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Free and Cr(CO)$_3$-Complexed Aminophosphine Phosphinite Ligands for Highly Enantioselective Hydrogenation of α-Functionalized Ketones

Corinne Pasquier, Said Naili, André Mortreux, Francine Agbossou,*
Lydie Pélinski, Jacques Brocard, Jürgen Eilers, Iris Reiners, Viola Peper, and
Jürgen Martens

Laboratoire de Catalyse de Lille, Groupe de Chimie Organique Appliquée, Ecole Nationale Supérieure de Chimie de Lille, BP 108, 59652 Villeneuve d'Ascq Cedex, France, and Laboratoire de Catalyse de Lille, Groupe de Synthèse Organométallique, Ecole Nationale Supérieure de Chimie de Lille, BP 108, 59652 Villeneuve d'Ascq Cedex, France, and Fachbereich Chemie der Universität Oldenburg, Ammerländer Heerstrasse 114-118, D-26129 Oldenburg i.O., Germany

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The synthesis and characterization of a new series of aryl- and cycloalkyl-substituted aminophosphine phosphinites (**1**−**8**) obtained from the reaction of the three precursors (*S*)-2-hydroxymethyl azetidine, (*S*)-3-hydroxymethyl-1,2,3,4-tetrahydroisoquinoline, and (*S*)-2-hydroxymethylindoline and chlorophosphines is described. The aromatic ring in (*S*)-2-hydroxymethylindoline has allowed the synthesis and isolation of tricarbonyl chromium complexed amino alcohols ***syn*-10** and ***anti*-10**, which were similarly converted into the corresponding aminophosphine phosphinites **11**−**13,** presenting a stereogenic center and a planar chirality. Ligand **5** ((*S*)-Cp,Cp-IndoNOP) revealed an unprecedented ^{31}P NMR fluxional behavior related to a rotation inhibition around the P-heteroatom (N and O) bonds. These new AMPP ligands were used in the enantioselective hydrogenation of various α-functionalized ketones, i.e., dihydro-4,4-dimethyl-2,3−furandione **14**, *N*-benzyl benzoylformamide **15**, ethylpyruvate **16**, and 2-(*N*,*N*-dimethyl)aminoacetophenone hydrochloride **17**. The stereoelectronic effects generated by the presence of the tricarbonyl chromium moiety onto the hydrogenations have been assessed. The beneficial effect of the matching chiralities in ligand ***syn*-12** associated with the use of the most appropriate nonchiral ligand Cl has resulted in a win of 13% of ee for the rhodium-based hydrogenation of **15**. While using the most suitable new chiral AMPP ligand from this study, the four above-mentioned substrates were converted into the corresponding optically active alcohols in >99% ee (**l4**/**5**), >99% ee (**15**/**6**), 87% ee (**16**/**5**), and >99% ee (**17**/**5**), respectively.

Introduction

Optically active transition metal complexes are playing a prominent role in the development of asymmetric catalysis.[1]Indeed, the latter constitutes one of the most progressing methodologies for the preparation of important bioactive intermediates. Among the processes, remarkable success has been achieved in the homogeneous asymmetric hydrogenation of a large range of substrates including enamides, imines, and ketones.[1,2] To achieve high degrees of activity and enantioselectivity in the hydrogenation of ketones, most of the strategies have focused on the construction of optically pure C_2 symmetric diphosphines bearing phenyl substituents on their phosphorus atoms. Such chiral modifiers have generally been devoted to ruthenium-catalyzed processes. Hence, tremendous success has been achieved in the hydrogenation of functionalized ketones with ruthenium catalysts associated with atropisomeric diphosphines (BINAP, BIPHEMP, ...)[3] and even more recently in the hydrogenation of arylalkyl ketones as well.[4] On the other hand, it is recognized that, for the hydrogenation of ketones, the use of rhodium complexes requires more electron-rich ligands in order to achieve high activities.[5] Thus, more basic diphosphanes have also become popular recently for enantioselective hydrogenations in the presence of either ruthenium or

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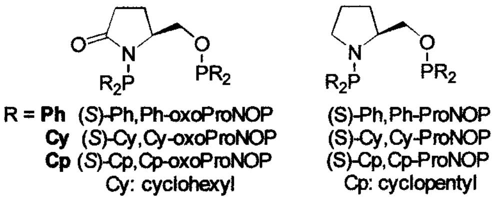
rhodium catalysts.[6] Furthermore, the use of such ligands was not restricted to the hydrogenation of ketones. For example, Duphos[7] and BICP[8] type ligands were also applied with success in the hydrogenation of various olefinic substrates. Finally, a very important contribution has been made recently by Zhang, who described the efficient hydrogenation of simple ketones in the presence of Rh−PENNPHOS catalysts and 2,6-lutidine as an additive.[9] For most of these new ligands, particular attention was paid to two properties in order to enlarge their applicability and to induce higher enantioselectivities. These are the ligand conformational rigidity and the basicity of the phosphorus atoms.

Over the years, we have been much concerned with the search and discovery of new efficient diphosphanes. In this context, we have an ongoing interest in the synthesis and application of aminophosphine phosphinites (AMPP), which are based on readily available enantiopure precursors.[10] One major attribute of the AMPP ligands described up to date is their synthesis as they are prepared in a single step from α-amino alcohols. The AMPP ligands found applications in various enantioselective catalytic processes.[10] Other groups also reported on the synthesis and use of analogous ligands.[10,11] Nevertheless, aryl groups generally substitute the phosphorus atoms of the latter, and they are uniformly examined in the enantioselective hydrogenation of olefinic substrates. We have demonstrated that a systematic modification of the phosphorus residues of the AMPPs opened the possibility of efficient hydrogenation of activated ketones.[12] In fact, the fulfillment of two key points, i.e., electron-donating phosphorus atoms and increased rigidity of the ligand framework, provided the most efficient and enantioselective AMPP type ligands for the rhodium-based hydrogenation of activated ketones. For example, the cyclohexyl-substituted ligand (*S*)-Cy,Cy-oxoProNOP (Scheme 1) derived from oxoprolinol, which certainly exhibits the most rigid backbone of the series, has also been by far the most enantioselective for the reduction of amino ketones and ketopantolactone to amino alcohols and pantolactone, respectively.[13] The latter compounds are key intermediates for the synthesis of chiral epoxystyrenes[14] and pantothenic acid,[15] which is a member of the vitamin B complex and a constituent of coenzyme A.

Scheme 1



As suggested above, while our earlier work focused especially on diphosphanes based on amino alcohols derived from proteinogenic amino acids, we thought to expand the scope of our investigations to new structurally related AMPPs with specific attention given to the rigidity and the steric attributes of the ligand core. As such, the exploration of closely related structures, even if not synthesized starting from natural precursors, can be of strong interest for a tuning of the ligands aimed at the access to optimized auxiliaries. Furthermore, as some new precursors possess an aromatic ring in their framework and because of the unique properties expected by arene-chromium-based species,[16,17] our attention was also drawn to adducts of AMPPs and $Cr(CO)_3$. Indeed, the tricarbonyl unit can coordinate above and below the plane of the arene, providing diastereomeric amino alcohols by virtue of planar chirality.[18] Actually, the close proximity of steric crowding and the complementary chirality exhibited by such species provide an excellent opportunity to introduce new features in the framework of the AMPP ligand. Such modifications (electronic and/or steric) will allow one to examine their impact on the properties (activities and enantioselectivities) of the corresponding catalysts. It is anticipated that these modified AMPP ligands might supply enhanced enantioselectivities. In this paper, we report the

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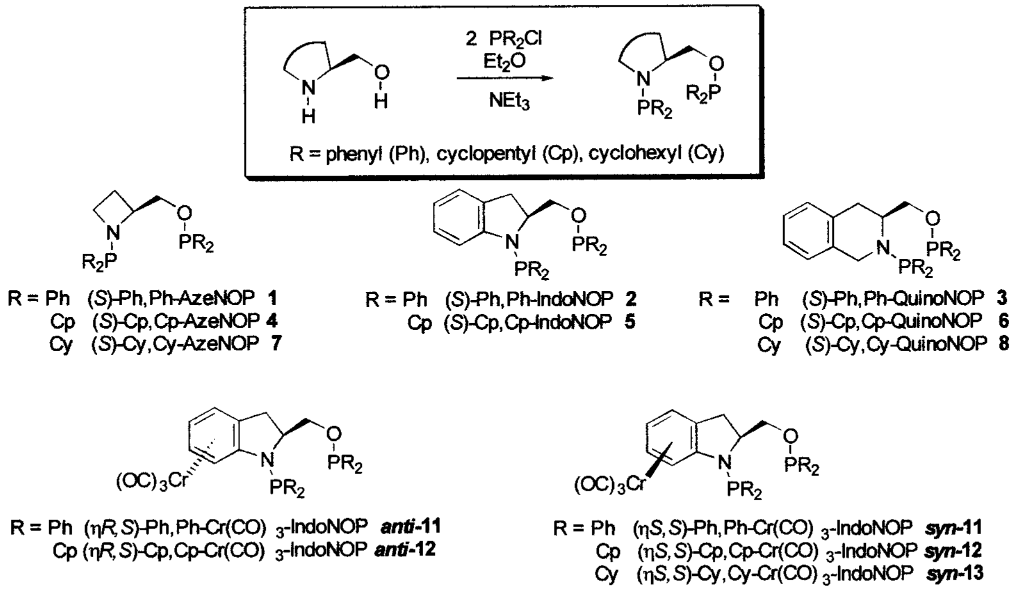
Scheme 2



R = Ph (*S*)-Ph,Ph-AzeNOP **1**
Cp (*S*)-Cp,Cp-AzeNOP **4**
Cy (*S*)-Cy,Cy-AzeNOP **7**

R = Ph (*S*)-Ph,Ph-IndoNOP **2**
Cp (*S*)-Cp,Cp-IndoNOP **5**

R = Ph (*S*)-Ph,Ph-QuinoNOP **3**
Cp (*S*)-Cp,Cp-QuinoNOP **6**
Cy (*S*)-Cy,Cy-QuinoNOP **8**

R = Ph (η*R*,*S*)-Ph,Ph-Cr(CO)$_3$-IndoNOP ***anti*-11**
Cp (η*R*,*S*)-Cp,Cp-Cr(CO)$_3$-IndoNOP ***anti*-12**

