 8.5 Hz, C$_6$H$_4$, *o* to P, 2H), 7.49–7.42, 7.38–7.31 (2 m, C$_6$H$_5$, 15H), 7.26 (dd, ^1J(H,P) = 472 Hz, ^3J(H,H) = 10.7 Hz, PH, 1H), 7.18 (dd, ^3J(H,P) = 12.1, ^3J(H,H) = 8.6 Hz, C$_6$H$_4$′, *o* to P, 2H), 6.80 (d, ^3J(H,H) = 8.6 Hz, C$_6$H$_4$, *m* to P, 2H), 6.62 (d, ^3J(H,H) = 8.6 Hz, C$_6$H$_4$′, *m* to P, 2H), 4.87 (s, C$_5$H$_5$, 5H), 3.07, 2.99 (2 s, CH$_3$ and CH$_3$′, 2 × 6H), 2.52–2.37 (m, CHH′, 2H); ^{13}C{^{1}H} (101 MHz, CD_2Cl_2) 90.8 (s, C$_5$H$_5$), −32.0 (dd, ^1J(C,P) = 33.3 Hz, ^2J(C,P) = 3.4 Hz, CHH′); PPh$_3$ at 134.7 (d, ^1J(C,P) = 53.7 Hz, *i*), 134.0 (d, ^2J(C,P) = 10.5 Hz, *o*), 131.5 (d, ^4J(C,P) = 2.0 Hz, *p*), 129.5 (d, ^3J(C,P) = 10.4 Hz, *m*); P(C$_6$H$_4$N(CH$_3$)$_2$)(C$_6$H$_4$N(CH$_3$)$_2$)′ at 154.2 (d, ^4J(C,P) = 1.9 Hz, *p* to P), 153.7 (d, ^4J(C,P) = 2.0 Hz, *p*′ to P), 134.0 (d, ^3J(C,P) = 11.5 Hz, *m* to P), 133.3 (d, ^3J(C,P) = 11.5 Hz, *m*′ to P), 112.6 (d, ^2J(C,P) = 13.3 Hz, *o* to P), 112.3 (d, ^2J(C,P) = 12.5 Hz, *o*′ to P), 108.2 (d, ^1J(C,P) = 79.9 Hz, *i* to P), 104.7 (d, ^1J(C,P) = 98.9 Hz, *i*′ to P), 40.3, 40.2 (2 s, CH$_3$ and CH$_3$′); ^{31}P{^{1}H} (162 MHz, CD_2Cl_2) 28.7 (d, ^3J(P,P) = 11.9 Hz, PH) 23.9 (d, ^3J(P,P) = 11.9 Hz, PPh$_3$), −142.9 (sept, ^1J(P,F) = 714 Hz, PF$_6$).

IR (thin film, cm^{-1}): 1645 (s, ν_{NO}). MS:[37] 830 (100) [**1d**-H]$^+$, 558 (62) [**1d**-P(*p*-C$_6$H$_4$N(CH$_3$)$_2$)$_2$H]$^+$.

(*S*)-[1d-H]$^+$ PF$_6^-$

Complex (*S*)-**2** (0.300 g, 0.538 mmol),[15] CH_2Cl_2 (15 mL), Ph_3C^+ PF_6^- (0.234 g, 0.603 mmol), **d** (0.175 g, 0.646 mmol),[17] and

CH_2Cl_2 (1 mL) were combined in a procedure analogous to that given for the racemate. After the reaction mixture was stirred at room temperature for 1 h, the sample was concentrated by oil pump vacuum (to *ca.* 3 mL). Then EtOH (7 mL) was added, and the mixture kept at −20 °C. After 2 h, the precipitate was collected by filtration, washed with EtOH (1 mL) and hexanes (2 × 3 mL), and dried by oil pump vacuum to give (*S*)-[**1d**-H]$^+$ PF_6^- as a yellow powder (0.400 g, 0.410 mmol, 76%), mp 180–182 °C, dec. Anal. calcd (%) for $C_{40}H_{43}F_6N_3OP_3Re$ (975.2): C 49.28, H 4.45, N 4.31; found: C 48.79, H 4.71, N 4.21. $[\alpha]_{25}^{589}$ = 202° ± 2° (*c* = 2.00 mg mL^{-1}, CH_2Cl_2). Spectroscopic data were similar to those of the racemate.

