Optically Active Transition-Metal Complexes. 9.[1] A General Stereoselective Route to α-Chiral (*R*)-Tricarbonyl(η^6-ethylbenzene)chromium Complexes. Novel Organometallic Phosphine Catalysts for the Asymmetric Hydrovinylation Reaction

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Treatment of (*R*)-[{α-(dimethylamino)ethyl}-η^6-benzene]Cr(CO)$_3$ with esters of chloroformic acid leads to stereoselective substitution of the dimethylamino group for a chloro substituent. The reaction can be extended to systems in which the chromium arene complex, after metalation, is diastereoselectively substituted in the *ortho* position with carbon and silicon electrophiles to generate planar chirality. The chloro group in turn can be replaced stereoselectively for various phosphorus, nitrogen, and oxygen nucleophiles. Both substitution reactions in the benzylic position proceed via retention of configuration. The addition of cyanide is not stereospecific. The phosphine derivatives are efficient catalysts for the enantioselective hydrovinylation of styrene to 3-phenyl-1-butene. X-ray crystal structures establish the absolute configuration of (*R*)-[(α-chloroethyl)η^6-benzene]Cr(CO)$_3$, (*R*)-[{α-(diphenylphosphanyl)ethyl}-η^6-benzene]Cr(CO)$_3$, and (*pS,S*)-[1-(α-cyanoethyl)-2-methyl-η^6-benzene]Cr(CO)$_3$.

Introduction

Optically active phosphines are among the most important ligands for homogeneous catalysis. Recently, particular attention has been paid to chiral phosphines based on substituted ferrocenes.[2] Such ligands have in fact found a number of industrial applications.[3] A major reason for this is the efficient methology developed by Ugi for the separation of {1-(dimethylamino)ethyl}-ferrocene[4] from racemic precursors and the contributions by Hayashi and Togni toward the stereoselective transformations into a variety of chelating phosphine ligands.[2]

Similar systems based on (arene)chromium tricarbonyl complexes have been introduced by Uemura.[5,6] (*R*)-[{α-(Dimethylamino)ethyl}-η^6-benzene]chromium tricarbonyl (**1a**) serves as the starting material, readily made from the commercially available optically active amine.[7,8] A method has been developed to introduce planar chirality by diastereoselective metalation and electrophilic substitution in the *ortho* position of the arene ring.[7]

No method has yet been found for the substitution of the dimethylamino group, which cannot be replaced, as in the ferrocene case, by nucleophilic substitution in acidic solution. In the ferrocene case, this is apparently favored by the stabilization of α-ferrocenyl carbocations,[9,10] while a similar stabilization in the α-position of (arene)chromium tricarbonyl complexes is less established. Stereoselective substitution in this position is therefore limited to special reaction conditions. There are only a few published examples.[6,11,12]

Recently we briefly reported a new methodology for the stereoselective replacement of the dimethylamino group of **1a** with chloroformic acid esters and the subsequent stereoselective nucleophilic substitution of the chloro substituent for a diphenylphosphanyl group.[13] We now wish to present a full report on the scope of this methology, which opens up a route to a large variety

(1) Part 8: Salzer, A.; Hosang, A.; Knuppertz, A.; Englert, U. *Eur. J. Inorg. Chem*., in press.
(2) Hayashi, T. in: *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995; p 105.
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(11) Davies, S. G.; Donohoe, T. J. *Synlett* **1993**, 323.
(12) Top, S.; Jaouen, G.; McGlinchey, M. *J. Chem. Soc., Chem Commun*. **1980**, 1110.
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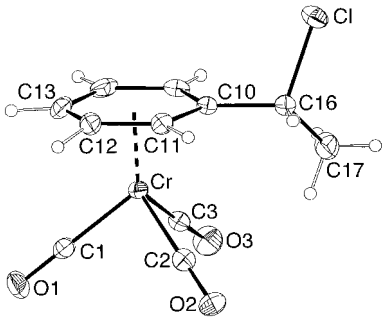


Figure 1. Molecular structure and crystallographic numbering scheme for (*R*)-[(1-chloroethyl)-η^6-benzene]Cr(CO)$_3$ (**2**; PLATON representation[15]). Ellipsoids are scaled to enclose 30% probability.

of (arene)chromium tricarbonyl complexes with both central and planar chirality.