R = Ph (η*S*,*S*)-Ph,Ph-Cr(CO)$_3$-IndoNOP ***syn*-11**
Cp (η*S*,*S*)-Cp,Cp-Cr(CO)$_3$-IndoNOP ***syn*-12**
Cy (η*S*,*S*)-Cy,Cy-Cr(CO)$_3$-IndoNOP ***syn*-13**

development of a series of conformationally rigid chiral AMPP bisphosphanes and we establish their utility in enantioselective hydrogenation of α-functionalized ketones.[19]

Results and Discussion

Synthesis and Characterization of the Chromium-Free Ligands. The three starting β-amino alcohols, i.e., (*S*)-2-hydroxymethylazetidine,[20] (*S*)-3-hydroxymethyl-1,2,3,4-tetrahydroisoquinoline,[21,22] and (*S*)-2-hydroxymethylindoline were obtained by standard reduction of the corresponding amino acids. Thus (*S*)-azetidinecarboxylic acid was reduced with lithium aluminum hydride, and (*S*)-1,2,3,4-tetrahydro-3-isoquinolinecarboxylic acid and (*S*)-indolinecarboxylic acid were reduced with borane−methyl sulfide. Then, the diphosphanes **1**−**8** were generated following the convenient standard procedure by reaction of the amino alcohols with the appropriate chlorophosphine ($ClPPh_2$, $ClPCp_2$ (Cp = cyclopentyl), or $ClPCy_2$ (Cy = cyclohexyl)) in the presence of an excess of triethylamine, as described in the Experimental Section (Scheme 2).[12] Despite extensive efforts, following the above route, we were unsuccessful in obtaining a cyclohexyl-substituted analogue of **5**.

The ligands **1**−**8** (Scheme 2) were isolated after a chromatographic workup through basic alumina as colorless oils in 56−92% yield. These ligands and other new compounds described below were characterized by ^1H, ^{31}P, and ^{13}C NMR spectroscopy and microanalysis, the data being summarized in the Experimental Section. The ^{31}P NMR data of the ligands are given in Table 1. Although the ^{31}P NMR data have been previously reported, some data are included in Table 1 in order to facilitate comparison. The general spectroscopic properties resemble those of the AMPP described earlier, and a single set of signals is generally observed.[12] Nevertheless, when recording the ^{31}P NMR spectra of (*S*)-Cp,-Cp-IndoNOP **5** at room temperature, we could observe a broadening of the signal for the P(O) resonance ($W_{1/2}$ = 69 Hz) and a splitting of the P(N) signal into two very large singlets ($W_{1/2}$ = 138 Hz). This trend has been attributed to the coexistence of two isomers in ca. 1:1 ratio resulting from a fluxionnal behavior on the NMR time scale. This had not been observed before with other AMPP ligands. Actually, a variable-temperature ^{31}P NMR study probed the thermal process giving most probably two rotamers derived from a rotational barrier

Table 1. Yields and $^{31}P\{^1H\}$ NMR Data for the Ligands[a]

ligand		yield (%)	δ (P_O) (ppm)	δ (P_N) (ppm)
(*S*)-Ph,Ph-ProNOP	*b*		113.5	45.6
(*S*)-Ph,Ph-oxoProNOP	*c*		116.9	36.2
(*S*)-Ph,Ph-AzeNOP	**1**	60	115.4	46.7
(*S*)-Ph,Ph-IndoNOP	**2**	79	114.2	41.6
(*S*)-Ph,Ph-QuinoNOP	**3**	86	114.1	61.4
(η*R*,*S*)-Ph,Ph-Cr(CO)$_3$-IndoNOP	***anti*-11**	74	116.9	43.1
(η*S*,*S*)-Ph,Ph-Cr(CO)$_3$-IndoNOP	***syn*-11**	100	113.9	46.5
(*S*)-Cp,Cp-ProNOP	*d*		142.0	57
(*S*)-Cp,Cp-oxoProNOP	*c*		146.5	60.9
(*S*)-Cp,Cp-AzeNOP	**4**	90	144.0	56.6
(*S*)-Cp,Cp-IndoNOP	**5**	90	145.9	65.3 and 58.4
(*S*)-Cp,Cp-QuinoNOP	**6**	72	143.5	78.0
(η*R*,*S*)-Cp,Cp-Cr(CO)$_3$-IndoNOP	***anti*-12**	55	149.5	55.2
(η*S*,*S*)-Cp,Cp-Cr(CO)$_3$-IndoNOP	***syn*-12**	84	146.0	67.3
(*S*)-Cy,Cy-ProNOP	*d*		146.5	53.9
(*S*)-Cy,Cy-oxoProNOP	*c*		150.4	58.1
(*S*)-Cy,Cy-AzeNOP	**7**	92	149.0	55.5
(*S*)-Cy,Cy-QuinoNOP	**8**	56	146.7	77.2
(η*R*,*S*)-Cy,Cy-Cr(CO)$_3$-IndoNOP	***anti*-13**	53	152.0	75.6

[a] $CDCl_3$. [b] Taken from ref 10a. [c] Taken from ref 13a. [d] Taken from ref 12b.

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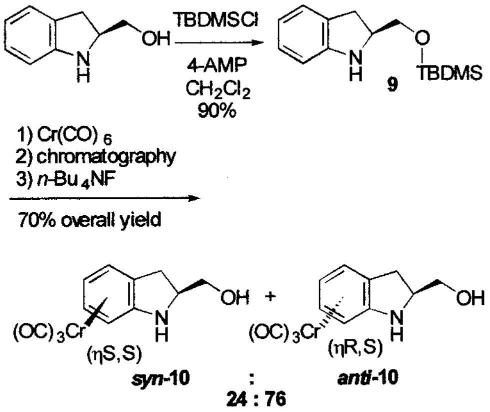
(22) In our preliminary communication (see ref 19a), we reported only on the use of QuinoNOP ligands based on the less easily accessible (*R*) precursor (see ref 21b). However, all the catalytic reactions were carried out with both optical antipodes providing equivalent results. Here, only those obtained while starting from the commercial precursor, (*S*)-1,2,3,4-tetrahydro-3-isoquinolinecarboxylic acid, are furnished.

Table 2. Selected $^{31}P\{^{1}H\}$ NMR Data for the P(N) Residue of the Ligands

	R		
ligand	Ph	Cp	Cy
(*S*)-R,R-oxoProNOP	36.2	60.9	58.1
(*S*)-R,R-AzeNOP	46.7	56.6	55.5
(*S*)-R,R-ProNOP	45.6	57	53.9
(*S*)-R,R-IndoNOP	41.6	65.3 and 58.4	
(*S*)-R,R-QuinoNOP	61.4	78	77.2

of the PCp_2 residue around the N−P bond. These isomers can be considered interconvertible non-biaryl atropisomers.[23] On going from 20 to −40 °C, the two signals decoalesced totally. The two coalescence temperatures were 18 °C for P(O) and 45 °C for P(N). Thus, the P(N) signal is more easily broadened than the P(O) one. From the data, the calculation[24] gave $\Delta G^{\ddagger}(T_c) =$ 13.5 kcal/mol for the process rendering the two P(N) and two P(O) equivalent. In addition, the isomeric ratio remained constant throughout the temperature range applied (−40 to +60 °C, $CDCl_3$). Such a phenomenon can be reasonably related to the structure of the ligand core. Hence, the bicyclic structure is probably seriously flattened with an additional coplanarity of the aryl ring and the nitrogen and phosphorus atoms. An overall rigidity of the chiral skeleton thus explains the rotation barrier of the P−N bond when the phosphorus is substituted by cyclopentyl groups. On the other hand, upon a careful examination of the chemical shift of the phosphorus atoms P(O) and P(N), some characteristic shift variations are observed which are related to the electronic and steric properties in the direct environment of the phosphorus atoms. When considering the several cyclic structures bearing identical substituents on the phosphorus atoms, we observe clearly that the chemical shifts of the P(O) moiety vary little compared with those of the P(N) residues (Table 1). On the other side, several factors influence the stereoelectronic properties of the nitrogen atom adjacent to the phosphorus atoms (ring size, conjugation). These properties have an influence on the phosphorus through modification of the partial double bond character arising from $N\pi-Pd\pi$ donor bonding, which in turn contributes to the s character of the P atom. The latter, which is also dependent upon the alkyl(P) group contribution, provides the final phosphorus shielding observed. As a result, the P(N) resonance of the QuinoNOP ligands **3** and **6** are downfield from those of the corresponding IndoNOP species **2** and **5** ($\Delta\delta$ ca. 20 ppm) and also from other previously described AMPP ligands,[12] which are all presenting, likewise, the nitrogen atom of the aminophosphine residue as part of a ring (average $\Delta\delta$ ca. 15 ppm for PPh_2N and 20 ppm for PCp_2N moieties) (Table 2, Schemes 1 and 2). Consequently, we propose a rough classification of the above ligands into three groups according to the stereoelectronic characteristic of the nitrogen atom. The first class contains the AzeNOP and ProNOP type ligands, where roughly only a ring size constraint intervenes. The second group is constituted by the IndoNOP and oxoProNOP type ligands, where the nitrogen is most influenced by the conjugation with the aryl and the carbonyl residues, respectively.

Scheme 3



Finally, there is the QuinoNOP type structure in which the nitrogen can present a small pyramidalization with a narrowing of the N−P−C(aryl) angle and a concomitant widening of the phosphorus cone angle.[25] There is also an additional deshielding of the phosphorus atoms substituted by cyclopentyl groups when compared with cyclohexyl, which is in direct line with a further widening of the phosphorus cone angle for Cp-AMPPs. One last contribution, i.e., diamagnetic aryl ring screening, is difficult to estimate because the overall conformation of the molecules is unknown. The ^{31}P NMR shielding of the P(N) phosphorus atoms provides therefore a convenient approach to the stereoelectronic properties of the chiral skeleton of the ligand.