(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_2$P(*p*-C$_6$H$_4$N(CH$_3$)$_2$)) (1d)

A Schlenk flask was charged with [**1d**-H]$^+$ PF_6^- (0.212 g, 0.217 mmol) and benzene (20 mL). The suspension was vigorously stirred and *t*-BuOK (0.0365 g, 0.326 mmol) added. After 1 h, the orange suspension was filtered through a plug of Celite. The plug was rinsed with benzene until the filtrate became colorless. The filtrate was concentrated by oil pump vacuum (to *ca.* 4 mL), layered with pentane (15 mL), and kept at 4 °C. After 48 h, the orange crystals were collected by filtration and dried by oil pump vacuum to give **1d** as a red solid (0.153 g, 0.185 mmol, 85%). Dec. pt. 157–158 °C. Anal. calcd (%) for $C_{41}H_{44}N_3OP_2Re$ (829.2): C 57.96, H 5.11, N 5.07; found: C 58.07, H 4.89, N 4.97.

NMR (C_6D_6, δ/ppm): ^{1}H (300 MHz) 7.82 (dd, ^3J(H,H) = 8.6 Hz, ^3J(H,P) = 6.3 Hz, $C_6\underline{H}_4$, *o* to P, 2H), 7.76 (dd, ^3J(H,H) = 8.6 Hz, ^3J(H,P) = 6.0 Hz, $C_6\underline{H}_4'$, *o* to P, 2H), 7.65–7.55 (m, *o*-$C_6\underline{H}_5$, 6H), 7.11–6.95 (m, *m*-, *p*-$C_6\underline{H}_5$, 9H), 6.72 (d, ^3J(H,H) = 8.6 Hz, $C_6\underline{H}_4$, *m* to P, 2H), 6.60 (d, ^3J(H,H) = 8.6 Hz, $C_6\underline{H}_4'$, *m* to P, 2H), 4.63 (s, $C_5\underline{H}_5$, 5H), 2.94 (dd, ^2J(H,H) = 11.5 Hz, J(H,P) = 9.7 Hz, C$\underline{H}$H′, 1H), 2.52, 2.50 (2 s, C$\underline{H}_3$ and C$\underline{H}_3$′, 2 × 6H), 2.25 (dd, ^2J(H,H) = 11.5 Hz, J(H,P) = 2.5 Hz, CH$\underline{H}$′, 1H); ^{13}C{^{1}H} (76 MHz) 89.9 (s, $\underline{C}_5H_5$), −16.6 (dd, ^1J(C,P) = 36.6 Hz, ^2J(C,P) = 4.8 Hz $\underline{C}$HH′); PPh$_3$ at 136.8 (d, ^1J(C,P) = 50.9 Hz, *i*), 134.1 (d, ^2J(C,P) = 10.4 Hz, *o*), 130.0 (d, ^4J(C,P) = 1.6 Hz, *p*), 128.5 (d, ^3J(C,P) = 10.0 Hz, *m*); P($\underline{C}_6H_4N(CH_3)_2$)($\underline{C}_6H_4N(CH_3)_2$)′ at 150.5, 150.2 (2 s, *p* and *p*′ to P), 134.8 (d, ^1J(C,P) = 19.8 Hz, *i* to P), 133.9 (d, ^1J(C,P) = 18.4 Hz, *i*′ to P), 134.4 (s (other line of expected d obscured), *o* to P), 133.8 (d, ^2J(C,P) = 15.9 Hz, *o*′ to P), 113.0 (d, ^3J(C,P) = 6.0 Hz, *m* to P), 112.7 (d, ^3J(C,P) = 7.1 Hz, *m*′ to P), 40.4, 40.3 (2 s, $\underline{C}H_3$ and $\underline{C}H_3$′); ^{31}P{^{1}H} (121 MHz) 27.2 (d, ^3J(P,P) = 6.7 Hz, $\underline{P}Ph_3$), 2.8 (d, ^3J(P,P) = 6.7 Hz, $\underline{P}$(*p*-$C_6H_4N(CH_3)_2)_2$).