Results and Discussion

1. Substitution of NMe$_2$ for Cl. Treatment of **1** with either ethyl chloroformate or chloroethyl chloroformate leads to clean substitution of the dimethylamino group and formation of (*R*)-[(1-chloroethyl)-η^6-benzene]Cr(CO)$_3$ (**2**) in 93% yield. The chloro ester reagents used are established for the conversion of tertiary amines into secondary amines, and it has been determined that the preference for leaving groups is benzyl > allyl > cyclohexyl > methyl.[14] The fate of the benzyl leaving group has not been investigated extensively, as the emphasis in this reaction has mainly been on the recovery of the amine. Therefore, it has never been established whether this reaction proceeds stereoselectively.

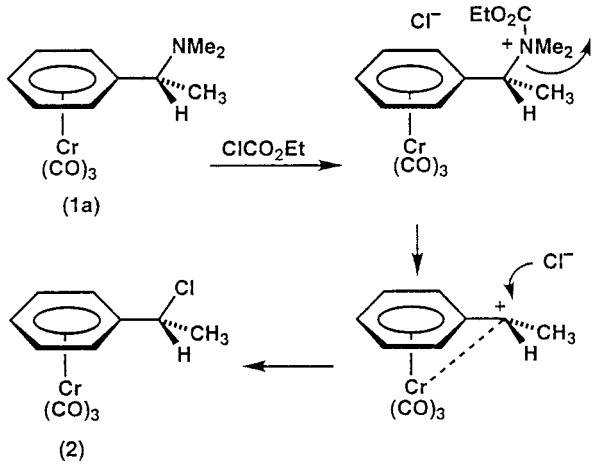
Compound **2** was found to be 96% enantiomerically pure by HPLC. As the organic amine also has an ee of 96%, the reaction is completely stereospecific.

We have performed the same reaction on uncoordinated (*R*)-{α-(dimethylamino)ethyl}benzene, but found among other products equal amounts of styrene and (α-chloroethyl)benzene. We were not able to completely separate these two compounds, but the sign of optical rotation of this mixture showed that the (α-chloroethyl)-benzene was mainly of the *S* configuration.

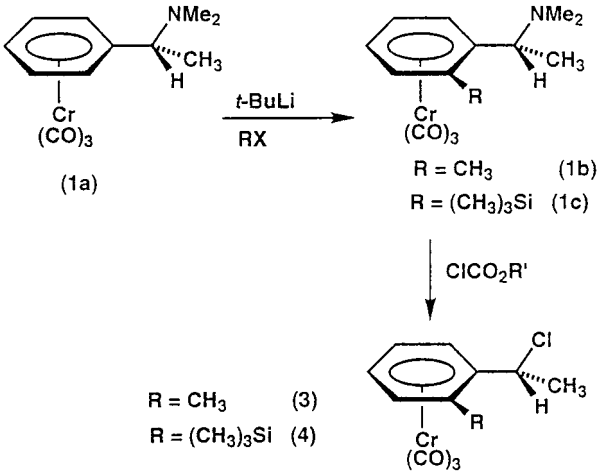
The absolute configuration of **2** could be determined by an X-ray crystal structure analysis and was found to be *R* (Figure 1). The reaction at the coordinated amine had therefore proceeded via retention of configuration. A possible mechanism is shown in Scheme 1.

