Design of New Hemilabile (P,S) Ligands for the Highly Diastereoselective Coordination to Alkyne Dicobalt Complexes: Application to the Asymmetric Intermolecular Pauson−Khand Reaction

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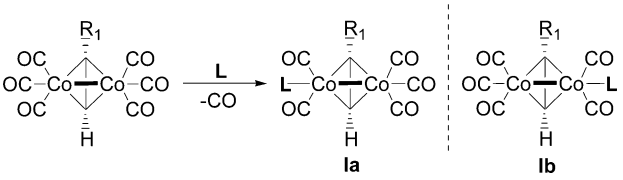
Here we synthesized a new generation of hemilabile P,S ligands designed for diastereoselective coordination to terminal alkyne-hexacarbonyldicobalt complexes. The camphor-derived CamPHOS (**2**) and MeCamPHOS (**12**) ligands were obtained in 68% and 59% yield in their borane-protected form starting from readily available 1,3-oxathiane **4**. Thermally induced coordination to dicobalt-hexacarbonyl-alkyne (HCCR, R = Ph, Bu^t, $SiMe_3$, $C(CH_3)_2$-OH) complexes was studied. MeCamPHOS (**12**) provided an unprecedented diastereoselectivity on coordination to terminal complexes (up to 90% de). The solid state structure of a coordinated CamPHOS ligand with $[Co_2(\mu\text{-}Bu^tSO_2C)_2(CO)_6]$ was determined and confirms the preference to coordinate the bimetallic cluster in a bridged manner. The resulting adducts were submitted to the intermolecular Pauson−Khand cyclization. Remarkably, CamPHOS and MeCamPHOS provided Pauson−Khand products of opposite absolute configurations. This behavior could be explained on the basis that **2** and **11** ligands lead to pseudo-enantiomeric tetracarbonyl complexes, as confirmed by circular dichroism analysis. Introduction of a CH_3− group on the carbon bridge between P and S increased CamPHOS selectivity dramatically from 33% to 90% de of the opposed sign with an overall destabilizing effect of 2.15 kcal/mol for **7b**.

Introduction

Diastereoselective ligand exchange reaction on hexacarbonyl complexes of terminal alkynes is an elusive goal. Cobalt atoms from dicobalt hexacarbonyl complexes of terminal alkynes are enantiotopic. Therefore, substitution of one cobalt atom for another metal or simply substitution of one CO for another ligand in one of the metal centers leads to chiral bimetallic complexes (Scheme 1). To date only phosphines and phosphites have been used for this purpose. Optically pure phosphine dicobalt hexacarbonyl complexes have been selectively synthesized in a number of ways: (a) using acetylenes with an adjacent chiral center,[1] (b) using monophosphines that contain chiral appendages,[2] (c) enantioselective coordination of an achiral phosphine induced with an external chiral promoter,[3] or (d) coordination of an appropriate chiral bidentate phosphine.[4] However, none of these methodologies has found wide application because of several drawbacks; for example, (a) coordination selectivities are low, usually close to 1:1, and separation of diastereomeric complexes is often difficult, (b) thermally induced phosphine isomerization can take place even at low temperatures, and (c) phosphine- or phosphite-substituted dicobalt complexes show lower reactivity than their parent complexes.[4a,5]

Scheme 1



Optically pure dicobalt hexacarbonyl complexes have synthetic applications, mainly in the development of

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enantioselective versions of the Pauson−Khand[6] and Nicholas reactions.[7] Accordingly, when a preparative use of these compounds is in mind, the reactivity toward these reactions is crucial. The use of chiral auxiliaries in the Pauson−Khand reaction has been extensively studied by our group.[8] We have previously introduced highly stereoselective inductors (Figure 1, **II**) capable of accelerating cyclopentenone formation by coordinating a hemilabile sulfide ligand.[9,10] To find easy-to-handle systems that can be used as promoters, we recently developed a new chiral bidentate (P,S) ligand derived from natural pulegone.[11] This approach allowed us to obviate the cumbersome steps needed for the introduction and elimination of a chiral auxiliary and demonstrate that a hemilabile P,S ligand accelerates the Pauson−Khand reaction. Nevertheless, despite achieving a significant level of selectivity (up to 60% de), the coordination diastereoselectivity to dicobalt complexes still has a major practical limitation.

Here we report the synthesis of a new generation of P,S ligands, their coordination behavior toward terminal alkyne dicobalt carbonyl complexes, and the structural features that lead to a highly diastereoselective coordination. Finally, the application of these ligands to the intermolecular asymmetric Pauson−Khand reaction is also discussed.

Results and Discussion

Design, Synthesis, and Coordination Behavior of CamPHOS. An important feature for the design of a new hemilabile bidentate ligand is to ensure coordination in a bridged (**III**) rather than chelated (**IV**) disposition in the dicobalt-alkyne cluster (Figure 1). We envisaged that the coordination of the sulfur and phosphorus to different cobalt atoms is crucial for the desired directing and accelerating effect in the Pauson−Khand cyclization.[10] To achieve this coordination pattern, the length between the two coordinative atoms is a key point. One carbon link between phosphorus and sulfur guarantees bridged type coordination (**III**).[12] In PuPHOS ligand (**1**), the sulfur atom is contained in an 1,3-oxathiane ring and the diaryl phosphine unit is linked to the thioacetal carbon in an equatorial position.[11] This structural motif provides the bridged tetracarbonyldicobalt complexes desired, but with low diastereoselectivities. We therefore assumed that the flat bicyclic backbone of pulegone was not the optimum scaffold for the differentiation of diastereotopic cobalt atoms in the bimetallic cluster. In an effort to find a more selective ligand, we reasoned that the camphor skeleton, bearing an out-of-the-plane gem-dimethyl group, could provide an extended diasteremeric bias compared to pulegone, and we therefore synthesized CamPHOS (**2**).The synthesis of CamPHOS (Scheme 2) started from commercially available (+)-camphorsulfonic acid. Thus, **3** was transformed into 1,3-oxathiane **4** in three steps, following procedures described in the literature.[13] Metalation of **4** at the 2 position was carried out with *sec*-BuLi at −78 °C since *n*-BuLi is not appropriate in this case.[14] Phosphinylation of 2-lithio camphorly-1,3-oxathiane with chlorodiphenylphosphine at −78 °C afforded a single 2-phosphino-1,3-oxathiane. On the basis of related alkylation of 1,3-oxathianes, we assumed that the absolute configuration was *S* (equato-

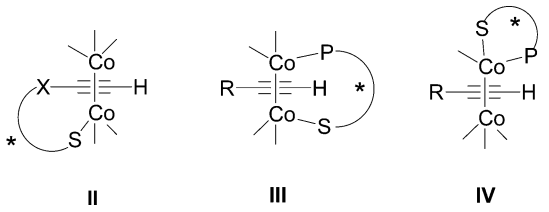

Figure 1.

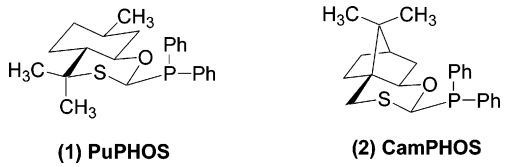

Figure 2.

Scheme 2

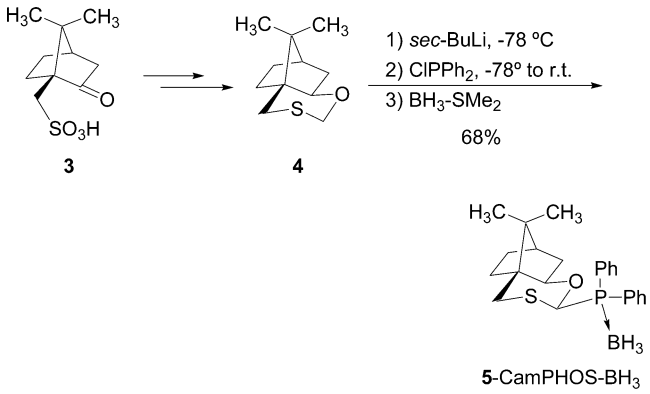

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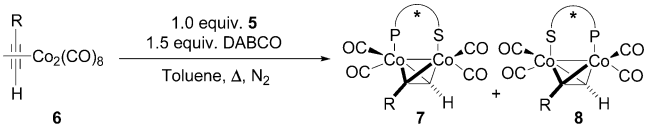
Table 1. Reactions of CamPHOS with Terminal Alkyne Dicobalt Hexacarbonyl Complexes



entry	R	starting complex	*T* (°C)	time (h)	yield (%)	dr[a]	product[c]
1	Ph	**6a**	65	24	85	1.5:1	**7a/8a**
2	*t*-Bu	**6b**	60	20	98	1:1	**7b/8b**
8[b]	*t*-Bu	**7b/8b** (1:1)	90	2	96	1.5:1	**7b/8b**
4[b,d]	*t*-Bu	**7b/8b** (1.5:1)	80	66	90	2:1	**7b/8b**

[a] Established by ^{1}H MNR spectroscopy of the resulting mixture of complexes. [b] Isomerization experiments were run with no added extra base or ligand. [c] Depicted absolute configurations of major/minor isomers are arbitrary. [d] Isomerization was conducted under CO.

