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N-Phosphino-*p*-tolylsulfinamide Ligands: Synthesis, Stability, and Application to the Intermolecular Pauson−Khand Reaction

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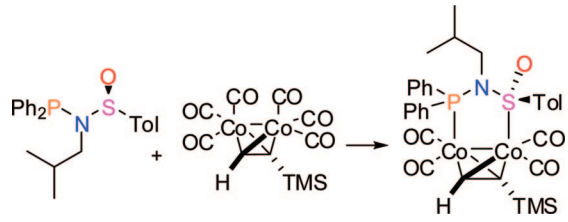
Received April 3, 2008



Here we synthesized a family of racemic and optically pure *N*-phosphino-*p*-tolylsulfinamide (PNSO) ligands. Their stability and coordination behavior toward dicobalt−alkyne complexes was evaluated. Selectivities of up to 3:1 were achieved in the ligand exchange process with (μ-TMSC$_2$H)Co$_2$(CO)$_6$. The resulting optically pure major complexes were tested in the asymmetric intermolecular Pauson−Khand reaction and yielded up to 94% ee. X-ray studies of the major complex **18a** indicated that the presence of an aryl group on the sulfinamide reduces the hemilabile character of the PNSO ligands.

Introduction

Interest in the preparation of chiral sulfur compounds in general and chiral sulfoxides and sulfinamides in particular has increased considerably since the beginning of the 1980s. This growth is attributed to the fact that chiral sulfoxides and sulfinamides are efficient chiral auxiliaries that can induce relevant asymmetric transformations.[1–3] Ligands that contain only sulfur as donor atom are of limited use in metal catalysis due to their poor coordination capacity with respect to phosphines and phosphites. This limitation has been addressed by preparing phosphine−sulfoxide or phosphine−sulfinamide ligands

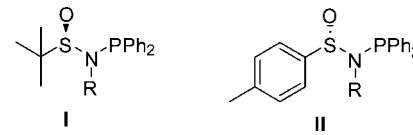


FIGURE 1. Phosphine−sulfinamide ligands.

in which the phosphorus atom provides metal affinity while the sulfur moiety is the source of chirality (Figure 1). Only a few P,S=O ligands have been described in the literature. This lack of information is probably due to the low stability of these ligands as a result of sulfur-to-phosphorus oxygen migration.[4–6] In the context of our project in the asymmetric Pauson−Khand reaction,[7–9] we recently provided the first report of the synthesis of *N*-phosphino-*tert*-butylsulfinamide ligands (**I**), which were found to be highly efficient in the intermolecular Pauson−Khand reaction.[10] Ligands of type **I** were synthesized in high yield and were stable toward oxygen migration in solution and solid form. A closely related family of ligands would arise from switching the *tert*-butyl group for an aryl group. We consider

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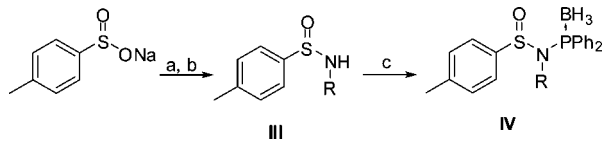
10.1021/jo800710n CCC: $40.75
Published on Web 08/26/2008

TABLE 1. Synthesis of Racemic PNSO Ligands



Entry	R	Yield of **III** (%)[d]	Yield of **IV** (%)	Ligand
1	Bn-	62	85	**1**-BH_3
2	1-Naph-CH_2-	87	55	**2**-BH_3
3	o-Me-$C_6H_4CH_2$-	78	81	**3**-BH_3
4	2-Pyr-CH_2-	41	30	**4**-BH_3
5	*p*-Bu^t-$C_6H_4CH_2$-	84	70	**5**-BH_3
6	*p*-F-$C_6H_4CH_2$-	73	76	**6**-BH_3
7	$(CH_3)_2CHCH_2$-	64	74	**7**-BH_3
8	$(CH_3)_2CH$-	53	70[e]	**8**-BH_3
9	*p*-Cl-C_6H_4-	74	66	**9**-BH_3
10	*p*-F-C_6H_4-	65	65	**10**-BH_3
11	*p*-CF_3-C_6H_4-	77	48	**11**-BH_3
12	*p*-MeO-C_6H_4-	–	–	**12**-BH_3

[a] $C_2O_2Cl_2$, toluene, rt, 1 h. [b] RNH_2, Et_3N, toluene, 0 °C. [c] BuLi or LiHMDS, THF, −78 °C, PPh_2Cl, then BH_3–SMe_2 at −30 °C. [d] Yield refers to crude material that was used without further purification in the next step. [e] Isolated as a 1/1.5 mixture of borane- and borane-free ligand.

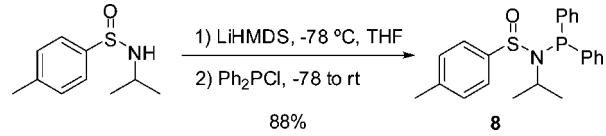
that *N*-phosphino-tolylsulfinamide ligands (**II**) would show different electronic and structural properties of interest with respect to type **I** ligands. Thus here we addressed the synthesis of racemic and optically pure *N*-phosphino-tolylsulfinamide ligands (**II**), their coordination behavior toward terminal alkyne−dicobalt carbonyl complexes, and their application in the intermolecular asymmetric Pauson−Khand reaction.

Results and Discussion

Synthesis of PNSO Ligands. We synthesized borane-protected *N*-phosphino-*p*-tolylsulfinamide ligands **1**−**11** following the scheme in Table 1. To prevent oxygen migration during the synthesis, the borane protection strategy reported for type **I** ligands was used.[10] Racemic PNSO ligands were prepared efficiently from sodium *p*-toluenesulfinate by conversion to the sulfinyl chloride with oxalyl chloride followed by aminolysis with several amines in toluene.[11] At this point, using parallel-chemistry techniques, a number of amines were used to yield up to 11 distinct sulfinamides (**III**). Benzylic amines (Table 1, entries 1−6) as well as aliphatic amines (Table 1, entries 7 and 8) provided good yields of the corresponding sulfinamide intermediates. In contrast, anilines provided a clear pattern in which electron-withdrawing groups on the aromatic ring stabilized the sulfinamide functional group while electron-releasing groups caused the opposite effect. Thus, while *p*-chloro-, *p*-fluoro-, and *p*-CF_3-anilines provided the corresponding sulfinamides with good yields, the use of p-methoxyaniline (Table 1, entry 12) led only to decomposition products, probably because of enhanced hydrolysis of the sulfinamide functionality.

Finally, sulfinamide deprotonation with either *n*-BuLi or LiHMDS at low temperature and subsequent addition of Ph_2PCl, followed by the addition of borane as a phosphine-protecting group afforded 11 examples of borane-protected PNSO ligands in good to moderate yields (Table 1). Most intriguingly, isopropyl amine-derived compound **8** was isolated as a mixture of protected and deprotected ligands. Interestingly the deprotected fraction of **8** displayed no oxygen migration from sulfur to phosphorus.

SCHEME 1. Synthesis of PNSO Ligand 8 without Borane Protection



Stability Evaluation of Free PNSO Ligands. *N*-Phosphinosulfinamides show a complex functionality that allows multiple decomposition pathways. First, sulfinamides can be easily hydrolyzed in acidic medium to provide the free amine. This is a desired property in asymmetric reductive amination with optically pure *tert*-butylsulfinamide and *p*-tolylsulfinamide, which allows the convenient isolation of the free primary amine.[12−14] Second, PNSO ligands bear a phosphinamide group that can also be hydrolyzed.[15] Finally, another undesired process for the use of these molecules as metal ligands is the aforementioned migration of the oxygen atom from sulfur to phosphorus.[16] Our previous studies on type **I** ligands bearing a *tert*-butylsulfinamide fragment indicated that protection by borane provided the stability required for purification after the introduction of the phosphinamide group. Once the borane-protected ligand was isolated, removal of borane with an amine (DABCO) was performed, with no decomposition of the molecule. At this point, the ligands were stable to oxygen migration and hydrolysis provided they were not exposed to acidic conditions, and thus they were shelf-stable solids.