This assumes that there is a stabilization of the benzylic carbocation through interaction with suitable metal orbitals, similar to the ferrocenyl moiety. The chloride then attacks the carbocation from the opposite side of the metal. This leads to overall retention of configuration but is occasionally referred to as "double inversion". Substitutions at the benzylic position of chromium arene complexes, as stated before, normally do not proceed with full retention of configuration, unless the nucleophile is present in large excess (i.e. the nucleophile is the solvent[12]) or if the carbocation is part of an annelated ring, where rotation of the side chain is impossible and the nucleophile always attacks from

Scheme 1



Scheme 2



the side opposite to the metal.[11] Neither condition is met in our case.

The reaction proceeds similarly if the arene ligand is substituted in the *ortho* position prior to amine to halide exchange. Diastereoselective metalation of **1a** with *t*-BuLi following the method by Davies[7] and subsequent electrophilic addition with MeI or (CH$_3$)$_3$SiCl leads to **1b** and **1c**, which were treated with ClCO$_2$R to generate (*pS*,*R*)-[1-(α-chloroethyl)-2-methyl-η^6-benzene]Cr(CO)$_3$ (**3**) and (*pR*,*R*)-[1-(α-chloroethyl)-2-(trimethylsilyl)-η^6-benzene]Cr(CO)$_3$ (**4**) in very good yields (Scheme 2).

2. Substitution of Cl for P, N, and O Nucleophiles. A chloride substituent, in contrast to the dimethylamino group, should be easily replacable by nucleophilic substitution. This proved to be the case, as treatment of **2** with lithium diphenylphosphide led to the formation of [{α-(diphenylphosphanyl)ethyl}-η^6-benzene]Cr(CO)$_3$ (**5**) in 61% yield. Enantiomeric excess was determined by complexation to bis[chloro{(*R*)-(dimethylamino-κN)phenyl-κC^1}palladium] to be 96% but after recrystallization reached >99%. The absolute conformation was also determined by X-ray structural analysis and was found to be *R*, which is somewhat contrary to expectation, as this type of reaction normally proceeds via a S_N2 mechanism and not via retention of configuration (Figure 2).

By the same method **3** can also be converted into the chiral phosphine (*pS*,*R*)-[1-{α-(diphenylphosphanyl)-

(14) Cooley, J. H.; Evain, E. J. *Synthesis* **1989**, 1.

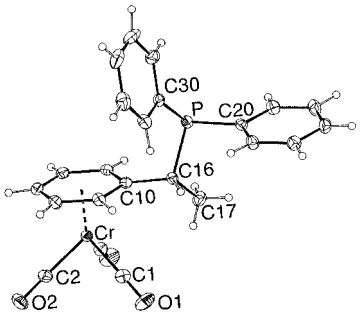
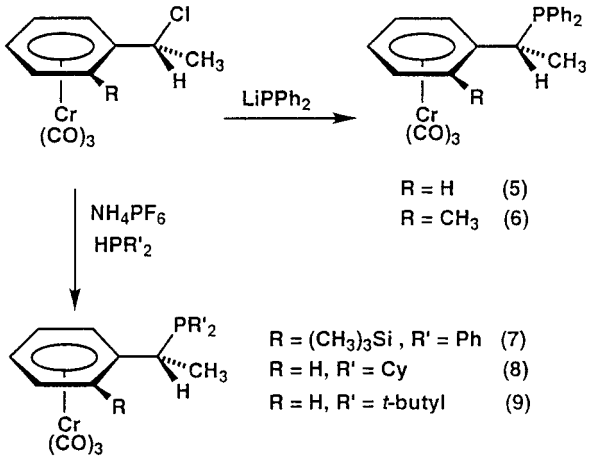


Figure 2. Molecular structure and crystallographic numbering scheme for (*R*)-[{α-(diphenylphosphanyl)ethyl}-η^6-benzene]Cr(CO)$_3$ (**5**; PLATON representation[15]). Ellipsoids are scaled to enclose 30% probability.