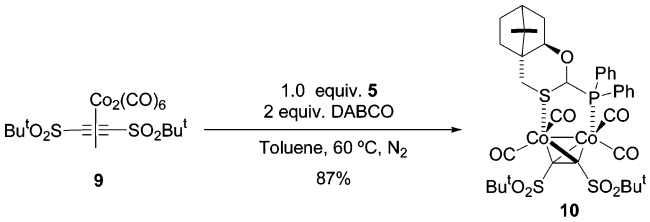
rial position). As a result of the electron-releasing oxathiane group, the new phosphine was highly prone to oxidation. Consequently, the new bidentate ligand was more conveniently isolated as its borane complex. Quenching the reaction mixture with borane-dimethylsulfide afforded BH_3-CamPHOS (**5**) in 68% yield (from **4**) as a white shelf-stable crystalline solid (Scheme 2).

Removal of the borane-phosphine protecting group can be done either by treatment with a nucleophilic amine or with a strong acid (TfOH, HBF_4).[15] In the case of BH_3-CamPHOS, reaction with 2 equiv of diazabicyclo-[3.3.0]octane (DABCO) in toluene at 50 °C provided the free phosphine within 30 min. This allowed the deprotection and complexation steps to be performed in one pot. When the dicobalt carbonyl complex of phenylacetylene **6a**, 1.0 equiv of BH_3-CamPHOS (**5**), and 1.5 equiv of DABCO were mixed in toluene at 65 °C, after 30 min, a brown intermediate was observed by TLC analysis (SiO_2), probably caused by the formation of a monodentate complex. Upon further reaction, this brown complex led to the emergence of two new purple spots. Further heating resulted in the purple complexes being the only visible products in the reaction mixture. Simple filtration on silica afforded a purple oil (85% yield). ^{1}H NMR analysis showed that the product consisted of a diastereomeric mixture of complexes **7a**/**8a** in a 1.5:1 ratio; this was established by integration of the terminal alkyne (doublet, *H*-CCCo$_2$) and acetal (singlet, *H*-CPSO) proton resonances (δ 4.70−6.00 ppm). IR analysis of the carbonyl region showed four absorption bands with an average frequency (ν) of 1992 cm^{-1}, which confirmed bridged double coordination of CamPHOS.[16]

Analogous reaction conditions (60 °C, 24 h) with *tert*-butylacetylene dicobalt complex (**6b**) resulted in no selectivity, yielding a 1:1 mixture of diastereomeric tetracarbonyl complexes

(Table 1, entry 2). This mixture, however, was isomerized: raising the temperature to 90 °C for 2 h shifted the equilibrium to a biased mixture of 1.5:1 (Table 1, entry 3). Further heating of the 1.5:1 mixture at 80 °C for 66 h under CO allowed the complexes to attain a final 2:1 ratio of **7b/8b** (Table 1, entry 4). Isomerization experiments with complexes **7b**/**8b** were run in toluene with no added DABCO or extra ligand.

Scheme 3



Crystal Structure of Coordinated CamPHOS. In contrast to our initial expectations, CamPHOS showed a lower diastereomeric excess than its PuPHOS predecessor. To gain further insight into the parameters that favor the formation of one complex with respect to its diastereomer, analysis of complexes **7a**/**8a** and **7b**/**8b** by X-ray diffraction was attempted. Unfortunately, suitable single crystals of these compounds for X-ray analysis could not be obtained. We therefore used the dicobalt hexacarbonyl complex of bis-*tert*-butylsulfonylethyne **9**, which, in our experience, tends to yield highly crystalline solids. Accordingly, the reaction of BH_3-CamPHOS with **9** in the presence of DABCO provided the desired tetracarbonyl adduct in 87% yield as a sole isomer (Scheme 3). Layering hexane over a toluene solution of **10** provided appropriate crystals for X-ray analysis. The unit cell contained four molecules of **10** and four of toluene. The solvent fragment and carbonyl O(3) are plagued with severe disorder. The corresponding ORTEP drawing of **10** is shown in Figure 3. Relevant crystal and structure refinement data are shown in Table 2. Selected atomic distances and angles are displayed in Table 3.

First, the X-ray structure of **10** allowed us to confirm that the phosphino group in CamPHOS is in an equatorial position in the 1,3-oxathiane chair ring. As expected, coordination of CamPHOS to the bimetallic cluster occurred in a bridged manner. The phosphorus and the sulfur were placed in two eclipsed pseudo-equatorial coordination sites. The cyclic sulfide was coordinated to cobalt through its equatorial lone pair. Both metal atoms, the two donor atoms, and the methyne in the ligand (Co−Co−P−C−S) formed a five-membered ring with an envelope-like conformation. It is important to note that the hydrogen in the methyne group is close to that of the *tert*-butylsulfonyl groups on the alkyne. The P,S ligand probably adopted this coordination in order to avoid unfavorable steric interactions between the gem-dimethyl bridge (CMe_2) in the camphor scaffold and the bulky *tert*-butyl groups in the alkyne backbone. Similarly, the *tert*-butylsulfonyl groups adopted a syn-

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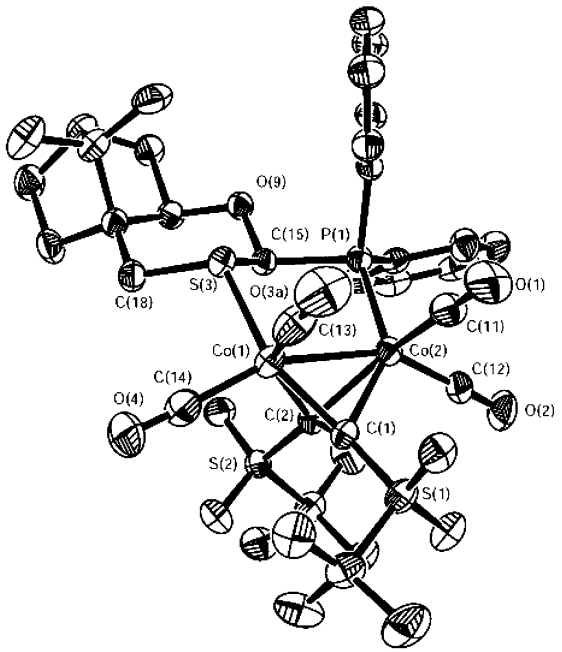


Figure 3. ORTEP drawing of **10** showing 30% ellipsoids. Solvent inclusion and hydrogen atoms have been omitted for clarity. Carbonyl O(3a) corresponds to half occupancy.