IR (thin film, cm^{-1}): 1633 (s, ν_{NO}). MS:[37] 830 (51) [**1d**]$^+$, 558 (100) [**1d**-P(*p*-$C_6H_4N(CH_3)_2)_2$H]$^+$.

(*S*)-1d

(*S*)-[**1d**-H]$^+$ PF_6^- (0.196 g, 0.201 mmol), *t*-BuOK (0.0338 g, 0.302 mmol), and benzene (20 mL) were combined in a procedure analogous to that given for the racemate. An identical workup gave (*S*)-**1d** as a red powder (0.149 g, 0.179 mmol, 89%), mp 130–135 °C, dec. Spectroscopic data were similar to those of the racemate.

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_2$P(2-biphen)$_2$H)]$^+$ PF_6^- ([**1e**-H]$^+$ PF_6^-)

A Schlenk flask was charged with racemic **2** (0.212 g, 0.380 mmol)[15] and CH_2Cl_2 (15 mL). The solution was cooled to −78 °C and Ph_3C^+ PF_6^- (0.162 g, 0.418 mmol) added with stirring. After 1 h, P(2-biphen)$_2$H (**e**, 0.167 g, 0.494 mmol) dissolved in CH_2Cl_2 (1.5 mL) was added dropwise. After 20 min, the cold bath was removed. After 1 h, the sample was concentrated by oil pump vacuum (to *ca.* 4 mL). A CH_3OH/EtOH mixture (4 mL, 1 : 1 v/v) was added. The solution was added dropwise to vigorously stirred hexanes (75 mL). The precipitate was collected by filtration, washed with hexanes (3 × 3 mL), and dried by oil pump vacuum to give [**1e**-H]$^+$ PF_6^- as an orange powder (0.376 g, 0.361 mmol, 95%), mp 236 °C, dec. Anal. calcd (%) for $C_{48}H_{41}F_6NOP_3Re$ (1041.2): C 55.38, H 3.97, N 1.35; found: C 55.28, H 4.05, N 1.37.

NMR (CD_2Cl_2, δ/ppm): ^{1}H (400 MHz) 7.79–7.67, 7.62–7.35, 7.26–7.17, 7.11–7.00 (4 m, aryl-$\underline{H}$, 33H), 6.48 (dd (other part of expected ddd obscured), ^3J(H,H) = 12.4 Hz, ^3J(H,H′) 3.1 Hz, P$\underline{H}$, 1H), 4.46 (s, $C_5\underline{H}_5$, 5H), 2.30–2.16 (m, C$\underline{H}$H′, 1H), 1.61–1.50 (m, CH$\underline{H}$′, 1H); ^{13}C{^{1}H} (101 MHz) 90.7 (s, $\underline{C}_5H_5$), −30.9 (dd, ^1J(C,P) = 28.8 Hz, ^2J(C,P) = 3.8 Hz, $\underline{C}$HH′); PPh$_3$ at 134.4 (d, ^1J(C,P) = 53.7 Hz, *i*), 133.8 (d, ^2J(C,P) = 10.7 Hz, *o*), 131.6 (d, ^4J(C,P) = 1.9 Hz, *p*), 129.4 (d, ^3J(C,P) = 10.7 Hz, *m*); P(2-biphen)(2-biphen)′ at[38] 147.8, (d, J(C,P) = 6.5 Hz), 146.6 (d, J(C,P) = 9.2 Hz), 139.6 (d, J(C,P) = 5.0 Hz), 139.5 (d, J(C,P) = 4.6 Hz), 134.3 (d, J(C,P) = 2.3 Hz), 134.0 (d, J(C,P) = 2.7 Hz), 133.5 (d, J(C,P) = 10.7 Hz), 132.7 (d, J(C,P) = 10.0 Hz), 132.4 (d, J(C,P) = 8.8 Hz), 132.1 (d, J(C,P) = 8.1 Hz), 129.78, 129.76, 129.7, 129.5, 129.4 (5 s), 129.2 (d, J(C,P) = 10.7 Hz), 128.7 (d, J(C,P) = 11.9 Hz), 125.4 (d, ^1J(C,P) = 65.2 Hz, *i* to P), 118.7 (d, ^1J(C,P) = 87.4 Hz, *i*′ to P); ^{31}P{^{1}H} (162 MHz) 24.0 (d, ^3J(P,P) = 20.8 Hz, $\underline{P}$H), 20.5 (d, ^3J(P,P) = 20.8 Hz, $\underline{P}Ph_3$), −142.9 (sept, ^1J(P,F) = 708 Hz, $\underline{P}F_6$).