Synthesis and Characterization of the Chromium-Complexed Ligands. As mentioned above, the presence of the arene ring in the ligands derived from the optically pure (*S*)-2-hydroxymethylindoline offers the possibility of $Cr(CO)_3$ complexation providing a mixture of diastereomers differing in the relative configuration of the stereogenic center and the chirality plane.[18] Unfortunately, a separation of the diastereomeric complexed amino alcohols could not be done straightforwardly. Thus, several routes were explored, and access to both isomers was best achieved following the procedure outlined in Scheme 3.

The amino alcohol (*S*)-2-hydroxymethyl indoline was first converted into the corresponding silyloxy derivative **9** in the presence of *tert*-butyldimethylsilyl chloride. Then, the chromium-complexed isomers were formed by heating **9** in the presence of $Cr(CO)_6$. The two diastereomeric complexes *anti* ($\eta R,S$) and *syn* ($\eta S,S$) are formed in a 76:24 ratio (^1H NMR), separated through silica gel chromatography, the *anti* isomer being eluted first, and isolated as yellow powders in 70% overall yield. Then, in separate experiments, both isomers were reacted with n-Bu_4NF to produce ***anti*-10** ($\eta R,S$) and ***syn*-10** ($\eta S,S$) complexed amino alcohols in quantitative yields. The corresponding *anti* and *syn* phenyl- and cycloalkyl-substituted AMPP ligands **11**−**13** (Scheme 2) were synthesized following the procedure described above for the uncomplexed ligands and isolated in 53−100% yield

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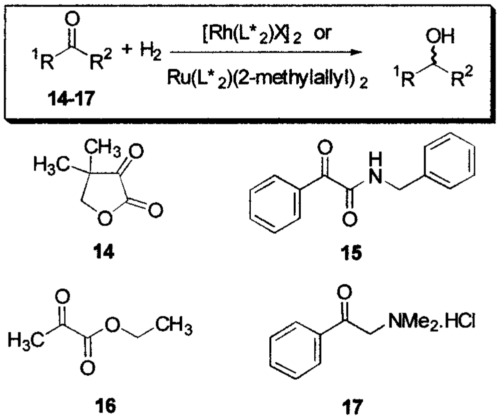
Scheme 4



after workup. The chromium-complexed AMPP ligands did not exhibit greatly distinctive ^{31}P NMR features. Nevertheless, there seems to be a tendency of shielding of the phosphorus of the *anti* isomers. Indeed, ligand ***anti*-12** presents a signal at 55.2 ppm for the P(N) residue as compared with 63 for the free ligand **5** and 67.3 for the diastereomer ***syn*-12** as reported in Table 1. Nevertheless, a rationalization of the stereoelectronic properties brought by the chromium tripod would be hazardous at this stage.

Hydrogenation of Functionalized Ketones. To evaluate the efficiency displayed by these new AMPP ligands in asymmetric hydrogenation, four functionalized ketones were selected and examined, i.e., dihydro-4,4-dimethyl-2,3-furandione **14**, *N*-benzyl benzoylformamide **15**, ethylpyruvate **16**, and 2-(*N*,*N*-dimethyl)aminoacetophenone hydrochloride **17** (Scheme 4).

Catalysts Precursors. Generally, the rhodium precatalysts were generated in situ by reacting $[Rh(COD)Cl]_2$[26] or $[Rh(COD)(OCOCF_3)]_2$[27] with 2 equiv of the ligand in the solvent used for the catalytic reaction. The ruthenium precatalysts Ru{AMPP}(2-methylallyl)$_2$ are formed prior to catalysis by heating Ru(COD)(2-methylallyl)$_2$[28] with 1 equiv of the AMPP in dichloromethane. ^{31}P NMR spectra recorded on the crude reaction mixtures showed that the formation of the ruthenium complexes was complete in the reported conditions.[29] The latter were used for the catalytic reactions without specific purification.

Hydrogenation of Dihydro-4,4-dimethyl-2,3-furandione 14. The results of the hydrogenation of **14** are summarized in Table 3. For comparison, earlier results involving (*S*)-Ph,Ph-oxoProNOP (entries 1 and 6) and (*S*)-Cp,Cp-oxoProNOP (entry 12) are also included. From a general standpoint, substrate **14** underwent quantitative hydrogenation under smooth conditions in the presence of the most representative ligands of the series. Phenyl-substituted AMPP ligands are best associated with ruthenium complexes, as they are giving higher activities and enantioselectivities than with rhodium catalysts (entry 1 vs 6, 3 vs 8, and 5 vs 11). Following previous conclusions,[29] cycloalkyl-substituted ligands were exclusively involved in rhodium-based hydrogenations. While taking the enantioselectivity standpoint, several remarks which are connected to the structure of the chromium-uncomplexed chiral framework emerge. Thus, the four-membered AzeNOP ligands provide very low enantioselectivities (entries 13 and 19).[30] It appears that the diastereomeric differentiation induced by the four-membered cycle of the AzeNOP ligands is certainly too small due to insufficient space crowding. As a matter of fact, a minimum—if not ideal—steric requirement has to be present for high levels of enantioselectivity. Among the three skeletons explored, the cyclopentyl-substituted IndoNOP is undoubtedly the most efficient of the series for the hydrogenation of **14** and provides an extremely high enantiocontrol as a total asymmetric induction is reached (entries 15 and 16). This efficiency can be related to the rigid planar structure around the nitrogen atom which induces the highest enantiodifferentiation through ideal balance between steric and electronic characteristics. The ligands of QuinoNOP type **6** and **8** are only slightly less enantioselective than the corresponding IndoNOP **5** (entry 17, 18, and 20 vs 16 and 15).

Next, interesting comments ensue from the results obtained with chromium-complexed ligands. A synergy was expected from the proper combination of the relative configuration of the stereogenic center and the chirality plane generated by the tricarbonyl unit. Indeed, when substrate **14** was hydrogenated in the presence of a Rh−Cl/**5** catalytic system, the resulting pantolactone was produced in 98% ee (entry14). When ***syn*-12** was used instead of **5** as the ligand, the enantioselectivity increased to >99% ee (entry 22). For a combination of Rh−TFA and ***syn*-12**, the enantioselectivity remained identical to that obtained with the uncomplexed ligand **5** (>99% ee) (entry 23). As a matter of fact, the parent ligand **5** induces a very high enantioselectivity when associated with either Rh−Cl or Rh−TFA catalyst precursors (entries 15 and 16).

The detrimental effect of the *mismatched* pair in ligand ***anti*-12** was more noticeable, giving a lower asymmetric induction, i.e., 84% ee for ***anti*-12** compared with >99% ee for ***syn*-12** (entry 21 vs 15). Also, the presence of the chromium unit takes some electron density from the adjacent P(N) phosphorus atom. It is

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(30) Even if such a process has not been observed so far with AMPP ligands, we sought to rule out any possible loss of stereochemical purity during the synthesis of the ligand. For that purpose, we checked the optical purity of (*S*)-Ph,Ph-AzeNOP **1**. This was achieved by converting the latter into its Pd complex [CN*Pd-**1**]BF$_4$ according to the reference given below. Thus, **1** was reacted in methanol with the optically pure dimeric orthometalated palladium complex di-μ-chlorobis[(*R*)-1-(dimethylamino)ethyl]-2-naphthenyl-C_2,*N*]dipalladiu(II) in the presence of 1 equiv of NaBF$_4$, providing complex [CN*Pd-**1**]Cl. The presence of a single set of signals, as assayed by careful examination of the ^{31}P NMR spectrum recorded on the crude reaction mixture (118 ppm, d and 126, d, J_{PP} = 50 Hz), was indicative of an optically pure AMPP ligand. Consequently, the basic conditions applied for the synthesis of the ligands are not inducing any racemization of the ligand and/or organic precursor. For the synthesis of the palladium complex see: (a) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254. (b) Salem, G.; Wild, S. B. *Inorg. Chem.* **1983**, *22*, 4049. (c) Martin, J.; Palmer, J.; Wild, S. B. *Inorg. Chem.* **1984**, *23*, 2664.

Table 3. Asymmetric Hydrogenation of Dihydro-4,4-dimethyl-2,3-furandione (14)[a]

entry	chiral ligand	complex[b]	$P_{H_2\,(bar)}$	*T* (°C)	time (h)[c]	conv (%)[d]	ee (%)[d]
1[e]	(*S*)-Ph,Ph-oxoProNOP	Ru	50	20	65	100	79.5
2	**1**	Ru	50	20	40	100	<1
3	**2**	Ru	50	20	42	100	70
4	***anti*-11**				43	43	20
5	**3**	Ru	50	20	48	91	43
6[f]	(**S**)-Ph,Ph-oxoProNOP	Rh−TFA	50	50	48	100	48
7	**1**	Rh−TFA	50	50	18	39	12
8	**2**	Rh−TFA	50	50	66	81	50
9	***anti*-11**	Rh−TFA	50	50	66	80	20
10	***syn*-11**	Rh−TFA	50	50	120	59	29
11	**3**	Rh−TFA	50	50	66	100	37
12[g]	(*S*)-Cp,Cp-oxoProNOP	Rh−TFA	1	20	0.1	100	98.7
13	**4**	Rh−TFA	50	20	0.3	100	8
14	**5**	Rh−Cl	50	20	0.5	100	98
15	**5**	Rh−TFA	50	20	0.3	100	>99
16	**5**	Rh−TFA	1	20	0.7	100	>99
17	**6**	Rh−Cl	50	20	1	100	92
18	**6**	Rh−TFA	1	20	1.5	100	95
19	**7**	Rh−TFA	50	20	0.3	100	1
20	**8**	Rh−TFA	1	20	1	100	97
21	***anti*-12**	Rh−TFA	1	20	1.5	100	84
22	***syn*-12**	Rh−Cl	1	20	1	100	>99
23	***syn*-12**	Rh−TFA	1	20	1	100	>99
24	***syn*-13**	Rh−TFA	1	20	2	80	>99
24[h]	**5**	Rh−TFA	1	20	5	100	97

[a] Hydrogenations were carried out in either a 200 mL flask or in a 50 mL double-walled stainless steel autoclave by using recrystallized **14** in toluene for rhodium-based catalyses and in dichloromethane for the ruthenium ones (0.4 M); substrate/Rh or Ru = 200:1. [b] Ru = Ru{AMPP}(2-methylallyl)$_2$. Rh−Cl = [Rh{AMPP}Cl]$_2$. Rh−TFA = [Rh{AMPP}(OCOCF$_3$)]$_2$. [c] The reaction times were not necessarily optimized. [d] Conversions and enantiomeric excesses were determined by GC analysis (FS-cyclodextrine β-I/P 25 m × 0.32 mm). All configurations are *R*. [e] Taken from ref 29. [f] Unpublished result. [g] Taken from ref 12b. [h] Subtrate/Rh = 5000.

thus not surprising to observe an influence of that moiety on the rate of the reaction. Indeed, a slight decrease of the reaction rate is effectively observed with ligand ***syn*-12** when compared with **5**. We noticed the following values for the turnover frequencies at 50% conversion (1 bar H_2, room temperature, Rh−OCOCF$_3$ catalysts) for the AMPP series (*S*)-Cy,Cy-oxoProNOP (3333 h^{-1}), **5** (2400 h^{-1}), ***syn*-12** (1500 h^{-1}). The enantioselectivity and activity induced by these AMPP ligands reinforce the fundamental outcome of the P(N) moiety on *both* the activity and enantioselectivity of the hydrogenations. It is thus not surprising that the ligand optimization is thus particularly efficiently accomplished on the PN side of the AMPP chelates. Finally, it has to be pointed out that the utilization of rhodium complexes is not prohibitive, as catalysis can be carried out with higher substrate/metal ratios under still mild conditions (entry 24). In the latter example, the high selectivity was maintained.