Following our previous procedure, deprotection of **1**-BH_3, bearing a benzyl group on nitrogen, was first examined. Treatment of **1**-BH_3 with DABCO in toluene provided a mixture of compounds from which no free ligand could be isolated by flash chromatography on SiO_2. However, a closer look at the deprotection step showed that product decomposition occurred during the purification procedure on SiO_2. ^1H NMR monitoring indicated that the free ligand was stable in solution under the deprotection conditions used (DABCO, toluene, 25−65 °C). These results suggest that decomposition is due to acidic hydrolysis on silica, rather than to oxygen migration. We next turned our attention to the *N*-isopropyl ligand **8**-BH_3 isolated as a 1:1.5 mixture of borane-containing and borane-free ligands. When this mixture was treated with DABCO, the corresponding borane-free ligand **8** was isolated as a sole product after filtration on SiO_2. This result indicates that ligand **8** is robust to hydrolytic decomposition and oxygen migration. To check whether the phosphine protection step was required in this case, the synthesis of **8** was repeated without the protection step. In this case, the free ligand **8** was isolated after flash chromatography with an improved 88% yield (Scheme 1).[6] The thermal stability of **8** was further

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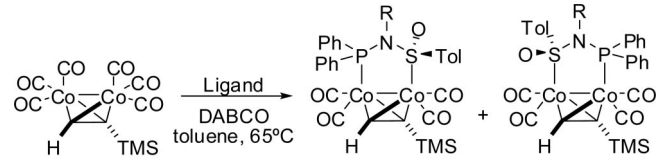
examined by heating a solution of the ligand at 65 °C in dry toluene under nitrogen atmosphere for 24 h. Under these conditions no substantial decomposition or oxygen transfer occurred since 93% of the ligand remained unaltered (^{1}H NMR). The robustness of ligand **8** appears to be related to the right steric bulk of the isopropyl group on nitrogen. Thus, neither the *N*-benzylic ligands (**1**−**6**), the *N*-isobutyl (**7**), nor the *N*-phenyl ligands (**9**−**11**) were isolated as borane-free ligands. These results indicate that *N*-phosphino-*p*-tolylsulfinamides are more prone to hydrolysis than their corresponding *tert*-butylsulfinamide counterparts. However, increasing the steric bulk on nitrogen provided enough stability against hydrolysis and oxygen transfer for isolation of the free PNSO ligands.

Reactions with (μ-Alkyne)$Co_2(CO)_6$ Complexes. Given that most of the PNSO ligands could not be isolated in their borane-free form, deprotection and ligand exchange reaction were performed in situ in the same reaction flask. Thus, cobalt complexes were prepared by treatment of trimethylsilylacetylene dicobaltcarbonyl with the corresponding borane-protected racemic PNSO ligands in the presence of 1.5 equiv of DABCO at 65 °C for 2 h (Table 2). This procedure afforded the corresponding diastereomeric mixture of complexes in good yield except for the *N*-phenyl ligands **9**−**11**, which produced consistently lower yields (16−32%), probably as a result of ligand decomposition on heating. No selectivity was observed for most of the ligand exchange reactions, even when extended reaction times and continued heating at 80 °C were used. The exception to this behavior were ligands **7** and **8** bearing an *N*-isobutyl and *N*-isopropyl fragment, which afforded a 2:1 and 3:1 mixture of diastereomeric complexes, respectively (Table 2, entries 6 and 7). To check whether this diastereoselectivity could be improved, the initial 2:1 mixture of **18a/18b** was subjected to thermodynamic equilibration in three experimental conditions: extended heating in toluene (65 °C, 18 h), heating in CO atmosphere (1 bar, 65 °C, 18 h), and heating in the presence of 0.1 equiv of dibenzyl sulfide (65 °C, 18 h). Both CO and sulfide should enhance equilibration through open nonbridged phosphine complexes.[17–19] Experimentally, heating alone resulted in no equilibration of the initial mixture; however, the use of CO or sulfide produced equilibration toward a 1:1 mixture of complexes **18a/18b**. These results suggest that tolylsulfinamide PNSO ligands equilibrate slowly compared to *tert*-butylsulfinamide ligands (**I**), and that the selectivity observed for ligands **7** and **8** is due to a kinetic control during the ligand exchange process rather than to thermodynamic equilibration of the final tetracarbonyl complexes.

Chiral *N*-Phosphino-*p*-tolylsulfinamide Ligands. After studying the coordination behavior of racemic PNSO ligands, we undertook the synthesis of the optically pure ligands **1**, **7**, and **8** (Table 3). Condensation of commercially available *S*-(+)-*p*-tolylsulfinamide **23** with the corresponding aldehyde/ketone reagent with $Ti(OEt)_4$ as a Lewis acid and water scavenger followed by in situ reduction with $NaBH_4$ afforded the corresponding sulfinamides in 87−58% yield.[20] Phosphinylation reaction and protection with borane provided the chiral ligands

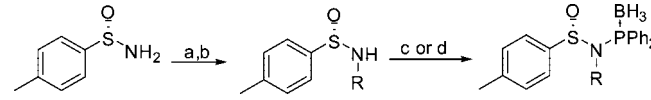
TABLE 2. Coordination of Racemic PNSO Ligands to a Dicobaltalkyne Complex



		13a-22a		13b-22b
Entry	L	Yield (%)	d.r.[a]	Complex
1	**1**-BH_3	88	1:1	**13a/13b**
2	**2**-BH_3	86	1:1	**14a/14b**
3	**3**-BH_3	80	1:1	**15a/15b**
4	**5**-BH_3	81	1:1	**16a/16b**
5	**6**-BH_3	69	1:1	**17a/17b**
6	**7**-BH_3	62	2:1	**18a/18b**
7	**8**[b]	80	3:1	**19a/19b**
8	**9**-BH_3	22	1:1	**20a/20b**
9	**10**-BH_3	32	1:1	**21a/21b**
10	**11**-BH_3	16	1:1	**22a/22b**

[a] As determined by ^{1}H NMR spectroscopy. [b] The borane-free ligand **8** was used; therefore DABCO was not employed in this case.

TABLE 3. Synthesis of Chiral PNSO Ligands[a]



(+)-23 (+)-III (−)-IV

Entry	R	III (%)	IV (%)	Ligand
1	benzyl	82	85	(−)-**1**-BH_3
2	isobutyl	87	74	(−)-**7**-BH_3
3	isopropyl	58	64	(−)-**8**[e]

[a] Reagents and conditions: (a) $Ti(OEt)_4$, CH_2Cl_2, Δ, 1.5 h with 1.3 equiv of one of the following: benzaldehyde (entry 1), isobutyraldehyde (entry 2), or acetone (entry 3). (b) $NaBH_4$, EtOH, rt, overnight. (c) BuLi, THF, −78 °C, Ph_2PCl, then BH_3–SMe_2 at −30°C. (d) BuLi, THF, −78 °C, Ph_2PCl. [b] Product 8 was isolated as borane-free ligand.

(−)-**1**-BH_3 and (−)-**7**-BH_3 in good yields. Alternatively, (−)-**8** was isolated as a stable borane-free ligand.