Scheme 3



ethyl}-2-methyl-η^6-benzene]Cr(CO)$_3$ (**6**), while **4** requires a somewhat modified method, namely the reaction with $HPPh_2$ in the presence of NH_4PF_6 (Scheme 3) to replace choride and generate (*pR,R*)-[1-{α-(diphenylphosphanyl)ethyl}-2-(trimethylsilyl)-η^6-benzene]Cr(CO)$_3$ (**7**) in 84% yield.

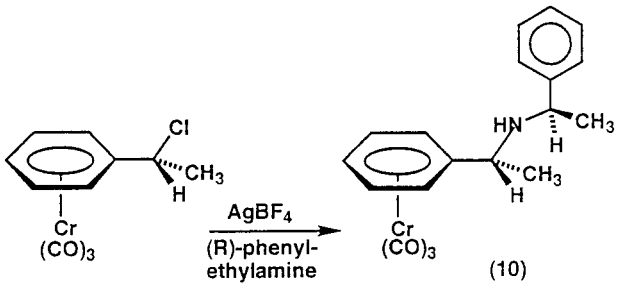
The same method also allows the introduction of alkylphosphines, which was not possible using lithium dialkylphosphides. By treatment of **2** with $HPCy_2$ or HP(*tert*-butyl)$_2$ in the presence of NH_4PF_6, the monophosphines(*R*)-[{α-(dicyclohexylphosphanyl)ethyl}-η^6-benzene]-Cr(CO)$_3$ (**8**) and (*R*)-[{α-(di-*tert*-butylphosphanyl)ethyl}-η^6-benzene]Cr(CO)$_3$ (**9**) could be isolated. Their enantiopurity was again checked by complexation to bis[chloro-{(*R*)-(dimethylamino-κN)phenyl-κC^1}palladium]. Only one diastereomer could be detected by ^{31}P NMR.

The diastereoselective formation of **3** and **4** as well as **6** and **7** is directly determined by NMR, as due to the presence of both planar and central chirality, any nonstereospecific substitution at the benzylic position would give rise to diastereomers. This is not the case, and all compounds are isolated with de > 98%.

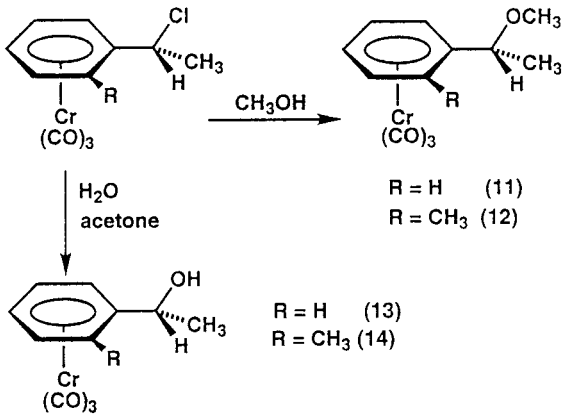
Compounds such as **2**−**4** are of considerable synthetic potential, as they should be suitable starting materials for the generation of other α-chiral arenes. We therefore investigated the substitution of the chloride substituent for nitrogen, oxygen, and carbon nucleophiles.

Reaction of **2** with (*R*)-α-phenylethylamine in the presence of $AgBF_4$ generated the amino complex **10**. The diastereomeric excess was determined by NMR to be between 89 and 92%, which is within the expected

Scheme 4



Scheme 5



range, considering that commercial (*R*)-α-phenylethylamine, incorporated twice into the molecule, has an ee of 96%. This replacement therefore is also diastereospecific (Scheme 4).