Hydrogenation of Substrates 15−17. The preceding ee data point out that ligands **5**, **6**, and ***syn*-12** are the most efficient of the series for the hydrogenation of substrate **14**. Thus, these new ligands were also evaluated in the hydrogenation of other representative α-functionalized ketones, i.e., a ketoamide **15**, a ketoester **16**, and an aminoketone hydrochloride **17,** where a gain in enantioselectivity is still achievable. The results are summarized in Table 4. It has to be pointed out that, as no special efforts were made to obtain hydrogen pressure and reaction time optimized catalytic conditions, only selectivity levels have been taken into consideration for the discussion. Compared with the previous best AMPP ligand, a clean beneficial effect could be achieved when using these new ligands for the hydrogenation of some of the above substrates (entries 30−38 vs 26−29 and 43 vs 42). As already stressed in previous reports,[13] the nonchiral ligand is of great importance for the hydrogenation of **15**, and the beneficial participation of the chloride is confirmed here. For the IndoNOP type ligands, when combining properly the *matched* planar and central chiralities of ligand ***syn*-12** and the appropriate nonchiral ligand (Cl), a significant selectivity improvement (Δee = 13%) could be achieved for the hydrogenation of **15** (entries 30−33) (Figure 1). This result is indicative of the particular ability of the IndoNOP type ligands to hydrogenate α-ketoacids derivatives as well. In addition, the *mismatched* pair present in ligand ***anti*-12** produced a lower enantioselectivity (82 vs 97% ee, entry 34 vs 33). The above results suggest that it is certainly the steric hindrance inherent to the Cr(CO)$_3$ pair in ***syn*-12** that leads to the increase of the stereodifferentiation between the catalytic diastereomeric intermediates responsible for the level of enantioselection. Finally, it has to be highlighted that for the hydrogenation of **15**, ligand **6** leads to a totally enantioselective transformation (entry 37). Consequently, the optimization of the AMPP ligands is tricky when a unique ligand is targeted for the transformation of a great variety of substrates. Meaningfully, from our studies on AMPP ligands, only a few easily accessible structures emerge as chiral auxiliaries applicable to a broader variety of ketonic susbtrates, i.e., oxoProNOP, IndoNOP, and QuinoNOP.

For the hydrogenation of ketoester **16**, the new ligands **5** and **6** provide levels of selectivity similar to those obtained earlier with oxoProNOP type ligands (entry 40 vs 39).[32] Even without condition optimization, ligand **5** produces ethyl lactate under mild conditions in 87% ee, which is close to the highest selectivity

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Table 4. Asymmetric Hydrogenation of Functionalized Ketones 15, 16, and 17[a]

entry	substrate	chiral ligand	complex	P_{H_2} (bar)	T (°C)	time (h)[b]	conv (%)[c]	ee (%)[d] (confign)
26[e]	**15**	(*S*)-Cp,Cp-oxoProNOP	Rh−TFA	1	20	0.5	100	67 (*S*)
27[e]		(*S*)-Cy,Cy-oxoProNOP	Rh−TFA	1	20	1.5	100	61 (*S*)
28[e]		(*S*)-Cp,Cp-oxoProNOP	Rh−Cl	1	20	2.3	100	80 (*S*)
29[e]		(*S*)-Cy,Cy-oxoProNOP	Rh−Cl	1	20	18	100	87 (*S*)
30		**5**	Rh-TFA	1	20	2.5	100	84 (*S*)
31		**5**	Rh−Cl	1	20	24	53	91 (*S*)
32		***syn*-12**	Rh−TFA	1	20	2	81	91 (*S*)
33		***syn*-12**	Rh−Cl	1	20	3	82	97 (*S*)
34		***anti*-12**	Rh−Cl	1	20	12	100	82 (*S*)
35		**6**	Rh−TFA	1	20	1.5	100	95 (*S*)
36		**8**	Rh−TFA	1	20	1.5	100	95 (*S*)
37		**6**	Rh−Cl	50	20	19	100	>99 (*S*)
38		**8**	Rh−Cl	50	20	1.75	55	90 (*S*)
39[f]	**16**	(*S*)-Cy,Cy-oxoProNOP	Rh−TFA	50	20	0.75	100	89 (*R*)
40		**5**	Rh−TFA	50	20	2	100	87 (*R*)
41		**6**	Rh−TFA	50	20	1	100	80 (*R*)
42[g]	**17**	(*S*)-Cy,Cy-oxoProNOP	Rh−TFA	50	20	24	65	96 (*S*)
43[h]		**5**	Rh−TFA	50	20	18	100	>99 (*S*)

[a] Hydrogenations were carried out in a 200 mL flask or in a 50 mL stainless steel autoclave using recrystallized **15** and **17** and distilled **16** in toluene; substrate/Rh = 200:1. [b] Reaction times were not necessarily optimized. [c] Determined by ^{1}H NMR for **15** and **17** and capillary GC, FS-cyclodextrineβ-I/P (25 m × 0.32 m) for **16**. [d] Determined on the basis of the specific rotation value $[\alpha]^{26}_D = +82.2$ (c 1.09, $CHCl_3$) for (*S*)-(+)-*N*−benzylmandelate[31] for the hydrogenation of **15**, by capillary GC, FS-cyclodextrine β-I/P (25 m × 0.32 m) for **16**, and HPLC analysis (chiralcel OD (Daicel)) of the free amine for **17**. [e] Taken from ref 13a. [f] Taken from ref 32. [g] Taken from ref 13b. [h] Ethanol as solvent.

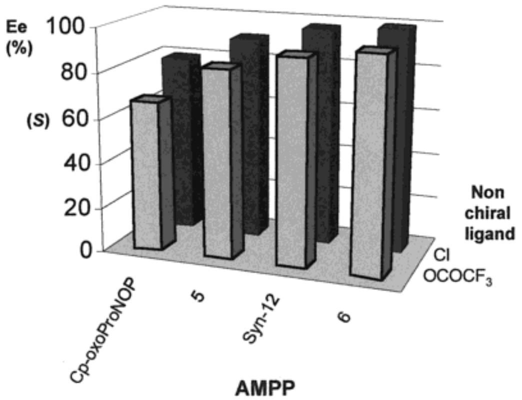

Figure 1. Comparison of the enantioselectivity obtained for the hydrogenation of **15** with respect to the chiral ligand and the effect of the nonchiral ligand.

reached for the hydrogenation of that substrate in the presence of rhodium catalysts.[32,33] It has to be noted that the highly enantioselective hydrogenation of that substrate is rather difficult.[32,33] Finally, the usefulness of the AMPP ligands for the production of β-amino alcohols via reduction of α-amino ketones, valuable intermediates for the production of chiral epoxystyrene,[14] is obvious from the result reported entry 42. Indeed, a total enantioselectivity is reached when using ligand **5**. In the latter case, ethanol has been used as solvent in order to dissolve the substrate, the latter being introduced as its hydrochloride salt.

Conclusion

In summary, we have established that the mean "optimized" aminophosphine phosphinites ligands and some of their tricarbonylchromium counterparts are available from easily accessible organic precursors and can be readily prepared in good yields. The ligands present particular ^{31}P NMR properties with respects to the stereoelectronic properties of their organic framework. The two series of electron-rich ligands based on (*S*)-3-hydroxymethyl-1,2,3,4-tetrahydroisoquinoline and (*S*)-2-hydroxymethylindoline and on the previously applied oxoprolinol provide the most enantioselective rhodium catalysts for the hydrogenation of several α-functionalized ketones. In that direction, the two new ligands **5** and **6** are the most efficient and versatile of the whole series of AMPPs developed so far for the hydrogenation of the above susbtrates, i.e., an α-ketolactone, an α-ketoamide, an α-ketoester, and an α-aminoketone. Also, the steric effects of the additionnal planar chirality obtained by $Cr(CO)_3$ complexation on the arene ring of the hydroxymethyl indoline in ligand ***syn*-12** provides enhanced enantioselectivities in some cases. The particularly efficient new ligands will be used for the hydrogenation of other ketonic substrates, and a mechanistic study will be reported soon.