With these optically pure ligands in our hands, the corresponding tetracarbonyl dicobalt complexes of $TMSC_2H$, PhC_2H, and $HO(CH_3)_2CC_2H$ were prepared (Table 4). For trimethylsilylacetilene complexes analogous yields and selectivity as observed for the racemic series were obtained (Table 4, entries 1−3). Reaction of ligands **7** and **8** with phenylacetylene and 2-methyl-3-butyn-2-ol dicobalt complexes provided the corresponding complexes with excellent yields but almost no selectivity (Table 4, entries 4−7). Most notably, optically pure diastereomeric complexes **18a**, **19a**, **24b**, and **25a** could be crystallized from hexane/toluene

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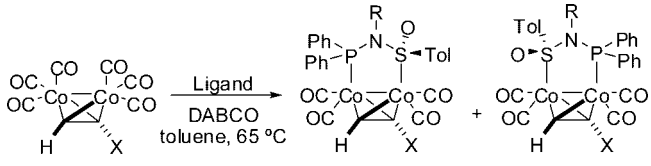
TABLE 4. Ligand Exchange Reaction with Optically Pure PNSO Ligands and Dicobaltalkyne Complexes



			Xa		Xb
Entry	**X**	**L**	**Yield (%)**	**d.r.[a]**	**Complex**
1	TMS	**(–)-1**-BH_3	88	1:1	**13a/13b**
2	TMS	**(–)-7**-BH_3	62	2:1	**18a/18b**
3	TMS	**(–)-8**[b]	80	3:1	**19a/19b**
4	Ph	**(–)-7**-BH_3	93	1:1	**24a/24b**
5	Ph	**(–)-8**[b]	80	1:1	**25a/25b**
6	$C(CH_3)_2OH$	**(–)-7**-BH_3	86	1:1	**26a/26b**
7	$C(CH_3)_2OH$	**(–)-8**[b]	81	1.3:1	**27a/27b**

[a] As determined by ^1H NMR spectroscopy. [b] The borane-free ligand **8** was used; therefore DABCO was not employed in this case.

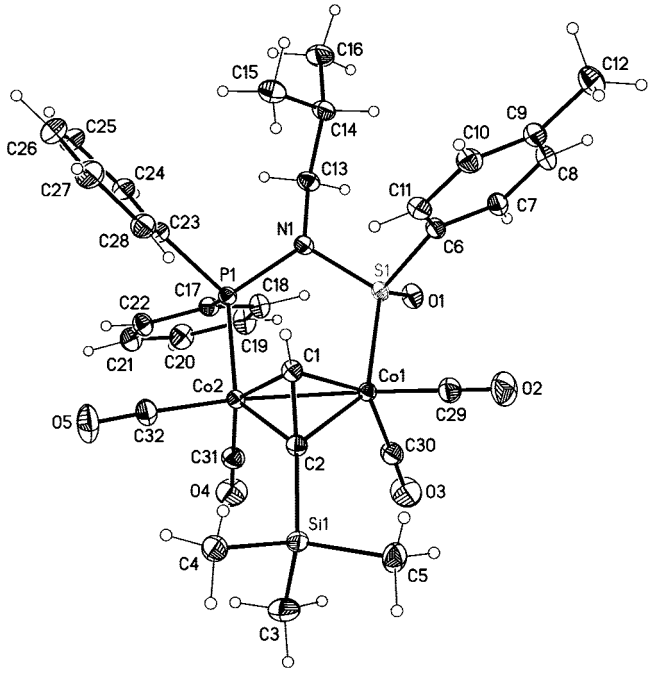
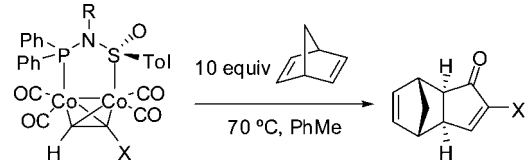


FIGURE 2. ORTEP plot for crystal structure of **18a**. The sulfur atom is bonded to the Pro-*R* cobalt atom (Co1).

mixtures.[21] Alternatively, diastereomeric mixtures **26a/26b** and **27a/27b** derived from 2-methyl-3-butyn-2-ol could be separated by flash chromatography.

The structure of the major isomer **18a** was firmly established by X-ray analysis (Figure 2). In a similar fashion as type **I** ligands, *N*-phosphino-*p*-tolylsulfinamides work as P,S bridged ligands. In the present case, the phosphorus was attached to cobalt Pro-*S*, while the sulfur atom was linked to the Pro-*R* center. The ligand and the alkyne substituent adopted an *anti* conformation to minimize steric interactions. The Co−S bond observed for **18a** (Figure 2) was shorter (2.17Å) than the same bond in *tert*-butylsulfinamide complexes (2.19 Å).[10] This shorter distance may be rationalized

TABLE 5. Pauson−Khand Reaction of Optically Pure Complexes with Norbornadiene



Entry	**Complex**	**X**	**Yield (%)[a]**	**ee[b]**	**Product**
1	**18a**	TMS	75	82	**(–)-28**
2	**19a**	TMS	60	50	**(–)-28**
3	**24b**	Ph	97	94	**(+)-29**
4	**25a**	Ph	88	89	**(–)-29**
5	**26a**	$C(CH_3)_2OH$	95	21	**(–)-30**
6	**26b**	$C(CH_3)_2OH$	89	28	**(+)-30**
7	**27a**	$C(CH_3)_2OH$	90	11	**(–)-30**

[a] Yield of isolated product after purification by flash chromatography. [b] Enantiomeric excess determined by either chiral GC or HPLC.

on the basis of higher backbonding within the metal and sulfur centers in the case of arylsulfinamide ligands, and is indicative of increased bond strength. Consequently, arylsulfinamide PNSO ligands are less hemilabile than their *tert*-butyl counterparts. This fact could explain why thermodynamic equilibration between the two diastereomeric complexes requires stronger reaction conditions (i.e., CO pressure, sulfur additive).

Finally, we tested the diastereomerically and optically pure tetracarbonyl complexes obtained in the asymmetric thermal intermolecular Pauson−Khand reaction with norbornadiene at 70 °C (Table 5). Complexes **18a** and **19a** produced (−)-cyclopentenone **28** in 82% ee and 50% ee, respectively (Table 5, entries 1 and 2). When a phenyl group is attached to the dicobalt−alkyne core, better selectivities were obtained with 94% and 89% ee (Table 5, entries 3 and 4). Finally, the complexes derived from 2-methyl-3-butyn-2-ol, a much more difficult substrate, provided selectivities between 11 and 28% ee (Table 5, entries 5 and 6). From the stereochemical point of view it is important to mention, that complexes of the **Xa** series always provided levorotatory products, while **Xb** complexes provided the (+) enantiomer. As previously determined, alkene reaction at the Pro-*R* cobalt atom provides levorotary products, while alkene reaction at the Pro-*S* center provides dextrorotatory products.[8,22] The levorotatory cyclopentenone produced from **18a** entail that norbornadiene reacts mainly at the Pro-*R* metal center where the sulfinamide was attached (see the X-ray, Figure 2). All the experiments described in Table 5 are in agreement with the stereochemical outcome observed for **18a**. Thus, diastereomers **18a**, **19a**, **25a**, **26a**, and **27a** (S bonded to Pro-*R* Co) provided levorotatory products, while **24b** and **26b** (S bonded to Pro-*S* Co) provided dextrorotatory ones.

With this in mind, two mechanistic scenarios are possible: either the *N*-phosphino-*p*-tolylsulfinamides operate as hemilabile

(21) Diastereomeric complexes can be distinguished from one another by ^1H NMR by means of the terminal alkyne resonance (5.53−6.25 ppm). The **Xa** series of diastereomers display 2−8 Hz coupling constant to phosphorus, while the **Xb** series display a coupling constant between 9 and 12 Hz.

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ligands, or alternatively the ligand functions as a solid bridged ligand while the alkene reaction occurs through a labilized CO ligand in the same metal center. The increased S−Co strength observed in the crystal structure of **18a** supports the second mechanistic hypothesis and could explain the lower selectivities observed for *N*-phosphino-*p*-tolylsulfinamides ligands (**II**) in the Pauson−Khand reaction compared to their *tert*-butyl PNSO analogues (**I**).