IR (thin film, cm^{-1}): 1660 (s, ν_{NO}). MS:[37] 896 (80) [**1e**-H]$^+$, 558 (100) [**1e**-P(2-biphen)$_2$H]$^+$.

(η^5-C_5H_5)Re(NO)(PPh$_3$)(CH$_2$P(2-biphen)$_2$) (1e)

A Schlenk flask was charged with racemic [**1e**-H]$^+$ PF_6^- (0.520 g, 0.500 mmol) and benzene (30 mL). The suspension was vigorously stirred and solid *t*-BuOK (0.0840 g, 0.749 mmol) added. After 1 h, the orange suspension was filtered through a plug of Celite. The plug was rinsed with benzene until the filtrate became colorless. The filtrate was concentrated by oil pump vacuum to *ca.* 5 mL and layered with pentane (35 mL). The orange precipitate was collected by filtration and dried by oil pump vacuum to give **1e** (0.406 g, 0.453 mmol, 91%), Dec. pt. 205 °C. Anal. calcd (%) for $C_{48}H_{40}NOP_2Re$ (895.2): C 64.42, H 4.50, N 1.57; found: C 64.15, H 4.11, N 1.64.

NMR (CD_2Cl_2, δ/ppm): ^{1}H (400 MHz) 7.41–7.33, 7.31–7.20, 7.14–6.98 (3 m, aryl-$\underline{H}$, 32H), 4.39 (s, $C_5\underline{H}_5$, 5H), 1.89 (apparent dt, ^2J(H,H) = 12.6 Hz, ^2J(H,P) = ^3J(H,P) = 8.6 Hz, C$\underline{H}$H′, 1H), 1.32 (ddd, ^2J(H,H) = 12.6 Hz, ^2J(H,P) = 8.6 Hz, ^3J(H,P) = 2.5 Hz, CH$\underline{H}$′, 1H); ^{13}C{^{1}H} (76 MHz) 90.9 (dd, ^2J(C,P) = 4.4 Hz, ^3J(C,P) = 1.2 Hz, $\underline{C}_5H_5$), −16.3 (dd, ^1J(C,P) = 39.6 Hz, ^2J(C,P) = 5.1 Hz, $\underline{C}$HH′); PPh$_3$ at 136.7 (d, ^1J(C,P) = 51.4 Hz, *i*), 134.1 (d, ^2J(C,P) =

10.5 Hz, *o*), 130.5 (d, ^4J(C,P) = 2.0 Hz, *p*), 128.8 (d, ^3J(C,P) = 10.1 Hz, *m*); P(2-biphen)(2-biphen)′ at[38] 149.2, 149.2, 148.8, 148.7, 146.5, 146.2, 144.3, 144.2, 144.0, 144.0, 139.8, 139.6, 135.8, 135.7, 131.3, 131.0, 131.0, 130.7, 130.7, 130.5, 130.4, 130.4, 130.3, 128.2, 128.1, 127.4, 127.3, 127.0, 126.9, 126.7; ^{31}P{^{1}H} (162 MHz) 24.6 (d, ^3J(P,P) = 6.9 Hz, PPh$_3$), −5.7 (d, ^3J(P,P) = 6.9 Hz, P(2-biphen)$_2$).