We had noted during our syntheses that **2**−**4** could be purified by chromatography over deactivated SiO_2 or Al_2O_3 without hydrolysis. This was in contrast to the analogous (α-chloroethyl)ferrocene, which we also prepared by the same method but which proved to be extremely sensitive to hydrolysis. Any reactions of the chromium complexes with oxygen nucleophiles were therefore expected to be rather slow. This was confirmed by the reaction of **2** with methanol, which required 2 h of reaction time in neat alcoholic solution. (*R*)-[(α-methoxyethyl)-η^6-benzene]Cr(CO)$_3$ (**11**) was again formed in quantitative yield in a completely stereoselective manner, as a comparison of $[\alpha]_D$ with the literature value[12] confirms. The same reaction was performed with planar-chiral **3**, which also established a de value of >98% for **12** (Scheme 5).

Jaouen had prepared compound **11** by starting from optically active (*R*)-[(α-hydroxyethyl)-η^6-benzene]Cr(CO)$_3$, which was protonated with H_2SO_4 in methanol as the solvent. This reaction proceeded with only 72% retention of configuration.[12] This clearly demonstrates that nucleophilic substitution at the benzylic position of chromium arene complexes is not always as selective as in the corresponding ferrocenyl compounds. The most likely explanation for this is a slow rotation around the $C_\alpha-C_{ipso}$ bond, as a competitive attack at the benzylic carbon from the *endo* side seems impossible.

The hydrolysis of benzyl chloride coordinated to Cr(CO)$_3$ according to Pettit[16] proceeds 10^4-10^5 times faster

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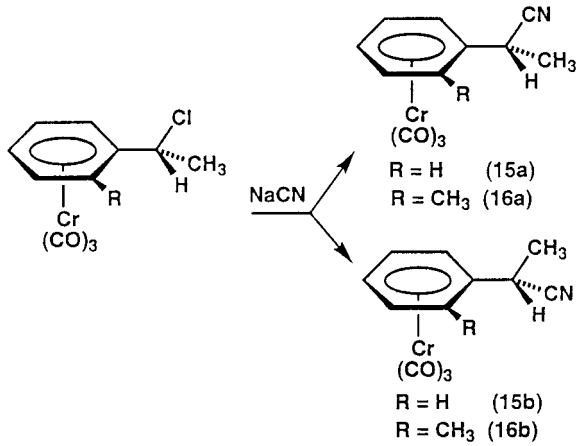
Scheme 6



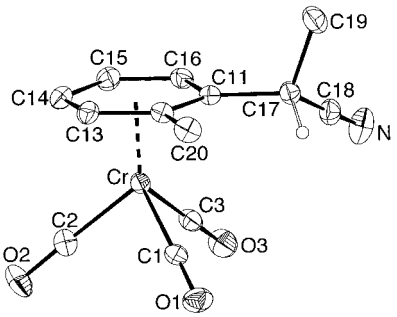
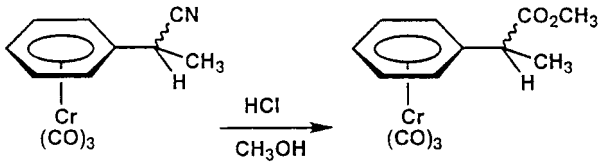


Figure 3. Molecular structure and crystallographic numbering scheme for (*pS,S*)-[1-(α-cyanoethyl)-2-methyl-η^6-benzene]Cr(CO)$_3$ (**16b**; PLATON representation[15]). Ellipsoids are scaled to enclose 30% probability.

Scheme 7



than that of uncomplexed benzyl chloride. Hydrolysis of **2**−**4**, as remarked before, is quite slow compared to that of the corresponding ferrocene. On reaction with water in acetone solution, **2** is completely hydrolyzed after 12 h to **13**. The $[\alpha]_D$ value confirms complete retention of configuration. **3** reacts likewise and (*pS,R*)-[1-(α-hydroxyethyl)-2-methyl-η^6-benzene]Cr(CO)$_3$ (**14**) is recovered in 91% yield as one single diastereomer (Scheme 5). Acetone is required in this reaction to make the chromium complex soluble.