Conclusions

We have synthesized a family of racemic and optically pure borane-protected *N*-phosphino-*p*-tolylsulfinamide ligands. Our results have shown that these ligands are stable in solution under the deprotection conditions (DABCO, 65 °C). The steric bulk on nitrogen is of major relevance and determines the final stability of the PNSO ligands. Thus, we have identified *N*-phosphino-*N*-isopropyl-*p*-tolylsulfinamide as the stable borane-free PNSO ligand. Coordination of this type of ligands with alkyne−dicobalt complexes provided, in general, low diastereoselectivities. The following experimental findings (a) hampered equilibration of diastereomeric complexes and (b) reduced the S−Co bond length with respect *tert*-butyl PNSO complexes, indicating that the presence of a tolyl group on sulfur reduces the hemilabile character of the PNSO ligands, which is detrimental for selectivity in the Pauson−Khand reaction. However, the alkene reaction still occurs predominantly at the metal center where the sulfinamide is bonded, as deduced from the absolute configuration of the resulting Pauson−Khand product.

Experimental Section

General Procedure for the Preparation of (*S*)-*N*-Alkyl-*p*-tolylsulfinamides. A 100 mL, two-necked, round-bottomed flask, equipped with a magnetic stirring bar and rubber septum, was charged with 3.22 mmol of *S*-(+)-*p*-tolylsulfinamide under a N_2 purge. Thirty milliliters of CH_2Cl_2 and 4.19 mmol of aldehyde were added. Immediately, 3.40 mL of $Ti(OEt)_4$ (16.1 mmol) was added via a syringe. The reaction mixture was heated to reflux during 1.5 h. The mixture was concentrated under vacuum and a yellow oil was obtained. This oil was then dissolved in 20 mL of EtOH and 3.86 mmol of $NaBH_4$ was added. The reaction mixture was kept at room temperature for 15 h. The resulting suspension was filtered through Celite and the solution was concentrated under vacuum. Flash chromatography on SiO_2 (80:20 hexane/EtOAc) afforded the desired (*S*)-*N*-alkyl-*p*-tolylsulfinamides.

(*S*)-(+)-*N*-Benzyl-*p*-tolylsulfinamide.[23] Following the general procedure, 500 mg of *S*-(+)-*p*-tolylsulfinamide (3.22 mmol), 0.42 mL of benzaldehyde (4.19 mmol), 3.36 mL of $Ti(OEt)_4$ (16.10 mmol), and 146 mg of $NaBH_4$ (3.86 mmol) were used. Chromatography on SiO_2 (80:20 hexane/EtOAc) afforded 650 mg (82%) of (*S*)-(+)-*N*-benzyl-*p*-tolylsulfinamide. Mp 84−86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.91 (dd, J = 15 and 8 Hz, 1H), 4.25 (m, 2H), 7.28−7.34 (m, 7H), 7.66 (m, 2H) ppm.

(*S*)-(+)-*N*-Isobutyl-*p*-tolylsulfinamide. Following the general procedure, 500 mg of *S*-(+)-*p*-tolylsulfinamide (3.22 mmol), 0.38 mL of isobutyraldehyde (4.19 mmol), 3.36 mL of $Ti(OEt)_4$ (16.10 mmol), and 146 mg of $NaBH_4$ (3.86 mmol) were used. Chromatography on SiO_2 (80:20 hexane/EtOAc) afforded 584 mg (87%) of (S)-(+)-*N*-isobutyl-*p*-tolylsulfinamide as a colorless oil. $[\alpha]_D$ +143.5 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 3214, 2956, 2870, 1087, 1057 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, J = 7 Hz, 3H), 0.90 (d, J = 7 Hz, 3H), 1.72 (m, 1H), 2.41 (s, 3H), 2.64 (m, 1H), 2.93 (m, 1H), 4.12 (br, 1H), 7.30 (d, J = 8 Hz, 2H), 7.58 (d, J = 8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2 ($2CH_3$), 21.4 (CH_3), 29.1 (CH), 48.7 (CH_2), 126.0 (CH), 129.5 (CH), 141.1 (C), 141.2 (C) ppm; MS (CI-NH_3) *m*/*z* 212 [(M + H)$^+$, 100%]. HRMS (ESI) calcd for $C_{11}H_{17}NOS$ + H 212.1103, found 212.1111.

(*S*)-(+)-*N*-Isopropyl-*p*-tolylsulfinamide. Following the general procedure, 1 g of *S*-(+)-*p*-tolylsulfinamide (6.443 mmol), 0.583 mL of dry acetone (8.376 mmol), 6.76 mL of $Ti(OEt)_4$ (32.241 mmol), and 293 mg of $NaBH_4$ (3.86 mmol) were used. Chromatography on silica gel (90:10 hexane/EtOAc) afforded 735 mg (58%) of (*S*)-(+)-*N*-isopropyl-*p*-tolylsulfinamide as a white solid. Mp 77−78 °C. $[\alpha]_D$ +96 (*c* 0.108, $CHCl_3$); IR (KBr) ν_{max} 3171, 1490, 1445, 1382, 1364, 1139, 1127, 1085, 1050, 1031, 1017, 989 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, J = 6 Hz, 3H), 1.29 (d, J = 6 Hz, 3H), 2.41 (s, 3H), 3.60 (oc, J = 6 Hz, 1H), 3.78 (d, J = 6 Hz, 1H), 7.29 (d, J = 8 Hz, 2H), 7.59 (d, J = 8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 (CH_3), 24.7 (CH_3), 25.1 (CH_3), 46.2 (CH), 125.9 (CH), 129.7 (CH), 141.3 (C), 142.5 (C) ppm; MS (ESI, H_2O:CH_3CN (1:1) 1% formic) *m*/*z* 417 [(2 M + Na)$^+$, 2%], 395 [(2 M + H)$^+$, 2%], 336 [6%], 220 [(M + Na)$^+$, 4%], 198 [(M + H)$^+$, 56%], 181 [(M − O)$^+$, 12%], 139 [(M − C_3H_8N)$^+$, 100%]; HRMS (ESI) calcd for $C_{10}H_{15}NOS$ + H 198.0947, found 198.0946.

General Procedure for the Synthesis of (*S*)-*N*-Phosphino-*p*-tolylsulfinamide Borane Complexes. An oven-dried, 100 mL, one-necked, round-bottomed flask, equipped with a magnetic stirring bar, was charged with the corresponding sulfinamide (1.89 mmol) under a N_2 purge. Anhydrous THF (20 mL) was added and the solution was cooled to −78 °C. *n*-BuLi 2.5 M (0.83 mL, 2.08 mmol) was added dropwise via a syringe, which resulted in the solution turning red. After the solution was stirred for 15 min at −78 °C, $ClPPh_2$ (2.08 mmol) was added via a syringe and the reaction mixture turned yellow. The solution was stirred for 1 h, during which time the temperature was warmed to −30 °C. At this point, 0.27 mL of BH_3−SMe_2 (2.83 mmol) was added. The solution was then allowed to warm to 0 °C. Et_2O (20 mL) and H_2O (10 mL) were carefully added in this order. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum. The crude product was purified on silica gel (90:10 hexane/EtOAc), affording the desired borane-protected (*S*)-*N*-phosphino-*p*-tolylsulfinamides.