Experimental Section

General Data. Unless otherwise stated, all the reactions were performed under an atmosphere of N_2 using standard Schlenk techniques. All reactions carried out with tricarbonylchromium complexes were performed in Schlenk tubes wrapped in an aluminum foil in order to avoid chromium decomplexation. Dry and oxygen-free solvents were treated as follows: CH_2Cl_2 distilled from CaH_2; toluene and Bu_2O distilled from sodium/benzophenone; Et_2O distilled from sodium/potassium (1Na/4K); and THF distilled from potassium. Reagents were used as received from common commercial sources. $[Rh(P_2)Cl]_2$, $[Rh(P_2)OCOCF_3]_2$, and $Ru(P_2)$(2-methylallyl)$_2$ were synthesized from $[Rh(COD)Cl]_2$,[25] $[Rh(COD)(OCOCF_3]_2$,[26] and Ru(COD)(2-methylallyl)$_2$,[27] respectively, as previously described. Catalytic hydrogenation reactions were carried out as reported previously in the presence of rhodium[13] and ruthenium[29] complexes. The conversions and enantiomeric excesses were determined using the following methods and conditions. Pantolactone: capillary GC, FS-cyclodextrine β-I/P (25 m ×

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(33) Burk et al. reported also very recently on the hydrogenation of **16** in the presence of cationic bis(phospholane)−Rh catalysts. See: Burk, M. J.; Pizzano, A.; Martin, J. A.; Liable-Sands, L. M.; Rheingold, A. L. *Organometallics* **2000**, *19*, 250. However, even if this catalyst is more active (compare: substrate/Rh = 500, H_2 ca. 4 bar, room temperature, 12 h, 100% conversion and entry 39 Table 3: substrate/catalyst = 200, H_2 ca. 50 bar, room temperature, 2 h, 100% conversion), the AMPP-based catalyst is more enantioselective (87% vs.76% ee).

0.32 mm). *N*-benzylmandelate: conversion determined by ^{1}H NMR. Enantiomeric excess determined by polarimetry, $[\alpha]_D^{26}$ +82.2 (*c* 1.09, $CHCl_3$) for (*S*)-(+)-*N*-benzylmandelate.[30] Ethyl lactate: capillary GC, FS-cyclodextrine β-I/P (25 m × 0.32 mm). 2-(*N,N*-dimethylamino)phenylethanol: conversion determined by ^{1}H NMR, enantiomeric excess determined by HPLC on the free amine, chiralcel OD (Daicel).

Routine ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker AC300 spectrometer operating at 300, 121, and 75 MHz for the three nuclei, respectively. Variable-temperature NMR was carried out on a Bruker AMX400 spectrometer. Chemical shifts are given in ppm, and coupling constants (*J*) are given in hertz. ^{1}H and ^{13}C{^{1}H} chemical shifts were referenced using the residual solvent resonance relative to tetramethylsilane (δ 0 ppm). ^{31}P{^{1}H} chemical shifts were referenced to external 85% H_3PO_4 in D_2O (0 ppm). Microanalyses were conducted by the Microanalytical Laboratory of the UST Lille and by Laboratories Wolf, Clichy, France. Mass spectra were carried out on a Finnigan MAT 311A (70 eV) or a Concept II H-H (Kratos Analytical Ltd) (FAB) at the Mass Spectroscopy Service of the UST Lille. Melting points were determined in open capillaries. HPLC analyses were performed on a Shimadzu apparatus equipped with a UV detector and a Chiralcel OD (5 × 250 mmm DAICEL) column. Optical rotations were measured on a Perkin-Elmer polarimeter in a 1 dm nonthermostated cell.

(*S*)-2-Hydroxymethylindoline. A 250 mL three-necked round-bottom flask equipped with a stir bar, a reflux condenser, and a dropping funnel was charged with (*S*)-indolinecarboxylic acid (2.5 g, 15 mmol) and THF (80 mL). Then, $BH_3 \cdot SMe_2$ (10 M, 12.5 mL) was placed in the funnel and added dropwise with stirring to the reaction mixture at room temperature over a period of 30 min. During the course of the addition, the amino acid dissolved and hydrogen was released. The mixture was stirred further at room temperature for an additional hour. Then, a solution of sodium hydroxide (80 mL, 0.5 M in H_2O) was added slowly over 30 min via the funnel. The reaction mixture was then heated at reflux for 3 h. After cooling, solid Na_2CO_3 was added to the mixture until saturation. Then, the reaction medium was extracted with Et_2O (3 × 50 mL). The combined organic phases were washed with water (3 × 10 mL) and dried with $MgSO_4$. After filtration, rotatory evaporation of the solvents, and drying under oil pump vacuum, (*S*)-2-hydroxymethylindoline was isolated as a white powder (2.28 g, 15 mmol, 100%), mp 73 °C, $[\alpha]_D$ +53.6 (*c* 0.89, EtOH). ^{1}H NMR (CDCl3, δ): 7.1 (d, J_{HH} = 7.3, 1H, *H*aro), 7.0 (t, J_{HH} = 7.6, 1H, *H*aro), 6.7 (t, J_{HH} = 7.3, 1H, *H*aro), 6.65 (d, J_{HH} = 7.6, 1H, *H*aro), 4.0 (m, 1H, NHC*H*), 3.7 (dd, J_{HH} = 10.7 and 3.5, 1H, C*H*H′OH), 3.6 (dd, J_{HH} = 10.7 and 6.3, 1H, CH*H*′OH), 3.1 (dd, J_{HH} = 15.9 and 9.0, 1H, CC*H*H′), 2.8 (dd, J_{HH} = 15.9 and 7.9, 1H, CCH*H*′). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 150.5, 128.9, 127.5, 124.9, 119.3, and 110.1 (*C*aro), 65.2 (*C*H_2OH), 60.3 (*C*H), 32.1 (*C*H_2Caro). Anal. Calcd for $C_9H_{11}NO$: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.02; H, 7.38; N, 9.40.

(*S*)-2-*tert*-Butyldimethylsilyloxymethylindoline 9. A 100 mL round-bottom flask was charged with a stir bar, (*S*)-hydroxymethylindoline (0.487 g, 3.3 mmol), *tert*-butyldimethylsilyl chloride (0.507 g, 3.4 mmol), and 4-(dimethylamino)-pyridine (0.038 g, 0.3 mmol). After nitrogen bubbling (5 min), dichloromethane (25 mL) and triethylamine (0.47 mL, 3.4 mmol) were added successively to the mixture. The solution was stirred overnight at room temperature. Then, 20 mL of an aqueous solution saturated with NH_4Cl was added. The reaction mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with water (20 mL) and dried with Na_2SO_4. After filtration and rotatory evaporation of the solvents, the residue was purified by silica gel chromatography (eluent petroleum ether/diethyl ether, 70:30). (*S*)-2-*tert*-butyldimethylsilyloxymethylindoline was obtained after oil pump vacuum-drying as an oil (0.789 g, 2.97 mmol, 90%). ^{1}H NMR (D2O, δ): 7.1 (d, J_{HH} = 7.3, 1H, *H*aro), 7.0 (t, J_{HH} = 7.6, 1H, *H*aro), 6.7 (t, J_{HH} = 7.4, 1H, *H*aro), 6.6 (d, J_{HH} = 7.75, 1H, *H*aro), 3.9 (m, 1H, C*H*), 3.6 (m, 2H, C*H*$_2$OH), 3.1 (dd, J_{HH} = 15.9 and 9.0, 1H, CC*H*H′), 2.6 (dd, J_{HH} = 15.9 and 5.8, 1H, CCH*H*′), 0.9 (s, 9H, (C*H*$_3$)$_3$C), 0.1 (s, 6H, (C*H*$_3$)$_2$Si). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 150.6, 128.3, 127.5, 125.0, 118.8, and 109.8 (*C*aro), 66.7 (*C*H_2OH), 60.6 (*C*H), 32.3 (*C*H_2C(aro)), 26.1 (C(*C*H_3)$_3$), −3.4 ((CH_3)$_3$*C*), −5.1 (*C*H_3Si). MS *m/z* (%): 263 (5.8) [M$^+$], 206 (12.4) [M$^+$ − *t*-Bu], 118 (100) [M$^+$ − CH_2 − OSiMe$_2$*t*-Bu].

(η*S*,*S*)- and (η*R*,*S*)-Tricarbonyl(2-*tert*-butyldimethylsilyloxymethylindoline)chromium. A 100 mL round-bottom flask equipped with a stir bar and a reflux condenser was charged with (*S*)-2-*tert*-butyldimethylsyliloxymethylindoline (0.789 g, 3 mmol), $Cr(CO)_6$ (0.862 g, 3.9 mmol), Bu_2O (15 mL), and THF (5 mL). After 15 min of nitrogen bubbling, the heterogeneous mixture was heated at 135 °C for 72 h. After cooling to room temperature, the reaction mixture was filtered through a fritted funnel and the solvents were removed under reduced pressure. The two diastereomers (η*R*,*S*) and (η*S*,*S*) were separated by silica gel chromatography (eluent petroleum ether/diethyl ether, 80:20) and isolated as yellow powders (0.640 g, 1.6 mmol and 0.200 g, 0.50 mmol, respectively, 70% overall).

(η*S*,*S*)-Tricarbonyl(2-*tert*-butyldimethylsilyloxymethylindoline)chromium. Mp: 163 °C. ^{1}H NMR ($CDCl_3$, δ): 5.6 (d, J_{HH} = 6.3, 1H, *H*aro), 5.3 (t, J_{HH} = 6.1, 1H, *H*aro), 5.0 (d, J_{HH} = 6.6, 1H, *H*aro), 4.8 (t, J_{HH} = 6.1, 1H, *H*aro), 4.1 (broad s, 1H, N*H*), 4.0 (m, 2H, C*H*H′O and C*H*), 3.6 (d, J_{HH} = 4.9, 1H, CH*H*′O), 3.1 (dd, J_{HH} = 16.2 and 9.6, 1H, C*H*H′C(aro)), 2.6 (dd, J_{HH} = 16.2 and 3.3, 1H, CH*H*′C(aro)), 0.9 (s, 9H, (C*H*$_3$)$_3$C), 0.1 (s, 6H, (C*H*$_3$)$_2$Si). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 234.9 (s, *C*O), 134.1, 97.3, 94.3, 93.1, 84.2, and 73.5 (*C*aro), 64.2 (s, *C*H_2O), 59.1 (*C*H), 30.5 (*C*H_2C(aro)), 25.9 (C(*C*H_3)$_3$), −5.3 (s, *C*H_3Si). MS *m/z* (%): 399 (4.1) [M$^+$], 343 (0.4) [M$^+$ − 2CO], 315 (38.0) [M$^+$ − 3CO], 263 (8.7) [M$^+$ − Cr(CO)$_3$], 118 (100) [M$^+$ − Cr(CO)$_3$ − CH_2−OSiMe$_2$*t*-Bu].