3. Substitution of Cl for CN. Even more important than the stereoselective addition of O, N, or P nucleophiles would be the addition of C nucleophiles, as this would open the route to a large variety of chiral organic compounds. We have as yet only investigated the reaction of **2** and **3** with the cyanide anion. This reaction again requires acetone/water as the solvent for solubility reasons. To prevent hydrolysis, compounds **2** and **3** were dissolved in absolute acetone and a concentrated aqueous solution of NaCN was then slowly added. A clear solution was obtained after all $NaCN_{aq}$ had been added. [(α-cyanoethyl)-η^6-benzene]Cr(CO)$_3$ (**15**) and (*pS*)-[(α-cyanoethyl)-2-methyl-η^6-benzene]Cr(CO)$_3$ (**16**) could be isolated after workup in reasonable to good yields, but as a racemic mixture for **15**, as deduced from a lack of optical rotation of the compound, and as a 1:1 mixture of diastereomers for **16a**,**b** (Scheme 6).

In the case of **16**, we were able to separate both diastereomers by chromatography. The second fraction, recrystallized from ether, gave crystals suitable for X-ray diffraction. Due to the known configuration of planar chirality, we were able to establish the *S* configuration for **16b** (Figure 3).

It is interesting to note that the cyano group in **16b** does not adopt the *exo* position away from the Cr(CO)$_3$ moiety similar to Cl or PPh_2 in **2** and **5**. A possible reason may be that for the *S* isomer in this conformation, the methyl group in the *ortho* position is now close to the hydrogen atom at C_α, which minimizes steric interaction. This also seems to be the preferred conformation in solution as determined by ^{1}H NMR spectroscopy, where we observed a strong NOE in the *o*-CH_3 group on irradiation into the α-hydrogen. This was greater than the NOE at the *ortho* proton on irradiation in the benzylic methyl group. The NOE of the two methyl groups was quite small, which is again compatible with the conformation observed in the solid state. Similar experiments on **16a** also showed that the α-hydrogen has a closer proximity to the *o*-methyl group than to the *o*-hydrogen atom, which would be compatible with a preferred conformation as shown in Scheme 6, with the cyano group now occupying the *exo* position.

We did not detect any products of hydrolysis under these conditions, although the nucleophile H_2O was of course present in large excess. This signifies that CN^-, as expected, is the far better nucleophile. This may also be the reason for the complete lack of stereoselectivity, as a strong nucleophile may react with **2** and **3** not only via the postulated benzylic carbocation, which may form through a dissociation equilibrium in polar solvents, but also in a competitive reaction via an S_N2 type of reaction. This does not happen to a similar extent with the softer and far bulkier PPh_2 nucleophile.

The alternative explanation, that the benzylic carbocation under these reaction conditions has a longer lifetime and will thus undergo slow rotation, can be rejected, as then hydrolysis products should also be observed in the acetone/water system, but this was not the case. There are other possible explanations for the nonselectivity of this reaction, which we want to clarify by reactions on related bicyclic systems and with other carbon nucleophiles. This study is currently in progress. We have also observed that when the *ortho*position is occupied by a PPh_2 group, a high stereoselectivity of cyanide addition with a de of 82% is found. This will be reported in a later paper dealing with chromium arene complexes with two functional groups.

We have also been successful in converting racemic **15** into the corresponding ester via hydrolysis as an entry into the chemistry of profen-type α-chiral arene esters. This proved to be quite difficult with conventional methods, and we were only successful when using high concentrations of HCl gas in methanol. [{α-(methoxycarbonyl)ethyl}-η^6-benzene]Cr(CO)$_3$ (**17**) was isolated in 41% yield as a racemic mixture (Scheme 7).