(*S*)-(−)-*N*-Benzyl-*N*-diphenylphosphino-*p*-tolylsulfinamide Borane Complex, (−)-1-BH_3. Following the general procedure, 500 mg of (*S*)-(+)-*N*-Benzyl-*p*-tolylsulfinamide (2.04 mmol), 0.90 mL of BuLi 2.5 M (2.24 mmol), 0.40 mL of $ClPPh_2$ (2.24 mmol), and 0.29 mL of BH_3−SMe_2 (3.06 mmol) were used. Chromatography on silica gel (90:10 hexane/EtOAc) afforded 768 mg (85%) of (−)-**1**-BH_3 as a white foam. $[\alpha]_D$ −59.0 (*c* 0.50, $CHCl_3$); IR (film) ν_{max} 3058, 2961, 2871, 2389, 2347, 1437 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90−1.89 (br, 3H, BH_3), 2.28 (s, 3H), 4.36 (dd, J = 16 and 16 Hz, 1H), 4.64 (dd, J = 16 and 8 Hz, 1H), 6.91−6.98 (m, 5H), 7.06 (m, 2H), 7.25 (m, 2H), 7.40−7.51 (m, 6H), 7.79 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (CH_3), 46.8 (d, J_P = 4 Hz, CH_2), 125.9 (CH), 126.7 (CH), 127.6 (CH), 128.6 (d, J_P = 59 Hz, C), 128.8 (d, J_P = 11 Hz, CH), 128.9 (CH), 129.0 (d, J_P = 11 Hz, CH), 129.6 (CH), 129.9 (d, J_P = 60 Hz, C), 131.9 (d, J_P = 2 Hz, CH), 132.3 (d, J_P = 2 Hz, CH), 133.0 (d, J_P = 11 Hz, CH), 133.3 (d, J_P = 11 Hz, CH), 136.6 (C), 139.6 (d, J_P = 5 Hz, C), 142.1 (C) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) 76.5 ppm; MS (QI, NH_3) *m*/*z* 430 [(M − BH_3)$^+$, 74%], 442 [(M − H)$^+$, 61%], 444 [(M + H)$^+$, 25%], 461 [(M + NH_4)$^+$, 11%]; HRMS (ESI) calcd for $C_{26}H_{27}BNOPS$-H 442.1566, found 442.1558.

(*S*)-(−)-*N*-Isobutyl-*N*-diphenylphosphino-*p*-tolylsulfinamide Borane Complex, (−)-7-BH_3. Following the general procedure, 400 mg of (*S*)-(+)-*N*-Isobutyl-*p*-tolylsulfinamide (1.89 mmol), 0.83 mL of BuLi (2.5 M, 2.08 mmol), 0.37 mL of $ClPPh_2$ (2.08 mmol), and 0.27 mL of BH_3−SMe_2 (2.83 mmol) were used. Chromatography on silica gel (90:10 hexane/EtOAc) afforded 569 mg (74%) of (−)-**7**-BH_3 as a white foam. $[\alpha]_D$ −161.7 (*c* 0.94, $CHCl_3$); IR (film) ν_{max} 3057, 2960, 2926, 2870, 2389, 2347, 1437 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.60 (d, J =

7 Hz, 3H), 0.90−1.87 (br, 3H, BH_3), 1.66 (m, 1H), 2.39 (s, 3H), 2.78 (ddd, J = 15, 15, and 8 Hz, 1H), 3.40 (ddd, J = 15, 9, and 6 Hz, 1H), 7.20 (m, 4H), 7.54 (m, 6H), 7.81 (m, 2H), 7.98 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2 (CH_3), 20.4 (CH_3), 21.5 (CH_3), 28.4 (CH), 52.7 (d, J_P = 6 Hz, CH_2), 125.8 (CH), 128.9 (d, J_P = 3 Hz, CH), 129.0 (d, J_P = 4 Hz, CH), 129.5 (d, J_P = 60 Hz, C), 129.9 (CH), 131.0 (d, J_P = 63 Hz, C), 132.0 (d, J_P = 2 Hz, CH), 132.3 (d, J_P = 2 Hz, CH), 132.9 (d, J_P = 10 Hz, CH), 133.4 (d, J_P = 11 Hz, CH), 139.8 (d, J_P = 5 Hz, C), 142.2 (C) ppm; ^{31}P NMR (121 MHz, $CDCl_3$) 74.6 ppm; MS (ESI, H_2O:CH_3CN (1:1) 1% formic) *m*/*z* 256 [($C_{11}H_{19}BNOPS$ + H)$^+$, 16%], 408 [(M − H)$^+$, 100%], 409 [(M)$^+$, 22%], 410 [(M + H)$^+$, 10%]; HRMS (ESI) calcd for $C_{23}H_{29}BNOPS$-H 408.1716, found 408.1721.

(*S*)-(−)-*N*-Isopropyl-*N*-diphenylphosphino-*p*-tolylsulfinamide, (−)-8. Following the general procedure, 630 mg of (*S*)-(+)-*N*-isopropyl-*p*-tolylsulfinamide (3.19 mmol), 3.51 mL of LiHMDS (1.0 M, 3.51 mmol), and 0.70 mL of $ClPPh_2$ (2.24 mmol) were used. No borane was required to stabilize the ligand in this case. Chromatography on silica gel (80:20 hexane/EtOAc) afforded 785 mg (65%) of (−)-**8** as a white foam. $[\alpha]_D$ −171.8 (*c* 0.1, $CHCl_3$); IR (film) ν_{max} 3053, 2996, 1481, 1433, 1381, 1132, 1087, 1067, 991 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (d, J = 7 Hz, 3H), 1.36 (d, J = 7 Hz, 3H), 2.32 (s, 3H), 3.84 (non, J = 7 Hz, 1H), 6.88 (d, J = 8 Hz, 2H), 7.08 (d, J = 8 Hz, 2H), 7.42 (m, 6H), 7.62 (td, J = 2 and 8 Hz, 2H), 7.70 (td, J = 1 and 8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (CH_3), 23.4 (d, J_P = 10 Hz, CH_3), 24.8 (d, J_P = 10 Hz, CH_3), 46.8 (d, J_P = 20 Hz, CH), 125.6 (CH), 128.5 (CH), 128.6 (d, J_P = 5 Hz, CH), 128.8 (d, J_P = 8 Hz, CH), 129.7(CH), 130.3 (CH), 131.3 (d, J_P = 19 Hz, CH), 134.7 (d, J_P = 24 Hz, CH), 137.7 (d, J_P = 11 Hz, C), 138.8 (d, J_P = 13 Hz, C), 140.9 (C), 141.7 (C). ppm; ^{31}P NMR (121 MHz, $CDCl_3$) 39.1 ppm; MS (ESI, H_2O:CH_3CN (1:1) 1% formic) *m*/*z* 260 [33%], 382 [(M + H)$^+$, 12%], 519 [(2[*i*PrNP(O)Ph_2] + H)$^+$, 100%], 541 [8%], 584 [7%], 800 [(3[*i*PrNP(O)Ph_2] + Na)$^+$, 11%]; HRMS (ESI) calcd for $C_{22}H_{24}NOPS$ + H 382.1389, found 382.1376.

Dicobalt−Tetracarbonyl Complexes of Optically Pure PNSO Ligands: General Procedure. A Schlenk tube equipped with a magnetic stirring bar was charged with 0.73 mmol of corresponding borane-protected PNSO ligand, 1.09 mmol of DABCO, and 0.80 mmol of trimethylsilylacetylene dicobalt complex. The reaction mixture was purged with N_2 and 10 mL of toluene was added. The mixture was kept at 65 °C for 2 h. The crude product was concentrated under vacuum and purified on silica gel (95:5 hexane/EtOAc), thereby obtaining PNSO dicobalt−tetracarbonyl complexes as red solids.