Table 2. Crystal Data and Structure Refinement for 10

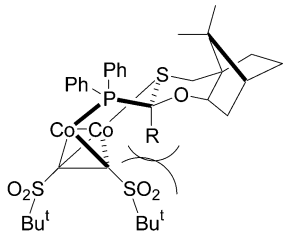
empirical formula	$C_{44}H_{58}Co_2O_9PS_3$
cryst syst	orthorhombic
space group	$P2_12_12_1$
a, Å	15.357(2)
b, Å	15.940(3)
c, Å	19.197(3)
α, deg	90
β, deg	90
γ, deg	90
volume, Å^3	4699.4 (13)
Z	4
density(calcd), mg/m^3	1.379
F(000)	2044
cryst size, mm	0.45 × 0.20 × 0.20
θ range, deg	1.70−26.39
index ranges	$-16 \le h \le 19$ $-19 \le k \le 12$ $-23 \le l \le 23$
no. of reflns collected	29 169
no. of ind reflns	9612 [$R_{int} = 0.0336$]
abs corr	semiempirical
max. and min. transmn	0.8367 and 0.6811
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	9612/0/531
goodness-of-fit on F^2	1.000
final *R* indices [$I>2\sigma(I)$]	$R(F) = 0.0332$ $R_w(F^2) = 0.0759$
R indices (all data)	$R(F) = 0.0462$ $R_w(F^2) = 0.0816$
abs struct param	−0.002(10)
largest diff peak/hole, e Å^{-3}	0.269/−0.187

clinal conformation instead of an antiperiplanar disposition with respect to the cluster C−C bond. This twisted conformation has been described for dicobalt pentacarbonyl complexes of **9** with sulfide ligands.[17]

A Modified CamPHOS Ligand: Design, Synthesis, and Coordination Behavior. To improve ligand performance, an analysis of the crystal structure of **10**

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Structure 10

Co(1)−C(2)	1.954(2)
Co(1)−S(3)	2.27712(9)
Co(2)−C(2)	1.1.946(2)
Co(2)−P(1)	2.2260(8)
S(3)−C(15)	1.839(3)
C(1)−C(2)	1.361(3)
Co(1)−C(1)	1.914(3)
Co(1)−Co(2)	2.4665(6)
Co(2)−C(1)	1.943(3)
P(1)−C(15)	1.842(3)
S(3)−Co(1)−Co(2)	95.29(2)
C(2)−Co(2)−P(1)	105.21(8)
C(2)−Co(1)−S(3)	106.79(8)
P(1)−Co(2)−Co(1)	96.42(2)
C(15)−S(3)−Co(1)	105.09(9)
C(15)−P(1)−Co(2)	107.22(9)
S(3)−C(15)−P(1)	105.4(1)
S(3)−Co(1)−Co(2)−P(1)	3.01(3)
C(13)−Co(1)−Co(2)−C(1)	1.9(2)
C(14)−Co(1)−Co(2)−C(12)	12.9(3)
S(1)−C(1)−C(2)−S(2)	48.0(6)
Co(2)−Co(1)−S(3)−C(15)	33.06(9)



CamPHOS, R=H
CO ligands are omitted for clarity

Figure 4.

led us to reason that increasing the steric bulk in the carbon bridge between the sulfur and phosphorus would have a major impact on stereoselectivity (Figure 4). The methyne in the 1,3-oxathiane ring is in close proximity to the diastereotopic bimetallic cluster, and the exchange of the small hydrogen for a larger group could affect the selectivity of the overall process. To test this hypothesis, we synthesized a methyl-substituted CamPHOS ligand.

Borane-protected dimethylarylphosphines and diarylmethylphosphines are good substrates for base-induced deprotonation of the methyl group with *n*-BuLi.[15c,18] Similarly, deprotonation of **5** with *sec*-BuLi at −78 °C led to the corresponding anion, which, in the presence of 12-crown-4, was alkylated with methyl iodide to furnish BH_3-MeCamPHOS (**11**) as a white crystalline solid in 87% yield. Alkylation with MeI produced a single isomeric compound. We assumed that the configuration of **11** is that depicted in Scheme 4, where the methyl group is placed in the axial position and the bulky boranodiphenylphosphine remains equatorial in the 1,3-oxathiane ring.[19]

Thus, we next studied the coordination behavior of the new MeCamPHOS (**12**) ligand toward several dicobalt hexacarbonyl complexes. After extended heating at 65 °C, the reaction of **11** with the dicobalt complex of

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Scheme 4

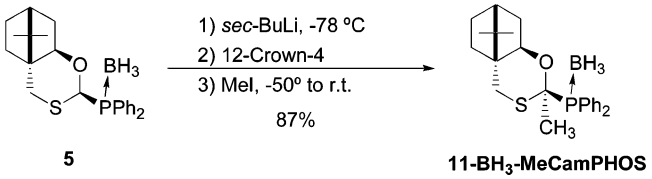
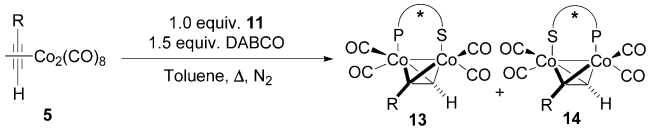


Table 4. Reaction of MeCamPHOS with Terminal Alkyne Dicobalt Hexacarbonyl Complexes



entry	R	starting complex	*T* (°C)	time (h)	yield (%)	dr[a]	product[c]
1	Ph	**6a**	65	48			**13a/14a**
2	*t*-Bu	**6b**	65	18	80	20:1	**13b/14b**
3	$SiMe_3$	**6c**	80[c]	19	64	12:1	**13c/14c**
4	CMe_2OH	**6d**	65	18	99	13:1	**13d/14d**

[a] Established by ^{1}H MNR spectroscopy of the resulting mixture of complexes. [b] Depicted absolute configurations of major/minor isomers are arbitrary. [c] The reaction was first heated at 80 °C (3 h) and then at 70 °C (16 h).

phenylacetylene in the presence of DABCO yielded (Table 4, entry 1) a mixture of several species. ^{1}H NMR analysis of the reaction mixture revealed four main resonances caused by the terminal alkyne hydrogen. These were assigned as follows: one triplet to a diphosphino adduct, two doublets to two diasteromeric monophosphino complexes in a 1:1 ratio, and a doublet to a single bridged complex. Further heating did not lead to the desired isomerization and caused decomposition. However, under the same conditions, the reaction of *tert*-butylethyne complex **5b** with MeCamPHOS after 18 h at 65 °C gave a mixture of bridged adducts **13b/14b** in a 20:1 (90% de) ratio (Table 4, entry 2). To our knowledge this is the highest diastereoselectivity observed in the coordination of a chiral phosphine to a dicobalt hexacarbonyl complex of a terminal acetylene. Moreover, the reaction of MeCamPHOS with the complexes **5c** and **5d** bearing, respectively, a trimethylsilyl and dimethylhydroxymethyl groups, yielded their corresponding tetracarbonyl complexes with remarkable selectivity: 85% and 86% de (Table 4, entries 3 and 4). None of the isomers for **13**/**14** mixtures could be isolated by either crystallization or chromatography.

Intermolecular Pauson−Khand Reactions of (μ-RC≡CH)Co_2(μ-P−S)*$(CO)_4$ Type Complexes. As previously established with PuPHOS, hemilabile ligands are excellent reagents for the highly enantioselective intermolecular Pauson−Khand reaction.[11] To test whether the new generation of P,S ligands could serve as inductors in the aforementioned cyclization, we studied the reaction of a diastereomeric mixture of complexes with norbornadiene. CamPHOS (**2**) adducts were first examined (Table 5, entries 1 and 2). Diasteromeric-bridged complexes derived from phenylacetylene (**7a**/**8a**) were separated by flash chromatography. The reaction of major isomer **7a** with norbornadiene was highly stereospecific and provided the corresponding (+)-cyclopentenone with 97% ee and 93% yield. Furthermore, CamPHOS exhibited a great accelerating effect since the reaction was complete within 30 min at

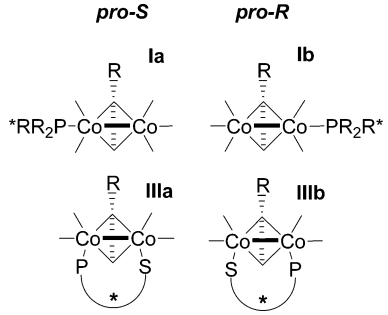


Figure 5. Subtituted dicobalt hexacarbonyl complexes.