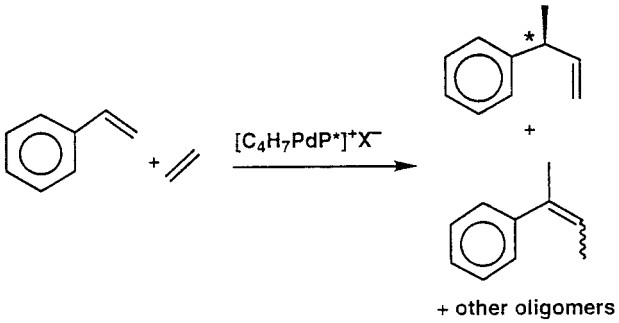
4. Asymmetric Hydrovinylation. Asymmetric hydrovinylation (Scheme 8) has been pioneered by

Table 1. Crystal Data, Data Collection Parameters, and Convergence Results for 2, 5, and 16b

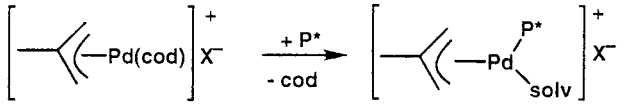
formula	$C_{11}H_9ClCrO_3$	$C_{23}H_{19}CrO_3P$	$C_{13}H_{11}CrNO_3$
fw	276.64	426.37	281.23
system	orthorhombic	orthorhombic	orthorhombic
space group (No.)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)
a, Å	9.311(3)	10.657(3)	8.657(3)
b, Å	9.316(2)	11.883(4)	11.192(2)
c, Å	12.838(7)	16.036(6)	12.505(7)
U, Å^3	1113.6(7)	2031(1)	1211.6(8)
Z	4	4	4
d_{calcd}, g cm^{-3}	1.65	1.39	1.54
μ, cm^{-1}	107.83	6.46	9.18
θ_{max}, deg	74.6	28	28
temp, K	203	203	273
λ, Å	1.5418	0.710 73	0.710 73
cryst dimens, mm^3	0.23 × 0.16 × 0.16	0.6 × 0.6 × 0.35	0.65 × 0.36 × 0.32
no. of rflns	3465	10232	6210
no. of indep obsd rflns with $I > 1.0\sigma(I)$	1950	4417	2686
no. of vars	145	329	163
Flack param	0.006(16)	−0.003(8)	−0.03(2)
R^a	0.044	0.032	0.034
$R_w{}^b$	0.050	0.031	0.037
GOF^c	1.099	0.801	0.914
res el dens, e Å^{-3}	0.466	0.438	0.515

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(F_o)$. ^{c} GOF $= [\sum w(|F_o| - |F_c|)^2/n_{observns} - n_{var}]^{1/2}$; $n_{observns}$ = no. of observations, n_{var} = no. of variables refined.

Scheme 8



Scheme 9



O°C, 60 min, solv = CH_2Cl_2

Bogdanovic[17] and Wilke[18] using nickel catalysts. Of special interest is the reaction between vinyl arenes and ethylene, as enantioselective codimerization provides a route to 2-arylpropionic acids.[19] A very efficient system was found using a ligand derived from myrtenal, which at −70 °C gave enantioselectivities of >95%.[18] In the Ni-catalyzed reaction, good results were also recently obtained by RajanBabu applying MOP ligands,[20] and the results obtained by Muller et al. are promising.[21]

We reported recently a catalytic system based on palladium for the hydrovinylation of styrene, leading to the codimer 3-phenyl-1-butene in high selectivity, yielding only small amounts of the isomerization products (*E*)- and (*Z*)-2-phenyl-2-butene. The ligand used was the diastereomerically pure *tert*-butyl(menthyl-*O*)-phenylphosphinite possessing a stereogenic P-atom, which gave ee values up to 87%.[22]

We had previously observed that phosphines with an optically active substituent based on an iron tricarbonyl moiety[23] gave very good product selectivity in the hydrovinylation reaction, but only moderate enantioselectivity.[24] We therefore tested our monophosphines **5**−**7** in the same reaction.