IR (thin film, cm^{-1}): 1621 (s, ν_{NO}). MS:[37] *m*/*z* (%): 896 (80) [**1e**-H]$^+$, 558 (100) [**1e**-P(2-biphen)$_2$]$^+$.

[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_2$P(α-naph)$_2$H)]$^+$ PF$_6^-$ ([**1f**-H]$^+$ PF$_6^-$)

A Schlenk flask was charged with racemic **2** (0.500 g, 0.896 mmol)[15] and CH_2Cl_2 (25 mL). The solution was cooled to −78 °C and Ph_3C^+ PF_6^- (0.382 g, 0.986 mmol)[18] added with stirring. After 1 h, P(α-naph)$_2$H (**f**, 0.308 g, 1.075 mmol) dissolved in CH_2Cl_2 (5 mL) was added. After 20 min, the cold bath was removed. After 1 h, the sample was concentrated by oil pump vacuum (to *ca.* 4 mL). A CH_3OH/EtOH mixture (4 mL, 1 : 1 v/v) was added. Then hexanes (*ca.* 20 mL) were added dropwise with vigorous stirring. The precipitate was collected by filtration, washed with hexanes (3 × 3 mL), and dried by oil pump vacuum to give [**1f**-H]$^+$ PF_6^- as an orange powder (0.772 g, 0.781 mmol, 87%), Dec. pt. 181–183 °C. Anal. calcd (%) for $C_{44}H_{37}F_6NOP_3Re$ (989.2): C 53.44, H 3.77, N 1.42; found: C 53.20, H 3.72, N 1.39.

NMR (CD_2Cl_2, δ/ppm): ^{1}H (400 MHz) 6.48 (dd; other part of expected ddd obscured), (^3J(H,H) = 12.3 Hz, ^3J(H,H′) = 3.0 Hz, PH, 1H), 8.45 (dd, ^3J(H,P) = 17.3 Hz, ^3J(H,H) = 7.1 Hz, 2-C$_{10}$H$_7$, 1H), 8.34 (dd, ^3J(H,P) = 16.0 Hz, ^3J(H,H) = 7.2 Hz, 2-C$_{10}$H$_7$′, 1H), 8.25, 8.17, 8.12, 8.02, 7.95, 7.82 (6 d, ^3J(H,H) = 8.2, 8.4, 8.4, 8.0, 8.0, and 8.3 Hz, 4-, 5-, 8-C$_{10}$H$_7$ and 4-, 5-, 8-C$_{10}$H$_7$′, 6 × 1H), 7.80–7.71, 7.69–7.60 (2 m, 6-, 7-C$_{10}$H$_7$ and 6-, 7-C$_{10}$H$_7$′, 2 × 2H), 7.55 (apparent t, ^3J(H,H) = 7.0 and 7.0 Hz, 3-C$_{10}$H$_7$, 1H), 7.49 (apparent t, ^3J(H,H) = 7.2 and 7.2 Hz, 3-C$_{10}$H$_7$′, 1H), 7.47–7.31 (m, C$_6$H$_5$, 15H), 4.62 (s, C$_5$H$_5$, 5H), 3.06–2.96, 2.87–2.74 (2 m, CHH′, 2 × 1H); ^{13}C{^{1}H} (101 MHz) 90.6 (s, C$_5$H$_5$), −33.9 (d, ^1J(C,P) = 27.4 Hz, CHH′); PPh$_3$ at 134.1 (d, ^1J(C,P) = 54.8 Hz, *i*), 133.8 (d, ^2J(C,P) = 10.5 Hz, *o*), 131.4 (d, ^4J(C,P) = 2.1 Hz, *p*), 129.4 (d, ^3J(C,P) = 10.5 Hz, *m*); P(α-naph)(α-naph)′ at[38] 135.8 (d, *J*(C,P) = 2.9), 135.6 (d, *J*(C,P) = 2.9 Hz), 135.5 (d, *J*(C,P) = 10.5 Hz), 135.2 (d, *J*(C,P) = 11.8 Hz), 134.0 (d, *J*(C,P) = 4.6 Hz), 133.9 (d, *J*(C,P) = 3.4 Hz), 132.8 (d, *J*(C,P) = 8.4 Hz), 132.3 (d, *J*(C,P) = 5.9 Hz), 130.4, 130.2, 129.6, 128.8, 128.1, 127.5 (6 s), 126.0 (d, *J*(C,P) = 11.4 Hz), 125.9 (d, *J*(C,P) = 11.4 Hz), 124.1 (d, *J*(C,P) = 8.0 Hz), 123.5 (d, *J*(C,P) = 8.0 Hz), 120.5 (d, ^1J(C,P) = 65.3 Hz, 1-C$_{10}$H$_7$), 119.6 (d, ^1J(C,P) = 83.5 Hz, 1-C$_{10}$H$_7$′); ^{31}P{^{1}H} (162 MHz) 22.7 (d, ^3J(P,P) = 12.9 Hz, PH), 20.3 (d, ^3J(P,P) = 12.9 Hz, PPh$_3$), −142.9 (sept, ^1J(P,F) = 708 Hz, PF$_6$).