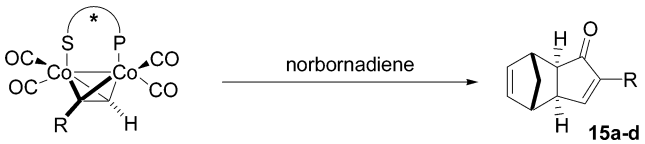
50 °C. On the other hand, switching from a phenyl to a *tert*-butyl group on the alkyne moiety resulted in decreased reactivity (Table 5, entry 2). Cycloaddition of the 2:1 mixture of **7b/8b** yielded the Pauson−Khand adduct with a loss of optical purity from a theoretical 33% to a mere 6% ee. MeCamPHOS showed a similar trend, and a reaction of a 20:1 (90% de) mixture of **13b/14b** afforded **15b** with only 40% ee. However, unexpectedly, the resulting cyclopentenone obtained from the MeCamPHOS complex held the opposite configuration of that obtained using CamPHOS. Similarly, complexes **13c/14c** and **13d/14d,** containing the MeCamPHOS ligand, led to the corresponding levorotatory cyclopentenones (Table 5, entries 4−7). Thermal activation induced unwanted isomerization during cyclization. Thus the reaction of **13c/14c** and **13d/14d** with norbornadiene at 60−65 °C resulted in cyclopentenones with a lower enantiomeric excess than their parent dicobalt complexes. This drawback was minimized by the use of *N*-methylmorpholine *N*-oxide (NMO) (entries 5 and 7, Table 5). For instance, the reaction of **13c/14c** (12:1 dr) with NMO in CH_2Cl_2 at room temperature led to **15c** with 79% ee and practically no loss of the original stereochemical integrity.

Chiroptical Properties of (μ-RC≡CH)Co_2(μ-P−S)*$(CO)_4$ Complexes. Having observed that CamPHOS (**2**) and MeCamPHOS (**12**) led to intermolecular Pauson−Khand adducts of opposite configuration, we next examined the absolute configuration of the bridged complexes that arose from **2** and **12**. Circular dichroism (CD) is an excellent tool for the study of chirally perturbed dicobalt-alkyne clusters.[20] We recently studied a series of alkyne complexes bearing chiral monodentate phosphines and found that the absolute configuration of the bimetallic cluster (i.e., whether the phosphine was coordinated to either a *pro-(S)* or *pro-(R)* cobalt atom (Figure 5, **Ia** and **Ib**)) could be directly ascertained by means of the positive or negative CD absorptions in the 450−650 nm region.[2d]

In this case, the C_2Co_2 chromophore bearing bridged P,S ligands exhibited a different coordination pattern (Figure 5, **IIIa** and **IIIb**), which should give rise to a distinct CD spectra. Therefore we studied whether this technique could be used to determine the absolute configuration of the present tetracarbonyl complexes. The CD spectrum of a diasteriomerically pure sample of major **7a** complex holding a coordinated CamPHOS ligand displayed several bands between 250 and 600 nm (Figure 6), most of which were in the positive region of

(20) Kajtár, M.; Kajtár-Miklós, J.; Giacomelli, G.; Gaál, G.; Váradi, G.; Horováth, I. T.; Zucchi, C.; Pályi, G. *Tetrahedron: Asymmetry* **1995**, *6*, 2177−2194.

Table 5. Pauson−Khand Cyclizations with Camphor-Derived Bridged P,S Ligands



entry	starting complex	dr[a]	R	conditions[b]	time	yield (%)	ee[c]	product[c]
1	**7a**	−	Ph	toluene/50 °C	30 min	93	97	(+)-**15a**
2	**7b/8b**	2/1	*t*-Bu	toluene/90 °C	3 h	75	6	(+)-**15b**
3	**13b/14b**	20/1	*t*-Bu	toluene/50 °C	18 h	80	40	(−)-**15b**
4	**13c/14c**	12/1	$Si(CH_3)_3$	C_6D_6/65 °C	3 h	68	56	(−)-**15c**
5	**13c/14c**	12/1	$Si(CH_3)_3$	CH_2Cl_2/NMO/r.t.	2 d	72	79	(−)-**15c**
6	**13d/14d**	13/1	CMe_2OH	toluene/60 °C	18 h	99	42	(−)-**15d**
7	**13d/14d**	13/1	CMe_2OH	CH_2Cl_2/NMO/rt	4 d	90	50	(−)-**15d**

[a] Diastereomeric ratio of starting complexes. [b] All reactions were conducted under nitrogen with 10 equiv of norbornadiene. [c] Enantiomeric excess (%) was determined either by HPLC (Chiracel-OD) or by GC (β-DEX).

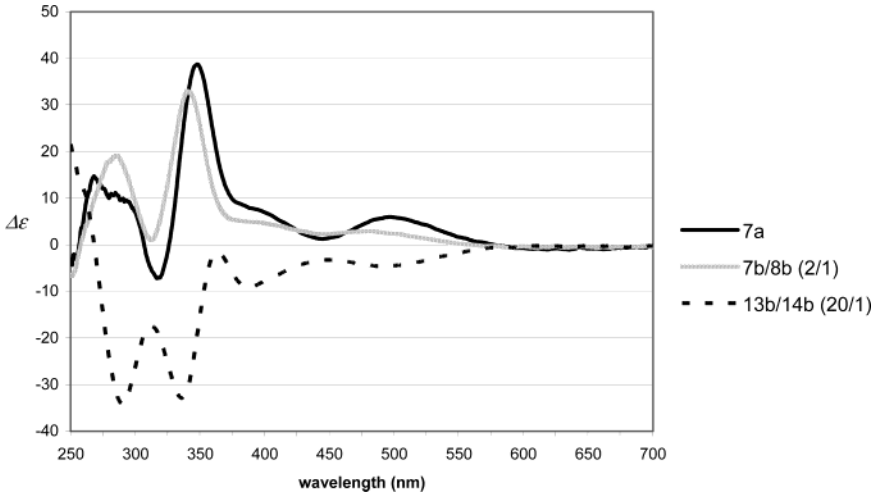
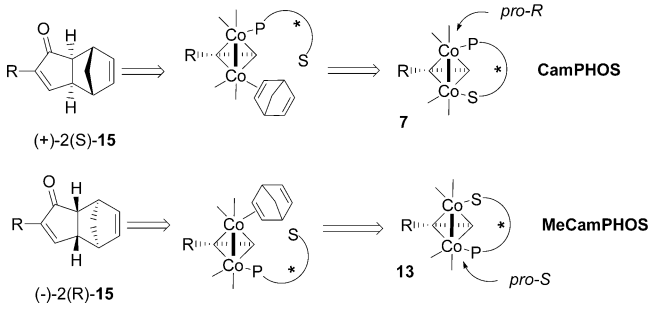


Figure 6. CD spectra of camphor-derived P,S bridged complexes.

$\Delta\epsilon$. Two characteristic absorption maximums were located at 348 nm ($\Delta\epsilon = +38.7$) and 500 nm ($\Delta\epsilon = +5.9$). By analogy, circular dichroism of a diastereomeric mixture of complexes **7b/8b** (2:1 ratio) displayed a parallel CD spectrum with **7a**, with all CD absorptions in the positive area. Interestingly, the CD of a dicobalt tetracarbonyl complex with the MeCamPHOS ligand (**13b**/**14b** in a 20:1 ratio) showed a totally pseudo-enantiomeric spectrum (Figure 6). Four negative absorption bands were identified at $\lambda = 290$ nm ($\Delta\epsilon = -34.1$), 336 nm ($\Delta\epsilon = -32.9$), 386 nm ($\Delta\epsilon = -9.1$), and 495 nm ($\Delta\epsilon = -4.6$). From this chiroptical behavior, we conclude that MeCamPHOS and CamPHOS led to pseudo-enantiomeric C_2Co_2 clusters with a coordination pattern as in **IIIa** and **IIIb** (Figure 5). Furthermore, since the lowest energy absorption between 450 and 600 nm can be clearly attributed to transitions in the C_2-$Co_2(CO)_4$ chromophore, we propose that it can be considered a diagnostic band to assign the configuration of P,S bridged complexes (vide infra).