(η*R*,*S*)-Tricarbonyl(2-*tert*-butyldimethylsilyloxymethylindoline)chromium. Mp: 92 °C. ^{1}H NMR ($CDCl_3$, δ): 5.6 (d, J_{HH} = 5.9, 1H, *H*aro), 5.4 (t, J_{HH} = 6.3, 1H, *H*aro), 4.9 (d, J_{HH} = 6.3, 1H, *H*aro), 4.8 (t, J_{HH} = 6.1, 1H, *H*aro), 4.1 (m, 1H, C*H*), 3.9 (broad s, 1H, N*H*), 3.7 (dd, J_{HH} = 9.8 and 4.0, 1H, C*H*H′O), 3.6 (dd, J_{HH} = 9.8 and 7.7, 1H, CH*H*′OH), 2.8 (dd, J_{HH} = 14.9 and 8.5, 1H, C*H*H′C), 2.58 (dd, J_{HH} = 14.9 and 10.6, 1H, CH*H*′C), 0.9 (s, 9H, (C*H*$_3$)$_3$C), 0.1 (s, 6H, (C*H*$_3$)$_2$Si). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 234.7 (s, *C*O), 133.6, 97.6, 94.7, 93.1, 83.8, and 73.2 (*C*aro), 66.0 (s, *C*H_2O), 60.9 (*C*H), 31.0 (*C*H_2C(aro)), 25.9 (C(*C*H_3)$_3$), −5.3 (s, *C*H_3Si). MS *m/z* (%): 399 (3.8) [M$^+$], 343 (0.7) [M$^+$ − 2CO], 315 (33.4) [M$^+$ − 3CO], 263 (9.5) [M$^+$ − Cr(CO)$_3$], 118 (100) [M$^+$ − Cr(CO)$_3$ − CH_2−OSiMe$_2$-*t*-Bu].

(η*S*,*S*)-Tricarbonyl(2-hydroxymethylindoline)chromium *syn*-10.[34] A 50 mL round-bottom flash was charged with a stir bar, (η*S*,*S*)-tricarbonyl(2-*tert*-butyldimethylsilyloxymethylindoline)chromium (0.220 g, 0.55 mmol), THF (30 mL), and 1 M *t*-Bu$_4$NF (0.66 mL, 0.66 mmol). After a few minutes of nitrogen bubbling, the reaction mixture was stirred at 0 °C for 4 h. After warming to room temperature, the reaction mixture was transferred into a funnel, washed with an aqueous solution saturated in NH_4Cl (30 mL), and extracted with diethyl ether (2 × 20 mL), and the combined organic layers were dried with Na_2SO_4. After filtration, rotatory evaporation of the solvent and drying under oil pump vacuum, ***syn*-10** was obtained as a yellow powder (0.157 g, 0.55 mmol, 100%), mp 108 °C, $[\alpha]_D$ −42.0 (*c* 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, δ): 5.6 (d, J_{HH} = 5.6, 1H, *H*aro), 5.4 (s, 1H, *H*aro), 5.0 (d, J_{HH} = 6.4, 1H, *H*aro), 4.8 (s, 1H, *H*aro), 4.1 (m, 2H, C*H* and C*H*H′OH), 3.6 (d, J_{HH} = 7.3, 1H, CH*H*′OH), 3.1 (dd, J_{HH} = 10.3 and 15.2, 1H, C*H*H′C(aro)), 2.6 (d, J_{HH} = 14.4, 1H, CH*H*′C(aro)). ^{13}C{^{1}H} NMR (CDCl3, δ): 237.4 (s, *C*O), 135.3, 98.7, 97.0, 96.0, 86.5, and 76.2 (*C*aro), 65.3 (*C*H_2OH), 60.5

(C*H*N), 32.7 (*C*H2C(aro)). MS *m*/*z* (%): 285 (5.0) [M^+], 201 (3.0) [$M^+ - 3CO$], 149 (10.9) [$M^+ - Cr(CO)_3$], 132 (17.1) [$M^+ - Cr(CO)_3 - OH$], 118 (100) [$M^+ - Cr(CO)_3 - CH_2OH$]. Anal. Calcd for $C_{12}H_{11}NO_4Cr$: C, 50.53; H, 3.89; N, 4.91. Found: C, 50.29; H, 4.04; N, 5.05.

(*ηR,S*)-Tricarbonyl(2-hydroxymethylindoline)chromium *anti*-10. (*ηR,S*)-Tricarbonyl(2-*tert*-butyldimethylsilyloxymethylindoline)chromium (0.620 g, 1.55 mmol) was reacted in a procedure analogous to that given for ***syn*-10**. An identical workup gave ***anti*-10** as a yellow powder (0.350 g, 1.24 mmol, 80%), mp 98 °C, $[\alpha]_D$ +263.2 (*c* 1, $CHCl_3$). ^1H NMR ($CDCl_3$, *δ*): 5.6 (d, $J_{HH} = 5.3$, 1H, *H*aro), 5.4 (s, 1H, *H*aro), 5.0 (d, $J_{HH} = 5.5$, 1H, *H*aro), 4.8 (s, 1H, *H*aro), 4.2 (m, 1H, C*H*), 3.8 (d, J = 7.3, 2H, C*H*H′OH and N*H*), 3.6 (s, 1H, CH*H*′OH), 2.8 (d, *J*HH = 8.7, 2H, C*HH*′C(aro)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, *δ*): 234.6 (s, *C*O), 133.1, 98.3, 97.0, 94.6, 84.5, and 74.0 (*C*aro), 63.9 (*C*H2-OH), 60.6 (*C*HN), 30.6 (*C*H2C(aro)). MS *m*/*z* (%): 285 (7.7) [M^+], 201 (4.8) [$M^+ - 3CO$], 149 (10.6) [$M^+ - Cr(CO)_3$], 132 (14.7) [$M^+ - Cr(CO)_3 - OH$], 118 (100) [$M^+ - Cr(CO)_3 - CH_2OH$]. Anal. Calcd for $C_{12}H_{11}NO_4Cr$: C, 50.53; H, 3.89; N, 4.91. Found: C, 50.67; H, 3.99; N, 4.92.

(*S*)-3-Hydroxymethyl-1,2,3,4-tetrahydroisoquinoline.[21a] A 250 mL round-bottom flask was equipped with a stir bar, a reflux condenser, and a dropping funnel and charged with (*S*)-1,2,3,4-tetrahydroisoquinolinecarboxylic acid (1 g, 5.6 mmol) and THF (35 mL). Then, $BH_3{\cdot}SMe_2$ (10 M, 4.5 mL) was added. The reaction mixture was heated at reflux for 2 h. During the reflux, the starting acid dissolved and a hydrogen release was observed. After removing the oil bath, the reaction mixture was cooled to 0 °C. NaOH (1 M, 50 mL) was added dropwise via the funnel over a period of 30 min. The reaction mixture was again heated at reflux for 3 h. After cooling to room temperature, the reaction mixture was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with water (40 mL) and dried with $MgSO_4$. After filtration, evaporation of the solvents under reduced pressure, and drying under oil pump vacuum, (*S*)-3-hydroxymethyl-1,2,3,4-tetrahydroisoquinoline was isolated as a white powder (0.80 g, 4.87 mmol, 87%). ^1H NMR ($CDCl^3$, *δ*): 7.2−7.0 (m, 4H, *H*aro), 4.0 (s, 2H, C*H2*N), 3.8 (dd, $J_{HH} = 10.8$ and 3.7, 1H, C*H*H′OH), 3.5 (dd, $J_{HH} = 10.8$ and 8.1, 1H, CH*H*′OH), 3.1 (m, 1H, C*H*), 2.7 (dd, $J_{HH} = 16.3$ and 4.2, 1H, C*H*H′C(aro)), 2.6 (dd, *J*HH = 16.3 and 10.7, 1H, CH*H*′C(aro)), 2.1 (s, 2H, N*H* and O*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, *δ*): 135.9, 134.1, 129.4, 126.3, 126.1, and 126.0 (*C*aro), 66.0 (*C*H2OH), 55.1 (*C*H), 47.9 (*C*H2N), 31.1 (*C*H2C(aro)). Anal. Calcd for $C_{10}H_{13}NO$: C, 73,59; H, 8.03; N, 8.58. Found: C, 73,32; H, 8.01; N, 8.25.

(*S*)-Ph,Ph-AzeNOP 1. This represents a typical experiment used for the synthesis of the ligands. A 100 mL Schlenk tube was charged with a stir bar, (*S*)-2-hydroxymethylazetidine (0.143 g, 1.6 mmol), THF (4 mL), and NEt_3 (2 mL). Then, chlorodiphenylphosphine (0.796 g, 3.6 mmol) in solution in THF (1 mL) was introduced via cannula. The mixture was stirred at room temperature overnight. The progress of the reaction mixture and the end of the reaction were checked by ^{31}P NMR. The stirring was continued if necessary until completion of the reaction.[35] The crude reaction mixture was then filtered under nitrogen through basic alumina (1 × 5 cm) and washed with Et_2O (2 × 10 mL). The solvents were evaporated under oil pump vacuum from the combined filtrates. The residue was dried further under oil pump vacuum, providing **1** (0.981 g, 0.96 mmol, 60%) as a colorless oil. ^1H NMR ($CDCl_3$, *δ*): 7.5−7.2 (m, 20H, *H*aro), 4.1 (m, 1H, C*H*), 4.0 (m, 2H, C*H*2O), 3.5 (m, 1H, C*H*H′N), 3.2 (m, 1H, CH*H*′N), 2.25 (m, 1H, C*H*H′CH), 2.1 (m, 1H, CH*H*′CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, *δ*): 133.3 (d, $J_{CP} = 20.1$, *C*aro), 131.7 (d, $J_{CP} = 18.1$, *C*aro), 130.4 (dd, $J_{CP} = 21.4$, $J_{CP} = 3.0$, *C*aro), 129.2 (d, $J_{CP} = 20.1$, *C*aro), 128.5 (m, *C*aro), 79 (d, $J_{CP} = 16.5$, *C*H2O), 63.5 (dd, $J_{CP} = 20.1$ and 7.9, *C*H), 46.3 (d, $J_{CP} = 3.0$, *C*H2N), 22.5 (d, $J_{CP} = 13.4$, *C*H2CH). Anal. Calcd for $C_{28}H_{27}NOP_2$: C, 73.84; H, 5.97; N, 3.08. Found: C, 73.51; H, 5.90; N, 3.05.