Co_2(μ-TMSC$_2$H)(CO)$_4$(μ-$C_{26}H_{24}NOPS$), 13a/13b. Following the general procedure, 196 mg of (−)-**1**-BH_3 (0.44 mmol), 74 mg of DABCO (0.66 mmol), and 185 mg of trimethylsilylacetylene dicobalt complex (0.37 mmol) were used. Chromatography on silica gel (95:5 hexane/EtOAc) afforded 283 mg (85%) of **13a/13b** (1:1) as a red solid. IR (film) ν_{max} 2961, 2035, 2002, 1978 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 0.35/0.39 (2s, 9H), 1.75/1.77 (2s, 3H), 4.11 (m, 1H), 4.75 (m, 1H), 5.92 (m, 1H), 6.03−6.13 (m, 2H), 6.48−6.55 (m, 4H), 7.01−7.14 (m, 7H), 7.63 (m, 2H), 7.63−7.84 (m, 3H), 7.94 (m, 1H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 0.8/0.9 (d, J_P = 2 Hz, $3CH_3$), 20.8/20.9 (CH_3), 48.5/49.6 (d, J_P = 5 Hz, CH_2), 85.4/86.5 (d, J_P = 12 Hz, CH), 93.7/95.1 (C), 125.9 (CH), 127.7 (m, CH), 127.9 (m, CH), 128.6 (br, CH), 128.6−129.1 (m, CH), 129.5/129.6 (CH) 130.3/131.3 (d, J_P = 15 Hz, CH), 130.9/131.0 (CH), 133.6/134.0 (d, J_P = 15 Hz, CH), 135.9/136.8 (m, C), 138.0 (d, J_P = 35 Hz, C), 141.2/141.4 (C), 147.3/147.5 (d, J_P = 10 Hz, C) ppm; ^{31}P NMR (121 MHz, C_6D_6) 115.9/118.5 ppm; MS (ESI, H_2O:CH_3CN (1:1) 1% formic) *m*/*z* 646 [(M − 4CO)$^+$, 100%], 674 [(M − 3CO)$^+$, 71%], 702 [(M − 2CO)$^+$, 44%], 730 [(M − CO)$^+$, 44%], 758 [(M + H)$^+$, 26%]; HRMS (ESI) calcd for $C_{35}H_{34}Co_2NO_5PSSi$ + H 758.0401, found 758.0365.

Co_2(μ-TMSC$_2$H)(CO)$_4$(μ-$C_{23}H_{26}NOPS$), 18a. Following the general procedure, 300 mg of (−)-**7**-BH_3 (0.73 mmol), 123 mg of DABCO (1.09 mmol), and 310 mg of trimethylsilylacetylene dicobalt complex (0.80 mmol) were used. Chromatography on silica gel (95:5 hexane/EtOAc) afforded 464 mg (88%) of **18a/18b** (2:1) as a red solid. Then 120 mg (23%) of major diastereomer **18a** was isolated by simple crystallization in a hexane/toluene solvent mixture. IR (film) ν_{max} 2960, 2034, 2002, 1978 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 0.03 (d, J = 6 Hz, 3H), 0.07 (d, J = 6 Hz, 3H), 0.37 (s, 9H), 0.98 (m, 1H), 1.90 (s, 3H), 2.54 (m, 1H), 3.39 (ddd, J = 15, 5, and 2 Hz, 1H), 5.98 (d, J = 8 Hz, 1H), 6.86 (d, J = 8 Hz, 2H), 7.01−7.14 (m, 6H), 7.81 (m, 4H), 7.90 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 0.9 ($3CH_3$), 19.1 (CH_3), 20.1 (CH_3), 21.1 (CH_3), 26.5 (CH), 54.7 (d, J_P = 5 Hz, CH_2), 86.1 (CH), 94.1 (C), 125.6 (CH), 128.7 (d, J_P = 10 Hz, CH), 129.1 (d, J_P = 10 Hz, CH), 129.5 (CH), 129.9 (CH), 130.7 (d, J_P = 13 Hz, CH), 131.3 (CH), 133.9 (d, J_P = 14 Hz, CH), 135.9 (d, J_P = 39 Hz, C), 138.5 (d, J_P = 35 Hz, C), 141.7 (C), 149.4 (d, J_P = 12 Hz, C) ppm; ^{31}P NMR (121 MHz, C_6D_6) 116.1 ppm; MS (ESI, H_2O:CH_3CN (1:1) 1% formic) *m*/*z* 612 [(M + H − 4CO)$^+$, 38%], 640 [(M + H − 3CO)$^+$, 25%], 668 [(M + H − 2CO)$^+$, 12%], 696 [(M + H − CO)$^+$, 42%], 724 [(M + H)$^+$, 62%]; HRMS (ESI) calcd for $C_{32}H_{36}Co_2NO_5PSSi$ + H 724.0558, found 724.0577.

Co_2(μ-TMSC$_2$H)(CO)$_4$(μ-$C_{22}H_{24}NOPS$), 19a. Following the general procedure, 200 mg (0.524 mmol) of (−)-**8** and 211 mg (0.577 mmol) of trimethylsilylacetylene dicobalt complex were used. No DABCO was used in this case. The reaction mixture was kept at 65 °C for 7 h. Flash chromatography on silica gel (95:5 hexane/EtOAc) afforded 346 mg (92%) of a **19a/19b** mixture (3:1) as a red solid. Crystallization in a mixture of hexane and toluene provided 227 mg (60%) of the major diastereomer **19a**. IR (KBr) ν_{max} 2031, 1996, 1969, 1978 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 0.17 (d, J = 7 Hz, 3H), 0.36 (s, 3H), 0.99 (d, J = 7 Hz, 3H), 1.91 (s, 3H), 3.69 (hep, J = 6 Hz, 1H), 6.04 (d, J = 8 Hz, 1H), 6.85 (d, J = 8 Hz, 2H), 7.10 (m, overloap with solvent peak, 6H), 7.91 (t, J = 8 Hz, 4H), 7.98 (d, J = 9.2 Hz, 4H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 0.9 (d, J = 2 Hz, $3CH_3$), 21.1 (CH_3), 23.5 (CH_3), 23.6 (CH_3), 58.3 (d, J_P = 5 Hz, CH), 85.5 (d, J_P = 11 Hz, CH), 93.4 (C), 126.3 (CH), 128.7 (d, J_P = 10 Hz, CH), 129.1 (d, J_P = 10 H, CH), 129.3 (CH), 129.8 (CH), 130.4 (d, J_P = 13 H, CH), 131.1 (CH), 133.6 (d, J_P = 14 Hz, CH), 136.4 (d, J_P = 38 Hz, C), 139.1 (d, J_P = 36 Hz, C), 141.6 (C), 149.7 (d, J_P = 12 Hz, C) ppm; ^{31}P NMR (121 MHz, C_6D_6) 114.5 ppm; MS (ESI, H_2O:CH_3CN (1:1) 1% formic) *m*/*z* 121 [100%], 282 [42%], 598 [(M + H − 4CO)$^+$, 79%], 626 [(M + H − 3CO)$^+$, 46%], 654 [(M + H − 2CO)$^+$, 20%], 682 [(M + H − CO)$^+$, 58%], 710 [(M + H)$^+$, 48%], 1436 [(2 M + NH_4)$^+$, 4%]; HRMS (ESI) calcd for $C_{31}H_{34}Co_2NO_5PSSi$+H 710.0401, found 710.0393.