Establishment of the Absolute Configuration of Complexes 7/8 and 13/14. The absolute configuration of the dicobalt tetracarbonyl complexes with P,S ligands can be ascertained from the corresponding Pauson−Khand products. As we previously demonstrated, dextrorotatory tricyclic pentenones arise from complexes where monophosphine ligands coordinate to the *pro-(R)* cobalt atom in the bimetallic cluster.[2d] Likewise, for

Scheme 5



bridged ligands, the positions of P and S on each cobalt atom determine the stereochemical course of the cyclization (Scheme 5). Consistent with the hypothesis that the labile sulfur ligand leaves a vacant coordination site for the incoming olefin (norbornadiene), the alkene coordination is directed to the metal center which is not bonded to phosphorus, as occurs for monodentate ligands. According to this model, dextrorotatory cyclopentenones produced when CamPHOS is used entail attachment of the phosphorus to the *pro-R* cobalt center (Scheme 5). Conversely, MeCamPHOS led to levorotatory Pauson−Khand products that arise from phosphine coordination at the *pro-S* metal. In further agreement with this model, the sign of the CD bands in the 450−600 region and the topicity of phosphorus coordination coincided with that observed for monodentate phosphines.[2d] Thus,

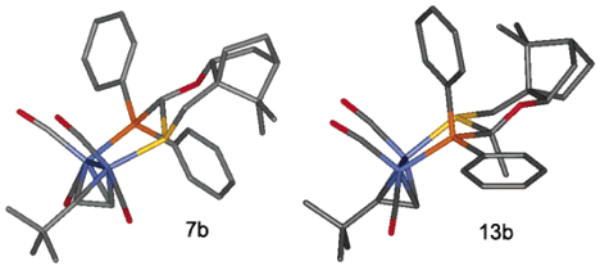


Figure 7. PM3 optimized structures of major diastereomers for CamPHOS and MeCamPHOS.

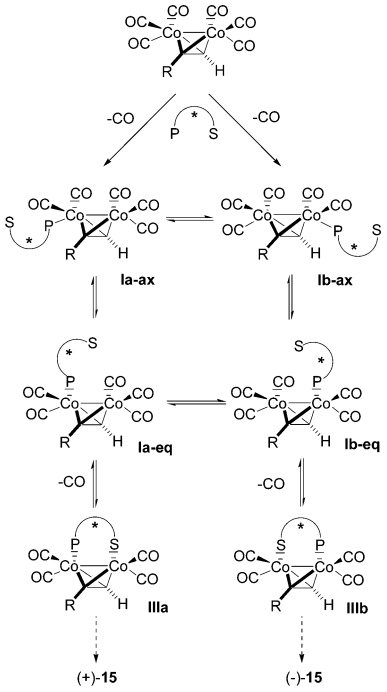
a negative (positive) CD absorption at around 500 nm implies phosphorus coordination at the *pro-S* (*pro-R*) cobalt atom. On the basis of these observations, we confirm that circular dichroism provides a simple and direct method to assess the absolute configuration of dicobalt complexes with bridged P,S ligands.

Chemical correlation with the Pauson−Khand products and the CD spectra permitted us to establish the absolute configuration of the major diastereomer in each diasteromeric pair of complexes **7**/**8** and **13**/**14**. When using CamPHOS, phosphorus is attached at the *pro-R* metal atom in the major diastereomeric complex **7** (Scheme 5 and Figure 7). On the other hand, the opposite configuration was obtained when MeCamPHOS was used and the major **13** bore the phosphine on the *pro-S* cobalt atom (Scheme 5 and Figure 7). Likewise, minor diastereomers **8** and **14** had the opposite configuration with respect to their major counterparts.

Remarkably, a relatively small methyl group had a huge effect on the coordination selectivity of P,S ligands. Introducing a CH_3− in the carbon bridge between phosphorus and sulfur produced a switch on selectivity. This change was significant, since diastereselectivity increased from 33% de for CamPHOS in **7b**/**8b** to 90% de of opposite sign for **13b**/**14b** when using MeCamPHOS. This observation implies that the overall destabilizing effect of the methyl group for major isomer **7b** was 2.15 kcal/mol. PM3-optimized structures of major anti-isomers for CamPHOS and MeCamPHOS are shown in Figure 7. CamPHOS in **7b** yielded a configuration analogous to that observed by X-ray crystallography for PuPHOS.[11] The camphor skeleton was too far from the bimetallic cluster to offer any efficient discrimination. Alternatively, the methyl group in **13b** was closer to the alkyne moiety and exerted a high diastereomeric bias.

Rationalization of the Coordination Pathway Observed. Experimental observations made during the reactions of P,S ligands with dicobalt hexacarbonyl complexes are consistent with the sequence of events depicted in Scheme 6. First, exchange of a CO ligand by the phosphine in CamPHOS should provide diastereomeric pentacarbonyl complexes **Ia-ax** and **Ib-ax**, in which the phosphorus atom reacts first because it is a better donor with respect to the sulfide. At this stage, the incoming phosphine is more likely to occupy a pseudo-axial coordination site on cobalt, as in other monodentate systems.[21] Little selectivity in the preference to bind either metal atom can be expected at this point, and an approximately 1:1 mixture of diastereomers **Ia-ax** and **Ib-ax** was found. From axial complexes, direct formation of a bridged structure like **III** is not feasible; the phosphorus atom must reach a pseudo-equatorial site as in **Ia-eq** and **Ib-eq**. Hence, from **I-ax** complexes, ligand pseudo-rotation would provide the needed pseudo-equatorially coordinated complexes **I-eq**, which can easily exchange a CO with sulfur to yield the final **IIIa** and **IIIb** tetracarbonyl complexes.[17,22]

Scheme 6. Postulated Equilibrium Process for Coordination of P,S Ligands



This behavior was experimentally confirmed by monitoring the reaction mixture of MeCamPHOS with **5c** by ^{1}H NMR early in the reaction. Thus, after heating the reaction mixture at 55 °C for 1 h the ^{1}H NMR spectrum showed, in an approximately 1:1 ratio, two resonances at δ 5.28 and 5.47 ppm, which corresponded to monodentate structures **Ia-ax** and **Ib-ax**. Moreover, in the same spectrum, additional signals belonging to the final bridged tetracarbonyl species **IIIa** and **IIIb** were already observed in a 6:1 ratio.

In an equilibrium process like the one proposed in Scheme 6, the relative energies of the end complexes **IIIa** and **IIIb** determine the final diastereomeric ratio observed. Isomerization between diasteromeric complexes is more likely to occur at the monodentate **I-ax** and **I-eq** structure level than at the bridged ones (**III**), in which concomitant migration of both donor atoms would be necessary. Isomerization between these complexes during the Pauson−Khand reaction would account for the decrease observed in stereospecificity during cyclization. Therefore, the appropriate choice of reaction conditions (NMO, CH_2Cl_2) could minimize the loss of stereochemical purity. In our case amine *N*-oxide did not have a clear effect on the reaction rate and probably prevented the presence of free CO in the reaction medium.

(21) (a) Bonnet, J. J.; Mathieu, R. *Inorg. Chem.* **1978**, *17*, 1973−1976. (b) Jeffrey, J. C.; Pereira, R. M. S.; Vargas, M. D.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1995**, 1805.

(22) Amouri, H. E.; Gruselle, M. *Chem. Rev.* **1996**, *96*, 1077−1103.

Conclusions

Here we have designed a new family of camphor-derived P,S ligands for bridged coordination to dicobalt hexacarbonyl complexes. To our knowledge, MeCamPHOS (**12**) exhibits the highest diastereoselectivity ever observed (up to 90% de) in the coordination process to hexacarbonyl dicobalt complexes. Experimental observations indicate that this is the result of thermodynamic equilibration that yields the more stable isomer. The absolute configuration of the new bridged complexes was established by chemical correlation from their intermolecular Pauson−Khand products. Along these lines, we also demonstrate the usefulness of circular dichroism to assign the absolute configuration of dicobalt clusters that bear bridged P,S ligands.

Experimental Section

General Procedures. All reactions were conducted under nitrogen or argon atmosphere using standard Schlenk techniques. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity-300 spectrometer. ^{1}H and ^{13}C NMR spectra were referenced relative to residual solvent peaks. ^{31}P were referenced with an external H_3PO_4 sample. In most alkyne dicobalt complexes the carbon signals corresponding to the cluster carbonyls do not appear in the ^{13}C NMR spectrum and have been omitted. The major part of alkyne-chelated cobalt complexes solidified to give amorphous solids, from which solvent could not be removed completely. This precluded satisfactory elemental analysis of these compounds. Infrared (IR) spectra were recorded on a Nicolette 510 FT spectrometer. Melting points were determined by differential scanning calorimetry (DSC) on a Mettler DSC-30 under nitrogen. Elemental analyses were performed at "Servei de microanàlisi del CSIC de Barcelona". High-resolution mass spectroscopy (HRMS) was conducted at "Unidade de Espectrometría de Masas de la Universidad de Santiago de Compostela". All anhydrous solvents were distilled under nitrogen, THF was distilled from sodium benzophenone ketyl, toluene was distilled from molten sodium, and CH_2Cl_2 was distilled from CaH_2. Silica gel used for filtration and flash chromatography of cobalt complexes was previously washed through with Et_2O. (+)-10-Thioisoborneol oxathiane was prepared according to a published literature procedure.[23] Complexes **6a**, **6b**, **6c**, and **6d** were prepared according to a standard procedure (1.0 equiv of $Co_2(CO)_8$, hexane, rt) from the corresponding commercially available alkynes.