IR (thin film, cm^{-1}): 1656 (s, ν_{NO}). MS:[37] 844 (45) [**1f**-H]$^+$, 558 (100) [**1f**-P(α-naph)$_2$H]$^+$.

(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_2$P(α-naph)$_2$) (**1f**)

A Schlenk flask was charged with [**1f**-H]$^+$ PF_6^- (0.361 g, 0.365 mmol) and benzene (22 mL). The suspension was vigorously stirred and solid *t*-BuOK (0.0613 g, 0.548 mmol) added. After 1 h, the orange suspension was filtered through a plug of Celite. The plug was rinsed with benzene until the filtrate became colorless. The filtrate was concentrated by oil pump vacuum (to *ca.* 5 mL), and pentane (35 mL) added dropwise with vigorous stirring. The precipitate was collected by filtration and dried by oil pump vacuum to give **1f** as a pale yellow powder (0.197 g, 0.234 mmol, 64%), mp 187–189 °C, dec. Anal. calcd (%) for $C_{44}H_{36}NOP_2Re$ (843.2): C 62.70, H 4.30, N 1.66; found: C 62.80, H 4.50, N 1.76.

NMR (CD_2Cl_2, δ/ppm): ^{1}H (400 MHz) 8.87–8.82, 8.78–8.72, 7.82–7.69, 7.52–7.28 (4 m, aryl-H, 29H), 4.62 (s, C$_5$H$_5$, 5H), 2.63 (dd, ^2J(H,H) = 11.5 Hz, *J*(H,P) = 9.6 Hz, CHH′, 1H), 1.91 (d, ^2J(H,H) = 11.5 Hz, CHH′, 1H); ^{13}C{^{1}H} (76 MHz) 90.4 (s, C$_5$H$_5$), −19.1 (dd, ^1J(C,P) = 36.8 Hz, ^2J(C,P) = 4.8 Hz, CHH′); PPh$_3$ at 136.3 (d, ^1J(C,P) = 51.9 Hz, *i*), 134.2 (d, ^2J(C,P) = 10.4 Hz, *o*), 130.7 (d, ^4J(C,P) = 2.1 Hz, *p*), 128.9 (d, ^3J(C,P) = 10.1 Hz, *m*); P(α-naph)(α-naph)′ at[38] 145.9, 145.5, 143.5, 143.2, 136.5, 136.5, 136.3, 136.2, 134.2, 133.9, 133.8, 130.8, 130.3, 129.1, 128.4, 128.4, 127.6, 127.3, 127.2, 126.9, 126.1, 126.0, 125.8, 125.8, 125.7; ^{31}P{^{1}H} (162 MHz) 26.5 (d, ^3J(P,P) = 6.9 Hz, PPh$_3$), −21.2 (d, ^3J(P,P) = 6.9 Hz, P(α-naph)$_2$).