Co_2(μ-PhC$_2$H)(CO)$_4$(μ-$C_{23}H_{26}NOPS$), 24b. Following the general procedure, 200 mg of (−)-**7**-BH_3 (0.49 mmol), 82 mg of DABCO (0.73 mmol), and 227 mg of phenylacetylene dicobalt complex (0.59 mmol) were used. Chromatography on silica gel (95:5 hexane/EtOAc) afforded 330 mg (93%) of **24a/24b** (1:1) as a red solid. This mixture was crystallized twice in hexane/toluene solvent mixtures to afford 60 mg of diastereomer **24b**. IR (film) ν_{max} 2038, 2007, 1982 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 0.01 (d, J = 7 Hz, 3H), 0.12 (d, J = 7 Hz, 3H), 1.13 (m, 1H), 1.87 (s, 3H), 2.64 (m, 1H), 3.44 (ddd, J = 15, 6, and 3 Hz, 1H), 5.99 (d, J = 10 Hz, 1H), 6.83 (d, J = 8 Hz, 2H), 6.96−7.16 (m, overloap with solvent peak, 9H), 7.70 (d, J = 8 Hz, 2H), 7.78 (m, 2H), 7.87−7.95 (m, 4H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 19.2 (CH_3), 20.1 (CH_3), 21.0 (CH_3), 26.9 (CH), 54.6 (d, J_P = 5 Hz, CH_2), 73.0 (d, J_P = 12 Hz, CH), 103.8 (d, J_P = 19 Hz, C), 125.7 (CH), 127.5 (CH), 128.7 (CH), 128.8 (CH), 128.9 (CH), 129.6 (CH), 130.1 (CH), 130.3 (d, J_P = 4 Hz, CH), 131.2 (CH), 131.6 (d, J_P = 12 Hz, CH), 133.4 (d, J_P = 15 Hz, CH), 136.5 (d, J_P = 37 Hz, C), 137.1 (d, J_P = 36 Hz, C), 141.0 (C), 142.0 (C), 148.8 (d, J_P = 10 Hz, C) ppm; ^{31}P NMR (121 MHz, C_6D_6) 114.1 ppm; MS (ESI, H_2O:CH_3CN (1:1) 1% formic) *m*/*z* 616 [(M − 4CO)$^+$, 66%], 644 [(M − 3CO)$^+$, 31%], 672 [(M − 2CO)$^+$, 24%], 700 [(M − CO)$^+$, 12%], 1477 [(2 M + Na)$^+$, 100%]; HRMS (ESI) calcd for $C_{35}H_{32}Co_2NO_5PS$ + Na 750.0295, found 750.0290.

$Co_2(\mu\text{-}PhC_2H)(CO)_4(\mu\text{-}C_{22}H_{24}NOPS)$, 25a. Following the general procedure, 200 mg (0.52 mmol) of (−)-**8** and 223 mg (0.58 mmol) of phenylacetylene dicobalt complex were used. The reaction mixture was kept at 65 °C for 2.5 h. Flash chromatography on silica gel (EtOAc) afforded 310 mg (83%) of a 1:1 mixture of diastereomers **25a** and **25b**. Crystallization in toluene/hexane mixtures provided pure **25a** (62 mg) as a red/brown solid. IR (KBr) ν_{max} 2035, 2005, 1984, 1971 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.24 (d, $J = 7$ Hz, 3H), 0.98 (d, $J = 7$ Hz, 3H), 1.92 (s, 3H), 3.75 (m, 1H), 5.90 (d, $J = 7$ Hz, 1H), 6.87 (d, $J = 8$ Hz, 2H), 7.06 (m, 6H), 7.16 (overlaps with solvent peak, 3H), 7.79 (d, $J = 8$ Hz, 2H), 7.89 (m, 5H), 7.99 (d, $J = 8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 21.1 (CH_3), 23.5 (CH_3), 23.6 (CH_3), 57.9 (d, $J_P = 5$ Hz, CH), 73.1 (CH), 102.0 (C), 126.3 (CH), 127.2 (CH), 128.3 (CH), 128.7 (d, $J_P = 10$ Hz, CH), 128.9 (CH), 129.1 (d, $J_P = 9$ Hz, CH), 129.3 (CH), 129.9 (CH), 130.1 (d, $J_P = 4$ Hz, CH), 130.7 (d, $J_P = 13$ Hz, CH), 131.1 (CH), 133.4 (d, $J_P = 14$ Hz, C), 136.4 (d, $J_P = 37$ Hz, C), 138.8 (d, $J_P = 37$ Hz, C), 141.7 (C), 149.5 (d, $J_P = 13$ Hz, C) ppm; ^{31}P RMN (121 MHz, C_6D_6) 114.0 ppm; MS (ESI, H_2O:CH_3CN (1:1) 1% formic) *m/z* 304 [100%], 602 [$(M + H - 4CO)^+$, 90%], 630 [$(M + H - 3CO)^+$, 7%], 658 [$(M + H - 2CO)^+$, 34%], 736 [$(M + Na)^+$, 31%], 1398 [$(2\,M - 2CO)^+$, 27%], 1449 [$(2\,M + Na)^+$, 37%]; HRMS (ESI) calcd for $C_{34}H_{30}Co_2NO_5PSNa$ 736.0138, found 736.0137.

$Co_2(\mu\text{-}HO(CH_3)_2CC_2H)(CO)_4(\mu\text{-}C_{23}H_{26}NOPS)$, 26a and 26b. Following the general procedure, 200 mg of (−)-**7**-BH_3 (0.49 mmol), 82 mg of DABCO (0.73 mmol), and 216 mg of 2-methyl-3-butyn-2-ol dicobalt complex (0.59 mmol) were used. This afforded 298 mg (86%) of **26a/26b** (1:1). Chromatography on silica gel (95:5 hexane/EtOAc) afforded 103 mg of pure **26a** and 80 mg of pure **26b** as red solids. **26a**: IR (film) ν_{max} 2973, 2037, 2005, 1979 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.07 (s, 3H), 0.09 (s, 3H), 1.32 (m, 1H), 1.75 (s, 3H), 1.79 (s, 3H), 1.91 (s, 3H), 2.61 (m, 1H), 3.13 (m, 1H), 3.54 (br, 1H), 5.80 (d, $J = 2$ Hz, 1H), 6.88 (d, $J = 8$ Hz, 2H), 7.05−7.16 (m, overlap with solvent peak, 6H), 7.71 (m, 2H), 7.96 (d, $J = 8$ Hz, 2H), 8.03 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 19.8 ($2CH_3$), 21.0 (CH_3), 27.1 (CH), 33.2 (CH_3), 34.7 (CH_3), 56.0 (CH_2), 73.4 (CH), 78.6 (C), 110.0 (C), 126.1 (CH), 128.7 (d, $J_P = 9$ Hz, CH), 128.9 (d, $J_P = 10$ Hz, CH), 129.7 (CH), 130.6 (CH), 130.7 (CH), 132.3 (d, $J_P = 13$ Hz, CH), 132.6 (d, $J_P = 14$ Hz, CH), 137.3 (d, $J_P = 36$ Hz, C), 137.4 (d, $J_P = 40$ Hz, C), 142.2 (C), 147.1 (d, $J_P = 11$ Hz, C) ppm; ^{31}P NMR (121 MHz, C_6D_6) 114.8 ppm; MS (ESI, H_2O:CH_3CN (1:1) 1% formic) *m/z* 580 [$(M - OH - 4CO)^+$, 5%], 608 [$(M - OH - 3CO)^+$, 6%], 636 [$(M - OH - 2CO)^+$, 8%], 664 [$(M - OH - CO)^+$, 11%], 692 [$(M - OH)^+$, 100%]; HRMS (ESI) calcd for $C_{32}H_{34}Co_2NO_6PS$-OH 692.0475, found 692.0484. **26b**: ^1H NMR (400 MHz, C_6D_6) δ −0.02 (d, $J = 6$ Hz, 3H), 0.11 (d, $J = 6$ Hz, 3H), 1.11 (m, 1H), 1.50 (s, 3H), 1.51 (s, 3H), 1.87 (s, 3H), 2.60 (m, 1H), 3.42 (m, 1H), 5.53 (d, $J = 10$ Hz, 1H), 6.84 (d, $J = 8$ Hz, 2H), 7.03−7.16 (m, overlap with solvent peak, 6H), 7.74 (m, 2H), 7.86−7.93 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 19.1 (CH_3), 20.1 (CH_3), 21.1 (CH_3), 26.8 (CH), 32.7 (d, $J_P = 3$ Hz, CH_3), 32.8 (d, $J_P = 2$ Hz, CH_3), 54.7 (d, $J_P = 6$ Hz, CH_2), 71.6 (d, $J_P = 11$ Hz, C), 72.9 (CH), 121.0 (d, $J_P = 17$ Hz, C), 125.7 (CH), 128.7 (d, $J_P = 9$ Hz, CH), 128.9 (d, $J_P = 10$ Hz, CH), 129.6 (CH), 130.2 (CH), 131.2 (CH), 131.6 (d, $J_P = 12$ Hz, CH), 133.3 (d, $J_P = 15$ Hz, CH), 136.4 (d, $J_P = 37$ Hz, C), 136.9 (d, $J_P = 36$ Hz, C), 142.1 (C), 148.7 (d, $J_P = 11$ Hz, C) ppm; ^{31}P NMR (121 MHz, C_6D_6) 113.4 ppm.