(−)-(1S,4S,6R,8R)-4-Diphenylphosphino-11,11-dimethyl-5-oxa-3-thiatricyclo[6.2.1.0^{1,6}]undecane Borane Complex, 5. To a cooled (−78 °C) solution of (+)-10-thioisoborneol oxathiane (1.0 g, 5.0 mmol) in THF (10 mL) was added dropwise 1.3 M *sec*-BuLi in cyclohexane (4.0 mL, 5.3 mmol). The temperature was allowed to rise to −30 °C, and next, the reaction was cooled back to −78 °C. Chlorodiphenylphosphine (0.99 mL, 5.5 mmol) was then added with a syringe, and the temperature was kept at −78 °C for 1 h and then allowed to reach room temperature. After 3 h the reaction was quenched at 0 °C by the addition of BH_3-$S(CH_3)_2$ (0.62 mL, 6.5 mmol). The reaction mixture was diluted with Et_2O, and water was added (CAUTION! bubbling occurs). The aqueous layer was washed with Et_2O, and the combined organic layers were washed with brine and dried ($MgSO_4$). Solvent removal under vacuum afforded a mixture of the desired boraphosphine complex and starting material (75% conv by ^{1}H NMR). Purification by flash chromatography (SiO_2, hexane/AcOEt, 10%), and crystallization from ether/hexane mixtures yielded 1.35 g (68%) of **5** as a colorless crystalline solid. Mp: 148−150 °C. $[\alpha]_D$ −92.5° (*c* 1.4, $CHCl_3$). IR (KBr): ν_{max} 688, 1043, 1437, 2348, 2386, 2967 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.40−1.80 (br m, BH_3), 0.85−1.06 (m, 2H), 0.84 (s, 3H), 1.03 (s, 3H), 1.40−1.50 (m, 1H), 1.62−1.74 (m, 3H), 1.78−1.88 (m, 1H), 2.73−2.79 (dd, J = 3 and 8 Hz, 1H), 3.09 (d, J = 14 Hz, 1H), 3.59−3.63 (dd, J = 3 and 8 Hz, 1H), 5.56 (s, 1H), 7.38−7.55 (m, 6H), 7.54−7.88 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.2, 22.5, 27.1, 29.4 (J_P = 7 Hz), 34.1, 37.5, 42.9, 45.2, 46.6, 79.2 (J_P = 44 Hz), 86.7 (J_P = 6 Hz), 125.7 (J_P = 55 Hz), 127.3 (J_P = 55 Hz), 128.1 (J_P = 10 Hz), 128.5 (J_P = 10 Hz), 131.3 (J_P = 2 Hz), 131.5 (J_P = 2 Hz), 133.2 (J_P = 9 Hz), 134.2 (J_P = 9 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 25.6 (br s) ppm. Anal. Calcd for $C_{23}H_{30}BOPS$: C 69.70, H 7.63, S 8.09. Found: C 69.79, H 7.70, S 7.80.

(+)-(1S,4S,6R,8R)-4-Diphenylphosphino-4,11,11-trimethyl-5-oxa-3-thiatricyclo[6.2.1.0 ^{1,6}]undecane Borane Complex, 11. To a cooled (−78 °C) solution of borane-phosphine complex **5** (1.0 g, 2.5 mmol) in THF (12 mL) was added dropwise 1.2 M *sec*-BuLi in cyclohexane (2.2 mL, 2.7 mmol), and this yielded an orange solution. 12-Crown-4 (0.99 mL, 5.5 mmol) was then added with a syringe, and the temperature was allowed to rise to −50 °C. At this temperature, methyl iodide (127 μL, 2.7 mmol) was added via syringe. This resulted in a change of color from orange to pale yellow. The reaction temperature was next allowed to reach room temperature. Solvent removal under vacuum afforded a single crude spot (TLC) of the desired boraphosphine complex. Purification by filtration on SiO_2 (hexane/AcOEt, 10%) and crystallization from hexane yielded 0.9 g (87%) of **11** as a colorless crystalline solid. Mp: 120 °C. $[\alpha]_D$ +74.0° (*c* 1.0, $CHCl_3$). IR (KBr): ν_{max} 698, 1105, 1437, 2392, 2954 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.40−1.90 (br m, BH_3), 0.66−0.80 (m. 1H), 0.79 (s, 3H), 0.82−1.01 (m, 1H), 1.08 (s, 3H), 1.22−1.32 (m, 2H), 1.52−1.66 (m, 2H), 1.76 (d, J = 12 Hz, 3H), 1.74−1.83 (m, 1H), 2.58−2.63 (dd, J = 3 and 14 Hz, 1H), 2.85−2.89 (d, J = 14 Hz, 1H), 3.10−3.17 (m, 1H), 7.37−7.59 (m, 6H), 7.89−7.96 (m, 2H), 8.11−8.18 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.9, 20.4, 26.2 (J_P = 4 Hz), 26.6, 27.3 (J_P = 11 Hz), 31.1, 36.8, 44.2, 46.6, 46.8, 81.6, 84.8 (J_P = 32 Hz), 126.6, (J_P = 51 Hz), 127.5 (J_P = 51 Hz), 127.0 (J_P = 9 Hz), 128.5 (J_P = 9 Hz), 131.1 (J_P = 2 Hz), 131.6 (J_P = 2 Hz), 133.9 (J_P = 8 Hz), 134.6 (J_P = 8 Hz) ppm. ^{31}P NMR (121 MHz, $CDCl_3$): δ 25.9−26.3 (br d, J = 48 Hz) ppm. HRMS (FAB+): calcd for $C_{24}H_{32}$-BOPS−H 409.1926, found 409.1918.

General Procedure for the Synthesis of Tetracarbonyl Complexes. $Co_2(\mu$-PhCCH$)(CO)_4(\mu$-$C_{23}H_{27}OPS)$, 7a and 8a. Dicobalt hexacarbonyl complex of phenylethyne **6a** (100 mg, 0.25 mmol), phosphine-borane complex **5** (102 mg, 0.25 mmol), DABCO (42 mg, 0.37 mmol), and toluene (1 mL) were charged in a Schlenk flask under nitrogen. The reaction mixture was heated to 65 °C for 24 h, removing periodically the CO by means of vacuum and nitrogen refilling. Complexation was monitored by TLC. Upon reaction completion the solvent was removed in vacuo. The residue was then purified by flash chromatography on SiO_2 to yield 156 mg (85%) of **7a**/**8a** as a red-purple viscous oil. ^{1}H NMR analysis revealed the existence of a 1.5:1 mixture of diastereomeric complexes. A pure fraction of the major diastereomer **7a** was purified by flash chromatography (SiO_2, hexane/AcOEt, 3%). IR (KBr): ν_{max} 1962, 1991, 2024 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6) major: δ 0.30−1.60 (m, 7H), 0.46 (s, 3H), 0.83 (s, 3H), 2.63 (d, J = 14 Hz, 1H), 2.69−2.76 (dd, J = 6 and 14 Hz, 1H), 2.94−2.98 (dd, J = 3 and 8 Hz,1H), 4.73 (s, 1H), 5.97 (d, J = 7 Hz, 1H), 7.00−7.30 (m, 9H), 7.73−7.79 (m, 2H), 7.86−7.93 (m, 4H) ppm; distinct signals from minor: δ 0.73 (s, 3H), 5.01 (s, 1H), 5.64 (d, J = 7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, C_6D_6) major: δ 19.9, 22.5, 27.0, 33.8, 37.1, 42.4 (J_P = 8 Hz), 44.4, 45.6, 46.5, 73.7 (J_P = 7 Hz, Co_2CCH), 86.9 (C_2OCH), 97.8 (J_P = 22 Hz, OPS*C*H),

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126.8, 128.8, 129.9, 130.0 (J_P = 3 Hz), 130.2, 130.4, 132.5 (J_P = 12 Hz), 132.5 (J_P = 35 Hz), 135.1 (J_P = 12 Hz), 135.6 (J_P = 35 Hz), 142.4, 203.0−206.2 (br, 4CO) ppm; distinct signals from minor: 69.4 (Co_2CCH), 87.3 (C_2OCH), 91.2 (J_P = 27 Hz, OPS*C*H) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ -27.4_{maj}, -30.4_{min} ppm. HRMS (FAB+): calcd for $C_{35}H_{33}Co_2O_5PS-CO$ 686.0501, found 686.0448.