(*S*)-Ph,Ph-IndoNOP 2. (*S*)-2-Hydroxymethylindoline (0.314 g, 2.1 mmol), Et_2O (2 mL), NEt_3 (1 mL), and chlorodiphenylphosphine (1.38 g, 6.3 mmol) in solution in Et_2O (1 mL) were reacted in a procedure analogous to that given for **1**. An identical workup gave **2** (0.861 g, 1.66 mmol, 79%) as a colorless oil. ^1H NMR ($CDCl_3$, *δ*): 7.5−7.3 (m, 24H, *H*aro), 7.1 (d, $J_{HH} = 7.1$, 1H, *H*aro), 6.9 (t, $J_{HH} = 7.6$, 1H, *H*aro), 6.7 (t, $J_{HH} = 7.3$, 1H, *H*aro), 6.6 (d, $J_{HH} = 7.9$, 1H, *H*aro), 4.3 (m, 1H, C*H*), 3.7 (m, 1H, C*H*H′OH), 3.6 (m, 1H, CH*H*′OH), 3.40 (dd, $J_{HH} = 16.1$ and 9.2, 1H, C*H*H′Caro), 3.1 (d, $J_{HH} = 16.1$, 1H, CH*H*′Caro). $^{13}C\{^1H\}$ NMR ($CDCl_3$, *δ*): 149.5 (d, $J_{CP} = 3.2$, *C*aro), 141.8 (dd, $J_{CP} = 17.4$ and 8.1, *C*P), 136.8 (dd, $J_{CP} = 12.7$ and 8.3, *C*P), 132.2−128.2 (m, *C*aro and *C*Caro), 126.3 (s, *C*aro), 124.8 (s, *C*aro), 19.4 (s, *C*aro), 111.8 (d, $J_{CP} = 8.5$, *C*aro), 71.9 (d, $J_{CP} = 17.4$, *C*H2OH), 64.1 (dd, $J_{CP} = 15.2$ and 8.9, *C*H), 33.3 (s, *C*H2Caro). Anal. Calcd for $C_{33}H_{29}NOP_2$: C, 76.65; H, 5.65; N, 2.71. Found: C, 76.20; H, 5.65; N, 2.57.

(*S*)-Ph,Ph-QuinoNOP 3. (*S*)-3-Hydroxymethyl-1,2,3,4-tetrahydroisoquinoline (0.148 g, 0.9 mmol), Et_2O (2 mL), NEt_3 (1 mL), and chlorodiphenylphosphine (0.437 g, 2.0 mmol) in solution in Et_2O (1 mL) were combined in a procedure identical to that given for **1**. After 48 h, an identical workup gave **3** (0.415 g, 0.77 mmol, 86%) as a colorless oil. ^1H NMR (CDCl3, *δ*): 8.0−6.9 (m, 24H, *H*aro), 4.2 (m, 1H, C*H*), 4.0 (dd, $J_{HH} = 16.7$, $J_{HH} = 2.3$, 2H, C*H*2N), 3.9 (m, 1H, C*H*H′O), 3.7 (m, 1H, CH*H*′O), 3.1 (dd, $J_{HH} = 16.1$ and 6.8, 1H, C*H*H′Caro), 2.9 (d, $J_{HH} = 16.1$, 1H, CH*H*′Caro). $^{13}C\{^1H\}$ NMR ($CDCl_3$, *δ*): 125.7−141.9 (m, *C*aro), 70.1 (dd, $J_{CP} = 5.5$ and 5.5, *C*H2O), 58.8 (d, $J_{CP} = 6.1$, *C*H), 31.5 (d, $J_{CP} = 5.5$, *C*H2CH). Anal. Calcd for $C_{34}H_{31}NOP_2$: C, 76.82; H, 5.88; N, 2.63. Found: C, 77.15; H, 5.62; N, 2.52.

(*S*)-Cp,Cp-AzeNOP 4. (*S*)-2-Hydroxymethylazetidine (0.054 g, 0.6 mmol), Et_2O (4 mL), NEt_3 (1 mL), and chlorodicyclopentylphosphine (0.281 g, 1.4 mmol) in solution in Et_2O (1 mL) were combined in a procedure identical to that given for **1**. After 18 h, an identical workup gave **4** (0.534 g, 1.26 mmol, 90%) as a colorless oil. ^1H NMR (CDCl3, *δ*): 4.0 (m, 1H), 3.8 (m, 1H), 3.6 (m, 2H), 3.5 (m, 1H), 2.3 (m, 1H, C*H*H′CH), 2.1 (m, 1H, CH*H*′CH), 2.0−1.2 (m, 36H, C*H*cyclopentyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$, *δ*): 75.3 (s, *J*CP = 14.5, *C*H2O), 63.7 (dd, $J_{CP} = 14.1$ and 7.1, *C*HN), 47.0 (*C*H2N), 40.9 (d, $J_{CP} = 4.5$, *C*cyclopentyl), 40.6 (d, $J_{CP} = 3.7$, *C*cyclopentyl), 37.8 (d, $J_{CP} = 6.0$, *C*cyclopentyl), 37.0 (d, $J_{CP} = 13.4$, *C*cyclopentyl), 30.7−25.0 (*C*cyclopentyl), 23.6 (d, $J_{CP} = 11.9$, *C*H2CH). Anal. Calcd for $C_{24}H_{43}NOP_2$: C, 68.06; H, 10.23; N, 3.31. Found: C, 68.43; H, 10.04; N, 3.23.

(*S*)-Cp,Cp-IndoNOP 5. (*S*)-2-Hydroxymethylindoline (0.150 g, 1 mmol), THF (2 mL), NEt_3 (1 mL), and chlorodicyclopentylphosphine (0.550 g, 2.7 mmol) in solution in THF (1 mL) were combined in a procedure analogous to that given for **1**. After 4 days, an identical workup gave **7** (0.371 g, 0.9 mmol, 90%) as a colorless oil. ^1H NMR (CDCl3, *δ*): 7.1 (d, $J_{HH} = 7.3$, 1H, *H*aro), 7.0 (t, $J_{HH} = 7.6$, 1H, *H*aro), 6.7 (t, $J_{HH} = 7.3$, 1H, *H*aro), 6.6 (d, $J_{HH} = 7.8$, 1H, *H*aro), 4.0 (m, 1H, C*H*), 3.7 (m, 1H, C*H*H′O), 3.5 (dd, $J_{HH} = 17.8$ and 9.5, 1H, CH*H*′O), 3.1 (dd, $J_{HH} = 15.9$ and 9.1, 1H, C*H*H′Caro), 2.97 (d, $J_{HH} = 15.9$, 1H, CH*H*′Caro), 2.0−1.2 (m, 36H, *H*cyclopentyl). $^{13}C\{^1H\}$ NMR ($CDCl_3$, *δ*): 150.5 (s, *C*aro), 127.9 (s, *C*aro), 126.9 (s, *C*aro), 124.8 (s, *C*aro), 118.6 (s, *C*aro), 109.4 (s, *C*aro), 72.4 (d, $J_{CP} = 9.8$, *C*H2O), 59.7 (d, $J_{CP} = 6.1$, *C*HN), 40.7 (d, $J_{CP} = 11.0$, *C*Hcyclopentyl), 40.6 (d, $J_{CP} = 15.3$, *C*Hcyclopentyl), 33.3−25.7 (m, *C*cyclopentyl). Anal. Calcd for $C_{29}H_{45}NOP_2$: C, 71.73; H, 9.34; N, 2.88. Found: C, 71.47; H, 9.22; N, 2.97.

(*S*)-Cp,Cp-QuinoNOP 6. (*S*)-3-Hydroxymethyl-1,2,3,4-tetrahydroisoquinoline (0.107 g, 0.6 mmol), THF (2 mL), NEt_3 (1

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(34) Jones, G. B.; Heaton, S. B.; Chapman, B. J.; Guzel, M. *Tetrahedron: Asymmetry* **1997**, *8*, 3625.

(35) When monitoring the reaction by ^{31}P NMR, the general trends reported earlier are observed,[13a] e.g., concomitant presence of OP−NH, NP−OH, and NP−OP species until complete conversion into the OP−NP ligands.

mL), and chlorodicyclopentylphosphine (0.295 g, 1.4 mmol) in solution in THF (1 mL) were combined in a procedure identical to that given for **1**. After 3 days, an identical workup gave **6** (0.214 g, 0.432, 72%) as a colorless oil in 72% yield. ^{1}H NMR ($CDCl_3$, δ): 7.1 (m, 3H, *H*aro), 6.9 (m, 1H, *H*aro), 4.1 (s, 2H, C*H*$_2$N), 3.7 (m, 1H, C*H*H′O), 3.6 (m, 1H, C*H*), 3.5 (m, 1H, CH*H*′O), 2.9 (dd, J_{HH} = 15.9 and 5.4, 1H, C*H*H′CH), 2.8 (dd, J_{HH} = 15.9 and 2.4, 1H, CH*H*′CH), 2.2−1.1 (m, 36H, *H*cyclopentyl). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 135.2 (s, *C*aro), 134.0 (s, *C*aro), 129.5 (s, *C*aro), 126.0 (s, *C*aro), 125.5 (s, *C*aro), 125.4 (s, *C*aro), 71.8 (dd, J_{CP} = 14.8 and 5.3, *C*H$_2$O), 58.3 (dd, J_{CP} = 29.3 and 7.9, *C*H), 44.9 (s, *C*H$_2$CH), 40.5 (d, J_{CP} = 15.9, *C*Hcyclopentyl), 38.7 (d, J_{CP} = 10.5, *C*Hcyclopentyl), 38.2 (d, J_{CP} = 13.6, *C*Hcyclopentyl), 31.1−25.7 (m, *C*H$_2$CH and *C*cyclopentyl). Anal. Calcd for $C_{30}H_{47}NOP_2$: C, 72.12; H, 9.41; N, 2.80. Found: C, 71.85; H, 9.40; N, 2.64.