$Co_2(\mu\text{-}HO(CH_3)_2CC_2H)(CO)_4(\mu\text{-}C_{22}H_{24}NOPS)$, 27a. Following the general procedure, 200 mg (0.524 mmol) of (−)-**8** and 213 mg (0.577 mmol) of 2-methyl-3-butyn-2-ol dicobalt complex were used. The reaction mixture was kept at 65 °C for 5.5 h. This afforded 297 mg (81%) of **27a/27b** mixture (1.3:1). Flash chromatography on silica gel (95:5 hexane/EtOAc) afforded 137 mg of diasteromer **27a** as a red/brown solid. IR (KBr) ν_{max} 2035, 2002, 1974, 1959 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.19 (d, $J = 7$ Hz, 3H), 0.98 (d, $J = 7$ Hz, 3H), 1.69 (s, 6H), 1.91 (s, 3H), 3.10 (br, 1H), 3.70 (m, 1H), 5.72 (d, $J = 2$ Hz, 1H), 6.85 (d, $J = 8$ Hz, 2H), 7.07 (m, 3H), 7.15 (overlaps with solvent peak, 3H), 7.86 (t, $J = 10$ Hz, 4H), 7.96 (d, $J = 8$ Hz, 2H), 8.05 (t, $J = 10$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ 21.1 (CH_3), 23.6 ($2CH_3$), 33.0 (CH_3), 34.3 (CH_3), 58.5 (d, $J_P = 5$ Hz, CH), 73.4 (CH), 76.3 (C), 126.2 (CH), 128.7 (d, $J_P = 10$ Hz, CH), 128.9 (d, $J_P = 10$ Hz, CH), 130.3(CH), 130.9 (CH), 131.8 (d, $J_P = 13$ Hz, CH), 132.7 (d, $J_P = 14$ Hz, CH), 137.1 (d, $J_P = 38$ Hz, C), 138.0 (d, $J_P = 35$ Hz, C), 141.9 (C), 148.7 (d, $J_P = 12$ Hz, C) ppm; ^{31}P NMR (121 MHz, C_6D_6) 114.5 ppm; MS (ESI, H_2O:CH_3CN (1:1) 1% formic) *m/z* 678 [$(M - OH)^+$, 100%], 718 [$(M + Na)^+$, 67%], 1413 [$(2\,M + Na)^+$, 23%]; HRMS (ESI) calcd for $C_{31}H_{32}Co_2NO_6PSNa$ 718.0244, found 718.0248.

4-(Trimethylsilyl)tricyclo[5.2.1.$0^{2,6}$]decadien-4,8-dien-3-one, 28.[7] **From 18a:** Optically pure tetracarbonyl complex **18a** (55 mg, 0.07 mmol), 76 μL of norbornadiene (0.75 mmol), and 2 mL of toluene were charged in a Schlenk flask under nitrogen and the reaction was stirred at 70 °C. The reaction was completed after 22 h. Purification by flash chromatography on SiO_2 (95:5 hexane/EtOAc) yielded 12 mg (75%) of (−)-**28** as a white solid (82% ee).

From 19a: Optically pure tetracarbonyl complex **19a** (50 mg, 0.07 mmol), 70 μL of norbornadiene (0.70 mmol), and 2 mL of toluene were charged in a Schlenk flask under nitrogen and the reaction was stirred at 70 °C. The reaction was stopped after 28 h. Purification by flash chromatography on SiO_2 (95:5 hexane/EtOAc) yielded 9 mg (60%) of (−)-**28** as a white solid (50% ee).

GC analysis: Beta-DEX, 160 °C, t_R (−) isomer = 16.8 min. t_R (+) isomer = 17.6 min.

4-Phenyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one, 29.[22] **From 24b:** Optically pure tetracarbonyl complex **24b** (55 mg, 0.07 mmol), 76 μL of norbornadiene (0.75 mmol), and 2 mL of toluene were charged in a Schlenk flask under nitrogen and the reaction was stirred at 70 °C. The reaction was completed after 2 h. Purification by flash chromatography on SiO_2 (97:3 hexane/EtOAc) yielded 16 mg (97%) of (+)-**29** as a white solid (94% ee).

From 25a: Optically pure tetracarbonyl complex **25a** (40 mg, 0.06 mmol), 57 μL of norbornadiene (0.56 mmol), and 2 mL of toluene were charged in a Schlenk flask under nitrogen and the reaction was stirred at 70 °C. The reaction was completed after 2 h. Purification by flash chromatography on SiO_2 (97:3 hexane/EtOAc) yielded 11 mg (88%) of (−)-**29** as a white solid (89% ee).

HPLC analysis: CHIRALCEL OD (25 cm), 2% IPA−98% heptane, 0.5 mL/min, $\lambda = 254$ nm. t_R (+) isomer = 16.4 min. t_R (−) isomer = 20.7 min.

4-(1-Hydroxy-1-methylethyl)tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one, 30. From 26a: Optically pure tetracarbonyl complex **26a** (41 mg, 0.06 mmol), 57 μL of norbornadiene (0.57 mmol), and 2 mL of toluene were charged in a Schlenk flask under nitrogen and the reaction was stirred at 70 °C. The reaction was completed after 18 h. Purification by flash chromatography on SiO_2 (90:10 hexane/EtOAc) yielded 11 mg (95%) of (−)-**30** as a white solid (21% ee).

From 26b: Optically pure tetracarbonyl complex **26b** (49 mg, 0.07 mmol), 70 μL of norbornadiene (0.69 mmol), and 2 mL of toluene were charged in a Schlenk flask under nitrogen and the reaction was stirred at 70 °C. The reaction was completed after 18 h. Purification by flash chromatography on SiO_2 (90:10 hexane/EtOAc) yielded 12 mg (89%) of (+)-**30** as a white solid (28% ee).

From 27a: Optically pure tetracarbonyl complex **27a** (50 mg, 0.07 mmol), 72 μL of norbornadiene (0.71 mmol), and 2 mL of toluene were charged in a Schlenk flask under nitrogen and the reaction was stirred at 70 °C. The reaction was completed after 21 h. Purification by flash chromatography on SiO_2 (90:10 hexane/EtOAc) yielded 13 mg (90%) of (−)-**30** as a white solid (11% ee).

HPLC analysis: CHIRALCEL OD (25 cm), 5% IPA−95% heptane, 1.0 mL/min, $\lambda = 254$ nm. t_R (−) isomer = 6.3 min. t_R (+) isomer = 7.0 min.

(23) García-Ruano, J. L.; Alonso, R.; Zarzuelo, M. M.; Noheda, P. *Tetrahedron: Asymmetry* **1995**, *6*, 1133–1142.

Acknowledgment. This work was supported by a MEC grant (CTQ2005-623). M.R. thanks MEC for a fellowship.

Supporting Information Available: General methods, procedures, and spectroscopic data for racemic ligands and complexes, copy of NMR spectra for new compounds, and X-ray refinement parameters and crystal data with a complete numbering scheme, atomic distances, and angles for **18a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO800710N