Co_2(μ-Bu^{t}CCH)(CO)$_4$(μ-$C_{23}H_{27}OPS$), 7b and 8b. According to the general procedure, dicobalt hexacarbonyl complex **6b** (100 mg, 0.27 mmol), phosphine-borane **5** (107 mg, 0.27 mmol), DABCO (45 mg, 0.4 mmol), and toluene (1 mL) were used. The reaction mixture was heated at 60 °C for 20 h. Purification by flash chromatography yielded 185 mg (98%) of **7b** and **8b** as a red viscous oil, which solidified upon standing. ^{1}H NMR analysis showed a 1:1 ratio of diastereomeric complexes. Further equilibration of the diastereomeric mixture at 80 °C under CO atmosphere for 66 h yielded a 2:1 mixture of diastereomers (90% yield). IR (KBr): ν_{max} 1958, 1985, 2020 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6) major: δ 0.30−1.6 (m, 7H), 0.45 (s, 3H), 0.77 (s, 3H), 1.47 (s, 9H), 2.68 (d, J = 12 Hz, 1H), 2.75−2.86 (dd, J = 6 and 11 Hz, 1H), 2.96−3.04 (dd, J = 3 and 9 Hz, 1H), 4.71 (d, J = 2 Hz, 1H), 5.66 (d, J = 7 Hz, 1H), 7.01−7.25 (m, 6H), 7.71−7.92 (m, 4H) ppm; distinct signals from minor: δ 0.66 (s, 3H), 0.44 (s, 3H), 4.99 (s, 1H), 5.19 (d, J = 9 Hz, 1H) ppm. ^{13}C NMR (75 MHz, C_6D_6) major: δ 19.9, 22.4, 27.0, 33.3, 33.8, 36.8, 42.3 (J_P = 11 Hz), 44.4, 45.7, 46.5, 72.8 (Co_2CCH), 86.7 (C_2OCH), 97.1 (OPS*C*H, J_P. = 21 Hz), 120.5 (br), 128.8, 129.6, 130.0, 130.4, 132.3 (J_P = 11 Hz), 135.4 (J_P = 13 Hz) ppm; distinct signals from minor: δ 67.0 (Co_2CCH), 87.2 (C_2OCH), 89.6 (OPS*C*H, J_P = 26 Hz) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ -27.8_{maj}, -29.1_{min} ppm. HRMS (FAB+): calcd for $C_{33}H_{37}Co_2O_5PS$ 694.0763, found 694.0747.

Co_2(μ-Bu^{t}SO$_2$C$_2$SO$_2$Bu^t)(CO)$_4$(μ-$C_{23}H_{27}OPS$), 10. According to the general procedure, dicobalt hexacarbonyl complex **9**[17] (65 mg, 0.11 mmol), phosphine-borane **5** (46 mg, 0.11 mmol), DABCO (19 mg, 0.17 mmol), and toluene (2 mL) were used. The reaction mixture was heated at 60 °C for 18 h. Filtration through a pad of silica (hexane/AcOEt, 20%) yielded 90 mg (87%) of **10** as a red cristalline solid. Mp: 181.4 °C. $[\alpha]_D$ 104.1° (*c* 0.02, CH_2Cl_2). IR (KBr): ν_{max} 1995, 2018, 2031, 2056 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 0.46−1.72, (m, 7H), 0.43 (s, 3H), 0.61 (s, 3H), 1.43 (s, 9H), 1.64 (s, 9H), 2.72−2.79 (dd, J = 6 and 13 Hz, 1H), 3.62 (d, J = 13 Hz, 1H), 3.67−3.75 (m, 1H), 6.98−7.18 (m, 7H), 7.72−7.51 (m, 2H), 7.53−7.63 (m, 2H) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ 19.9, 22.3, 24.8, 25.1, 26.9, 33.6, 37.0, 38.2, (J_P = 9 Hz), 44.7, 45.7, 46.6, 62.1, 62.2, 86.6 (C_2OCH, J_P = 4 Hz), 88.4 (OPS*C*H, J_P = 28 Hz), 128.8, J_P = 9 Hz), 129.4 (J_P = 36 Hz), 130.3, 131.0, 132.3, (J_P = 36 Hz), 132.6 (J_P = 10 Hz), 134.3 (J_P = 10 Hz) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ −33.3 (br s) ppm. HRMS (FAB+): calcd for $C_{37}H_{45}Co_2O_9PS_3$+H 879.0705, found 879.0702.

Co_2(μ-Bu^{t}CCH)(CO)$_4$(μ-$C_{24}H_{29}OPS$), 13b and 14b. According to the general procedure, dicobalt hexacarbonyl complex **6b** (97 mg, 0.26 mmol), phosphine-borane **11** (100 mg, 0.24 mmol), DABCO (40 mg, 0.36 mmol), and toluene (2 mL) were used. The reaction mixture was heated at 65 °C for 18 h. Filtration through a pad of silica (hexane/AcOEt) yielded 141 mg (80%) of **13b**/**14b** as a red viscous oil, which solidified upon standing. ^{1}H NMR analysis showed that diastereomeric complexes were found in a 20:1 ratio. IR (KBr): ν_{max} 1958, 1987, 2020 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6) major: δ 0.35−1.70 (m, 7H), 0.46 s, 3H), 0.84 (s, 3H), 1.52 (s, 9H), 1.83 (d, J = 12 Hz, 3H), 2.07−2.12 (dd, J = 2 and 14 Hz, 1H), 2.61−2.66 (dd, J = 1 and 14 Hz, 1H), 2.84−2.92 (m, 1H), 5.86 (d, J = 5 Hz, 1H), 6.95−7.21 (m, 6H), 8.09−8.19 (m, 2H), 8.30−8.40 (m, 2H) ppm; distinct signals from minor: δ 5.06 (d, J = 5 Hz, 1H) ppm. ^{13}C NMR (75 MHz, C_6D_6) major: δ 19.7, 20.3, 23.9 (J_P = 14 Hz), 26.6, 31.8, 32.3 (J_P = 10 Hz), 33.3, 36.9, 37.1, 44.4, 47.0, 49.3, 75.4 (J_P = 6 Hz, Co_2CCH), 82.2 (C_2OCH), 102.5 (J_P = 15 Hz, CH_3OPSC), 127.6 (J_P = 9 Hz), 128.8 (J_P = 9 HZ), 130.2, 130.7, 133.6 (J_P = 31 Hz), 134.0 (J_P = 30 Hz), 135.3 (J_P = 11 Hz), 135.5 (J_P = 12 Hz), 203.5−207.5 (4 CO) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ -20.0_{maj} (br s) ppm. HRMS (FAB+): calcd for $C_{34}H_{39}Co_2O_5PS-CO$ 680.0971, found 680.0978.

Co_2(μ-Me$_3$SiCCH)(CO)$_4$(μ-$C_{24}H_{29}OPS$), 13c and 14c. According to the general procedure, dicobalt hexacarbonyl complex **6c** (51 mg, 0.13 mmol), phosphine-borane **11** (50 mg, 0.12 mmol), DABCO (21 mg, 0.18 mmol), and toluene (2 mL) were used. The reaction mixture was heated at 80 °C for 3 h and then at 70 °C for 16 h. Purification by flash chromatography (hexane/AcOEt, 1%) afforded 57 mg (64%) of **13c**/**14c** as a viscous red oil. ^{1}H NMR analysis showed the corresponding diastereomeric complexes were found in a 1:12 ratio. IR (KBr): ν_{max} 1960, 1989, 2022 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6) major: δ 0.12−1.70 (m, 7H), 0.45 (s, 3H) 0.57 (s, 9H), 0.83 (s, 3H), 1.75 (d, J = 13 Hz, 3H), 2.06−2.65 (AB, J = 14 Hz, 2H), 2.90−2.98 (m, 1H), 6.33 (d, J = 5 Hz, 1H), 6.95−7.25 (m, 6H), 8.12−8.18 (m, 2H), 8.31−8.37 (m, 2H) ppm; distinct signals from minor: δ 5.72 (d, J = 5 Hz, 1H) ppm. ^{13}C NMR (75 MHz, C_6D_6) major: δ 1.0, 19.7, 20.3, 23.8 (J_P = 14 Hz), 26.6, 31.9, 32.6, (J_P = 10 Hz), 36.9, 44.5, 47.1, 49.6, 82.2 (C_2OCH), 88.7 (Co_2CCH), 103.3, (J_P = 16 Hz, CH_3OPSC), 128.8 (J_P = 9 Hz), 130.3, 130.8, 133.8 (J_P = 31 Hz), 134.0 (J_P = 30 Hz), 135.3 (J_P = 13 Hz), 135.5 (J_P = 13 Hz) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ -14.2_{maj} (br s) ppm. HRMS (FAB+): calcd for $C_{33}H_{39}Co_2O_5PSSi-CO$ 696.0740, found 696.0761.