IR (thin film, cm^{-1}): 1644 (s, ν_{NO}). MS:[37] 842 (30) [**1f**-H]$^+$, 558 (100) [**1f**-P(α-naph)$_2$]$^+$.

(*S*$_{Re}$*S*$_C$)-[(η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH(CH$_3$)PPh$_2$H)]$^+$ PF$_6^-$ ((*S*$_{Re}$*S*$_C$)-[**9a**-H]$^+$ PF$_6^-$)

A Schlenk flask was charged with (*S*)-(η-C$_5$H$_5$)Re(NO)(PPh$_3$)(CH$_2$CH$_3$) (0.114 g, 0.199 mmol)[23] and CH_2Cl_2 (5 mL). The solution was cooled to −78 °C and Ph_3C^+ PF_6^- (0.0722 g, 0.219 mmol) added with stirring. After 1 h, the orange mixture had turned bright yellow. Then PPh_2H (0.0555 g, 0.299 mmol) dissolved in CH_2Cl_2 (0.6 mL) was added. After 1 h, the mixture was allowed to warm to room temperature over the course of 1 h. The solution was concentrated (to *ca.* 1 mL) and pentane added. The oil-like precipitate was isolated by decantation and dissolved in CH_2Cl_2/*t*-BuOH (7 mL, 2 : 5 v/v). The solvent was concentrated by oil pump vacuum with vigorous stirring. A yellow powder precipitated, which was collected by filtration, washed with pentane (2 × 0.5 mL), and dried by oil pump vacuum to give (*S*$_{Re}$*S*$_C$)-[**9a**-H]$^+$ PF_6^- as a pale yellow powder (0.0920 g, 0.102 mmol, 51%), Dec. pt. 125–128 °C. Anal. calcd (%) for $C_{37}H_{35}F_6NOP_3Re$ (902.8): C 49.22, H 3.91, N 1.55; found: C 49.17, H 4.06, N 1.52. $[\alpha]_{25}^{589}$ = 105° ± 1° (*c* = 1.00 mg mL^{-1}, CH_2Cl_2).

NMR (δ/ppm): ^{1}H (400 MHz, $CDCl_3$) 7.79–7.30 (m, C$_6$H$_5$, 25H), 7.48 (dd, ^1J(H,P) = 493 Hz, ^3J(H,H) = 9.0 Hz, PH, 1H), 5.06 (s, C$_5$H$_5$, 5H), 3.46–3.35 (m, CHCH$_3$, 1H), 1.27 (dd, *J*(H,P) = 24.5 Hz, ^3J(H,H) = 7.5 Hz, CHCH$_3$, 3H); ^{13}C{^{1}H} (76 MHz, CD_2Cl_2; the ReCH signal was not observed) 91.6 (s, C$_5$H$_5$); PPh$_3$ at 133.9 (d, ^1J(C,P) = 54.0 Hz, *i*), 133.7 (d, ^2J(C,P) = 10.6 Hz, *o*), 131.5 (d, ^4J(C,P) = 2.2 Hz, *p*), 129.5 (d, ^3J(C,P) = 10.4 Hz, *m*); PPhPh′ at 134.6 (d, ^4J(C,P) = 2.6 Hz, *p* to P), 134.1 (d, ^4J(C,P) = 2.6 Hz, *p*′ to P), 133.2 (d, ^2J(C,P) = 9.1 Hz, *o* to P), 132.6 (d, ^2J(C,P) = 9.1 Hz, *o*′ to P), 130.5 (d, ^3J(C,P) = 11.5 Hz, *m* to P), 130.3 (d, ^3J(C,P) = 11.7 Hz, *m*′ to P), 122.4 (d, ^1J(C,P) = 57.7 Hz, *i* to P), 121.5 (d, ^1J(C,P) = 68.1 Hz, *i*′ to P), 20.4 (s, CH$_3$); ^{31}P