(*S*)-Cy,Cy-AzeNOP 7. (*S*)-2-Hydroxymethylazetidine (0.130 g, 1.5 mmol), Et_2O (4 mL), NEt_3 (1 mL), and chlorodicyclohexylphosphine (0.763 g, 3.3 mmol) in solution in Et_2O (1 mL) were combined in a procedure identical to that given for **1**. After 18 h, an identical workup gave **7** (0.662 g, 1.38 mmol, 92%) as a colorless oil. ^{1}H NMR ($CDCl_3$, δ): 3.9 (m, 1H), 3.8−3.5 (m, 4H), 2.3 (m, 1H, C*H*H′CH), 2.1 (m, 1H, CH*H*′CH), 1.9−1.0 (m, 44H, C*H*cyclohexyl). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 75.9 (d, J_{CP} = 15.0, *C*H2O), 64.9 (dd, J_{CP} = 20.1 and 8.2, *C*HN), 47.7 (d, J_{CP} = 5.2, CH$_2$N), 38.3 (d, J_{CP} = 5.6, *C*H$_2$CH), 38.0 (d, J_{CP} = 5.2, *C*cyclohexyl), 35.6 (d, J_{CP} = 7.1, *C*cyclohexyl)**,** 33.2 (d, J_{CP} = 14.1, *C*cyclohexyl), 30.1−24.9 (m, *C*cyclohexyl), 23.9 (d, J_{CP} = 11.5, *C*H$_2$CH). Anal. Calcd for $C_{28}H_{51}NOP_2$: C, 70.11; H, 10.72; N, 2.92. Found: C, 69.88; H, 10.53; N, 2.88.

(*S*)-Cy,Cy-QuinoNOP 8. (*S*)-3-Hydroxymethyl-1,2,3,4-tetrahydroisoquinoline (0.103 g, 0.6 mmol), THF (2 mL), NEt_3 (1 mL), and chlorodicyclohexylphosphine (0.323 g, 3.6 mmol) in solution in THF (1 mL) were combined in a procedure identical to that given for **1**. After 3 days an identical workup gave **8** (0.189 g, 0.34 mmol, 56%) as a colorless oil. ^{1}H NMR ($CDCl_3$, δ) 7.1−6.9 (m, 4H, *H*aro), 4.1 (m, 2H, C*H*$_2$N), 3.7 (m, 1H, C*H*H′O), 3.5 (m, 1H, C*H*), 3.4 (m, 1H, CH*H*′O), 2.9 (dd, J_{HH} = 15.4 and 4.9, 1H, C*H*HCH), 2.8 (dd, J_{HH} = 15.4 and 1.6, 1H, CH*H*′CH), 2.0−0.8 (m, 44H, *H*cyclohexyl). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 135.2, 133.9, 129.6, 125.9, 125.5, and 125.4 (*C*aro), 73,0 (d, J_{CP} = 23.5, *C*H$_2$O), 59.0 (dd, J_{CP} = 23.5 and 7.3, *C*H), 46.1 (s, CH$_2$CH), 37.9 (d, J_{CP} = 16.6, *C*Hcyclohexyl), 36.1 (d, J_{CP} = 13.4, *C*Hcyclohexyl), 35.0 (d, J_{CP} = 15.9, *C*Hcyclohexyl), 30.7−26.1 (*C*H$_2$C and *C*cyclohexyl).

(η*R*,*S*)-Cr(CO)$_3$-Ph,Ph-IndoNOP *anti*-11. (η*R*,*S*)-Tricarbonyl(2-hydroxymethylindoline)chromium ***anti*-10** (0.0538 g, 0.19 mmol), THF (2 mL), NEt_3 (1 mL), and chlorodiphenylphosphine (0.133 g, 0.6 mmol) in solution in THF (1 mL) were combined in a procedure identical to that given for **1**. After 46 h of stirring at 60 °C, an identical workup gave ***anti*-11** (0.092 g, 0.14 mmol, 74%) as a yellow oil. ^{1}H NMR ($CDCl_3$, δ): 7.5−7.2 (m, 20H, *H*phenyl), 5.4 (d, J_{HH} = 6.0, 1H, *H*aro), 5.1 (dt, J_{HH} = 6.5, J_{HP} = 1.1, 1H, *H*aro), 5.0 (dd, J_{HH} = 6.6, J_{HP} = 1.4, 1H, *H*aro), 4.8 (dt, J_{HH} = 6.1, J_{HP} = 0.7, 1H, *H*aro), 4.1 (m, 1H, C*H*), 3.9 (m, 1H, C*H*H′O), 3.7 (m, 1H, CH*H*′O), 3.2 (dd, J_{HH} = 16.0 and 9.9, 1H, C*H*H′CH), 3.0 (dd, J_{HH} = 16.0 and 5.5, 1H, CH*H*′CH). Anal. Calcd for $C_{36}H_{29}NCrO_4P_2$: C, 66.16; H, 4.47; N, 2.14. Found: C, 66.65; H, 4.36; N, 2.06.

(η*S*,*S*)-Cr(CO)$_3$-Ph,Ph-IndoNOP *syn*-11. (η*S*,*S*)-Tricarbonyl(2-hydroxymethylindoline)chromium ***syn*-10** (0.050 g, 0.17 mmol), Et_2O (2 mL), NEt_3 (1 mL), and chlorodiphenylphosphine (0.083 g, 0.38 mmol) in solution in Et_2O (1 mL) were combined in a procedure identical to that given for **1**. After 4 days, an identical workup gave ***syn*-11** (0.112 g, 0.17 mmol, 100%) as a yellow oil. ^{1}H NMR (CDCl3, δ): 7.3−7.2 (m, 20H, *H*Phenyl), 5.5 (d, J_{HH} = 5.8, 1H, *H*aro), 5.4 (dd, J_{HH} = 6.8, J_{HP} = 1.7, 1H, *H*aro), 5.2 (dt, J_{HH} = 6.8, J_{HP} = 1.2, 1H, *H*aro), 4.8 (t, J_{HH} = 6.1, 1H, Haro), 4.1 (m, 1H, C*H*), 4.0 (m, 1H, C*H*H′OH), 3.3 (m, 1H, CH*H*′OH), 3.2 (dd, J_{HH} = 16.3 and 9.5, 1H, C*H*H′CH), 3.0 (dd, J_{HH} = 16.3 and 5.5, 1H, CH*H*′CH).

(η*R*,*S*)-Cr(CO)$_3$-Cp,Cp-IndoNOP *anti*-12. (η*R*,*S*)-Tricarbonyl(2-hydroxymethylindoline)chromium ***anti*-10** (0.067 g, 0.235 mmol), Et_2O (2 mL), NEt_3 (1 mL), and chlorodicyclohexylphosphine (0.205 g, 1 mmol) in solution in Et_2O (1 mL) were combined in a procedure identical to that given for **1**. After 4 days, an identical workup gave ***anti*-12** (0.123 g, 0.20 mmol, 55%) as a yellow powder.

(η*S*,*S*)-Cr(CO)$_3$-Cp,Cp-IndoNOP *syn*-12. (η*S*,*S*)-Tricarbonyl(2-hydroxymethylindoline)chromium ***syn*-10** (0.0602 g, 0.2 mmol), THF (2 mL), NEt_3 (1 mL), and chlorodicyclopentylphosphine (0.0946 g, 0.46 mmol) in solution in THF (1 mL) were combined in a procedure analogous to that given for **1**. After 4 days, an identical workup gave ***syn*-12** (0.068 g, 0.11 mmol, 84%) as a yellow oil. ^{1}H NMR ($CDCl_3$, δ): 5.4 (d, J_{HH} = 6.0, 1H, *H*aro), 5.2 (m, 2H, *H*aro), 4.6 (t, J_{HH} = 6.1, 1H, *H*aro), 3.9 (m, 1H, C*H*), 3.8 (m, 1H, C*H*H′OH), 3.6 (m, 1H, CH*H*′OH), 3.0 (dd, J_{HH} = 16.5 and 9.6, 1H, C*H*H′CH), 2.7 (dd, J_{HH} = 16.5 and 2.4, 1H, CH*H*′CH), 2.3−0.9 (m, 36H, *H*cyclopentyl). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 233.8 (s, *C*O), 93.9 (s, *C*aro), 92.2 (s, *C*aro), 83.8 (s, *C*aro), 76.6 (s, *C*aro), 70.4 (d, J_{CP} = 11.6, *C*H$_2$O), 60.5 (s, *C*HN), 40.6 (d, J_{CP} = 17.7, *C*Hcyclopentyl), 40.3 (d, J_{CP} = 16.5, *C*Hcyclopentyl), 32.7−25.7 (m, *C*H$_2$cyclopentyl). MS: *m*:*z* (%): 593 (1.1) [$M^+ - CO$], 537 (5.8) [$M^+ - 3CO$], 416 (2.5) [$M^+ - Cr(CO)_3 - Cp$], 103 (52.6), 69 (100) [Cp^+]. Anal. Calcd for $C_{32}H_{45}NCrO_4P_2$: C, 61.83; H, 7.3; N, 2.25. Found: C, 61.42; H, 7.18; N, 2.15.

(η*S*,*S*)-Cr(CO)$_3$-Cy,Cy-IndoNOP *syn*-13. (η*S*,*S*)-Tricarbonyl(2-hydroxymethylindoline)chromium ***syn*-10** (0.0795 g, 0.28 mmol), THF (2 mL), NEt_3 (1 mL), and chlorodicyclohexylphosphine (0.170 g, 0.73 mmol) in solution in THF (1 mL) were combined in a procedure analogous to that given for **1**. After 3 days, an identical workup gave ***syn*-13** (0.102 g, 0.39 mmol, 53%) as a yellow oil. ^{1}H NMR ($CDCl_3$, δ): 5.6 (d, J_{HH} = 5.4, 1H, *H*aro), 5.4 (t, J_{HH} = 5.8, 1H, *H*aro), 4.9 (d, J_{HH} = 6.1, 1H, *H*aro), 4.8 (t, J_{HH} = 5.8, 1H, Haro), 4.1 (m, 1H, C*H*), 3.9 (m, 1H, C*H*H′O), 3.7 (m, 1H, CH*H*′O), 2.9 (dd, J_{HH} = 14.9, J_{HH} = 8.6, 1H, C*H*H′CH), 2.6 (dd, *J* = 14.9 Hz, J_{HH} = 11.2, 1H, CH*H*′CH), 2.1−1.1 (m, 44H, *H*cyclohexyl).

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