Co_2(μ-HOMe$_2$CC$_2$H)(CO)$_4$(μ-$C_{24}H_{29}OPS$), 13d and 14d. According to the general procedure, dicobalt complex **6d** (18 mg, 0.048 mmol), phosphine-borane **11** (20 mg, 0.048 mmol), DABCO (8 mg, 0.072 mmol), and toluene (1 mL) were used. The reaction mixture was heated to 65 °C for 18 h. Purification by flash chromatography (hexane/AcOEt, 10%) afforded 35 mg (99%) of **13d**/**14d** as a red viscous oil, which solidifies upon standing. ^{1}H NMR analysis showed a 13:1 ratio of diastereomeric complexes. IR (KBr): ν_{max} 1962, 1991, 2024 cm^{-1}.^{1}H NMR (300 MHz, C_6D_6) major: δ 0.0.40−1.80 (m, 7H), 0.45 (s, 3H) 0.82 (s, 3H), 1.75 (s, 3H), 1.78 (s, 3H), 1.79 (d, J = 12 Hz, 3H), 2.06−2.64 (AB, J = 14 Hz, 2H), 2.82−2.91 (m, 1H), 5.74 (d, J = 5 Hz, 1H), 6.95−7.20 (m, 6H), 8.06−8.14 (m, 2H), 8.27−8.35 (m, 2H) ppm; distinct signals from minor: δ 5.00 (d, J = 5 Hz, 1H) ppm. ^{13}C NMR (75 MHz, C_6D_6) major: δ 19.7, 20.2, 23.9 (J_P = 15 Hz), 26.5, 31.8, 32.3, (J_P = 10 Hz), 33.0, 33.2, 36.9, 44.4, 47.0, 49.3, 73.3, 74,0 (Co_2CCH), 82.2 (C_2OCH), 102.7 (J_P = 16 Hz, CH_3OPSC), 106.5 (J_P = 15 Hz), 128.8 (J_P = 9 Hz), 130.4, 130.9, 133.3 (J_P = 31 Hz), 133.7 (J_P = 28 Hz), 135.3 (J_P = 11 Hz), 135.5 (J_P = 12 Hz) ppm. ^{31}P NMR (121 MHz, C_6D_6): δ -17.0_{maj} (br s) ppm. HRMS (FAB+): calcd for $C_{33}H_{37}Co_2O_6PS$+H 711.0790, found 711.0719.

(+)-(3a*S*,4*R*,7*S*,7aS)-2-Phenyl-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one, 15a.[24] Diastereomerically pure major **7a** (49 mg, 0.068 mmol), norbornadiene (68 μL, 0.68 mmol), and toluene (2 mL) were charged in a Schlenk flask under nitrogen and heated to 50 °C with stirring. TLC monitoring showed the reaction was complete after 30 min. Purification by flash chromatography on SiO_2 (hexane/AcOEt, 2.5%) yielded 14 mg (93%) of (+)-**15a** as a white solid (97% ee). HPLC analysis: CHIRALCEL OD (25 cm), 2% IPA−98% hexane, 0.5 mL/min, λ = 254 nm. t_R (+) isomer = 16.8 min. t_R (−) isomer = 20.6 min.

(+)-(3a*S*,4*R*,7*S*,7a*S*)- and (−)-(3a*R*,4*S*,7*R*,7a*R*)-2-*tert*-Butyl-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one, 15b.[25] From CamPHOS: A 2:1 diastereomer mixture of **7b**/**8b** (55 mg, 0.079 mmol), norbornadiene (79 μL, 0.79 mmol), and toluene (2 mL) was charged in a Schlenk flask under nitrogen and heated initially at 60 °C for 1 h and then 90 °C for 3 h. Purification by flash chromatography on SiO_2 (hexane/AcOEt,

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1%) yielded 12 mg (75%) of (+)-**15b** (6% ee). From MeCamPHOS: A 20:1 diastereomer mixture of **13b**/**14b** (79 mg, 0.1 mmol), norbornadiene (100 μL, 1.0 mmol), and toluene (2 mL) were charged in a Schlenk flask under nitrogen and heated initially at 50 °C for 18 h and then 80 °C for 1 h. Purification by flash chromatography on SiO_2 (hexane/AcOEt, 5%) yielded 16 mg (80%) of (−)-15b (40% ee). HPLC analysis: CHIRALCEL OD (25 cm), 0.5% IPA−95.5% hexane, 1.0 mL/min, λ = 254 nm. t_R (+) isomer = 8.4 min. t_R (−) isomer = 10.3 min.

(−)-(3a*S*,4*S*,7*R*,7a*R*)-2-Trimethylsilanyl-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one, 15c.[2d] Thermal conditions: A 12:1 diastereomer mixture of **13c**/**14c** (15 mg, 0.02 mmol), norbornadiene (20 μL, 0.2 mmol), and C_6D_6 (0.75 mL) was charged in a NMR tube under nitrogen and heated at 65 °C for 3 h. This resulted in complete conversion of the starting complex (TLC) and yielded 3 mg (68%) of (−)-**15c** in 56% ee as calculated by GC analysis. *N*-Oxide conditions: A 12:1 diastereomer mixture of **13c**/**14c** (40 mg, 0.054 mmol), norbornadiene (50 μL, 0.5 mmol), *N*-methylmorpholine *N*-oxide (38 mg, 0.32 mmol), and CH_2Cl_2 (2 mL) was charged in a Schlenk flask under nitrogen and stirred at room temperature for 2 days to yield 8 mg (72%) of (−)-**15c** in 79% ee as calculated by GC analysis. GC analysis: Supelco β-DEX 120, 30m, 150 °C. t_R (−) isomer = 31.7 min. t_R (+) isomer = 33.4 min.

(−)-(3a*R*,4*S*,7*R*,7a*R*)-2-(1-Hydroxy-1-methylethyl)-3a,4,7,7a-tetrahydro-4,7-methanoinden-1-one, 15d.[2c,26] Thermal conditions: A 13:1 diastereomer mixture of **13d**/**14d** (25 mg, 0.035 mmol), norbornadiene (35 μL, 0.35 mmol), and toluene (1 mL) was charged in a Schlenk flask under nitrogen and heated at 60 °C for 18 h. This resulted in complete conversion of the starting complex (TLC) and yielded 7 mg (99%) of (−)-**15d** in 42% ee as calculated by HPLC analysis. *N*-Oxide conditions: A 13:1 diastereomer mixture of **13d**/**14d** (27 mg, 0.038 mmol), norbornadiene (38 μL, 0.38 mmol), *N*-methylmorpholine *N*-oxide (26 mg, 0.22 mmol), and CH_2Cl_2 (3 mL) was charged in a Schlenk flask tube under nitrogen and stirred at room temperature for 4 days to yield 7 mg (90%) of (−)-**15d** in 50% ee as calculated by HPLC analysis. HPLC analysis: CHIRALCEL OD (25 cm), 5% IPA−95% hexane, 1.0 mL/min, λ = 254 nm. t_R (−) isomer = 6.5 min. t_R (+) isomer = 7.3 min.

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Supporting Information Available: Tables of complete X-ray crystal data: ORTEP drawings, refinement parameters, atomic coordinates, and bond distances and angles for **10**. ^{1}H NMR of ligand **11** and complexes **7a**, **7b**/**8b**, **13b**/**14b**, **13c**/**14c**, and **13d**/**14d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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