{^{1}H} (122 MHz, CD_2Cl_2) 22.7 (d, ^3J(P,P) = 14.9 Hz, $\underline{P}Ph_3$), 31.9 (d, ^3J(P,P) = 14.6 Hz, $\underline{P}H$), −142.8 (sept, ^1J(P,F) = 713 Hz, $\underline{P}F_6$).

IR (thin film, cm^{-1}): 1668 (s, ν_{NO}). MS:[37] 758 (18) [**9a**-H]$^+$, 572 (100) [**9a**-PPh_2H]$^+$.

($S_{Re}S_C$)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH(CH_3)PPh_2H) (($S_{Re}S_C$)-9a)

This complex was generated by first treating ($S_{Re}S_C$)-[**9a**-H]$^+$ PF_6^- with *t*-BuOK (1.5 equiv.) in benzene. The mixture was filtered through a plug of Celite. The filtrate was concentrated and pentane added. The ($S_{Re}S_C$)-**9a** precipitated and was collected by filtration, dried by oil pump vacuum, and used without further characterization.

Crystallography

(A) Racemic [**1c**-H$^+$]PF_6^- was dissolved in CH_2Cl_2 and layered with pentane. After 7 d at 4 °C, orange prisms had formed. Data were collected as outlined in Table 1. Cell parameters were obtained from 10 frames using a 10° scan and refined with 8286 reflections. Lorentz, polarization, and absorption corrections[39] were applied. 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.[40] 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 literature.[41] (B) Orange prisms of [**1d**-H$^+$]PF_6^- were similarly obtained, and the structure was solved analogously (10 frames using a 10° scan and refined with 9467 reflections). The PH hydrogen atom (P2) was located and free isotropically refined.

Catalytic reactions

(A) Racemic catalysts. A Schlenk flask was charged with the substrate (typically 0.060–0.080 g). Then benzene or chlorobenzene solutions that were 0.0125 M in $ClCH_2CH_2Cl$ (internal standard, ^{1}H NMR integration) were added to give 0.100 M substrate solutions. These were equilibrated to 20 °C using a cryostat. Solutions of benzene or chlorobenzene that were 0.0100 M in catalyst and 0.0125 M in $ClCH_2CH_2Cl$ were cooled to 0 °C. Equal volumes, corresponding to 10 mol% loading, were added dropwise over *ca.* 5 min to the substrate solutions. An aliquot (0.6 mL) was transferred to an NMR tube, and ^{1}H NMR spectra were periodically recorded. When the reaction was complete (or no further reaction took place), five volumes of hexane were added with stirring. The mixture was filtered through a short plug of silica gel (removing catalyst), which was washed with hexane/ethyl acetate (9 : 1 v/v). The solvent was removed from the filtrates by rotary evaporation to give the product, characterized as summarized in the ESI.† Yields: see text and Scheme 4. Reactions conducted in chlorobenzene were further purified by silica gel column chromatography, except in the case of **6j**. (B) Enantiopure catalysts. The preceding reactions were repeated on 0.0010–0.0020 g scales. The products were analyzed by HPLC using Chiralcel OD, Chiralpak AD-H or Chiralpak AS-H columns and a Thermo Quest instrument package (pump/autosampler/detector P4000/AS3000/UV6000LP).

Data availability

Electronic supplementary information (ESI) available: General procedures, syntheses of secondary phosphines and organic substrates and products, additional NMR data, and ee determinations. CCDC 2423133 ([**1c**-H]$^+$ PF_6^-) and 2423134 ([**1d**-H]$^+$ PF_6^-).† For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d2dt02680e.

Conflicts of interest

There are none to declare.

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