The catalysts applied were generated in situ by ligand exchange using [(η^3-C_4H_7)Pd(cod)]BF_4[22] as a precursor (Scheme 9). Results of the hydrovinylation reaction are shown in Table 2.

Even at room temperature, high activity and selectivity toward the codimers were observed with all ligands. Stability, activity, and chemo- and enantioselectivity increase with increasing steric demand of the *ortho* substituent R. Introduction of the trimethylsilyl group at this position (ligand **7**) therefore resulted in an excellent enantioselective system which belongs to the best Pd catalysts described so far for asymmetric hydrovinylation. Almost 70% conversion was observed within 15 min. The product was obtained in 78.5% ee, and only a small amount of isomerization products was detected in the reaction mixture. However, at higher conversions, isomerization of the product to internal achiral olefins took place. Therefore, after 0.5 h and at complete conversion, selectivity toward 3-phenylbut-1-ene has dropped to 48.5%. But even at those high conversions, chemoselectivity toward the codimers remained very good (∼98%). As we had previously observed, the consecutive isomerization reaction goes along with a kinetic resolution.[25] Due to this, the ee of

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Table 2. Results of Hydrovinylation Reactions

ligand	*t*/h	conversn[a]/%	yield$_{codim}$[b]/%	yield$_{3Ph1B}$[c]/%	S_{codim}[d]/%	S_{3Ph1B}[e]/%	ee/%
5	2	17.8	15.8	15.7	88.7	99.1	17.8
6	0.5	93.5	92.2	75.7	98.6	82.2	33.8
7	0.25	67.3	61.9	58.7	91.9	94.8	78.5
7	0.5	99.9	97.8	47.5	97.9	48.5	92.0

[a] Conversion of styrene. [b] Yield of codimers. [c] Yield of 3Ph1Bu. [d] ∑(codimers)/conversn. [e] (3Ph1Bu)/∑(codimers).

the product rises to 92% within 0.5 h. Another important feature is the remarkable stability of the catalytic system. No Pd (black) formation was observed after the reaction, which is quite unusual when using a monodentate phosphine ligand. It is assumed that the steric bulk of ligand **7** prevents the mixture from forming binuclear palladium species which can then lead to Pd (black) formation. The increasing stability and activity of the catalytic system as one goes from ligand **5** to **7** agrees with this explanation.

With the phosphorus attached to the palladium, the chromium tricarbonyl arene moiety can rotate around the C−C single bond of the ethyl group. Via this rotation, it is plausible that ligand **7** most efficiently shields one side of the active palladium species. This is believed to be the reason for both the excellent chemo- and enantioselectivity of the catalyst derived from **7**.

Experimental Section

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by standard methods. Chromatography was carried out with Merck silica gel 60. NMR spectra were recorded on a Varian Mercury 200 (200 MHz, ^{1}H; 50 MHz, ^{13}C; 81 MHz, ^{31}P) and a Varian Unity 500 (500 MHz, ^{1}H; 125 MHz, ^{13}C; 202 MHz, ^{31}P; 160 MHz, ^{11}B) at ambient temperature. Chemical shifts (δ) are given in ppm relative to $SiMe_4$. Melting points were measured on a H. Heidolph/Kelheim Typ 101.30 melting point apparatus. IR spectra were recorded on a Perkin-Elmer FT-IR Model 1720 X spectrometer. Optical rotations were measured in 1 dm cells on a Perkin-Elmer Model 241 polarimeter at ambient temperature. Mass spectra were obtained with a Finnigan MAT 95 spectrometer. Elemental analyses were obtained on a Carlo Erba Strumentazione element analyzer, Model 1106. The compounds (*R*)-[{(NMe_2)CHMe}C_6H_5]Cr$(CO)_3$ (**1a**), (*R,S*)-[{(NMe_2)CHMe}(Me)C_6H_4]Cr$(CO)_3$ (**1b**), and (*R,R*)-[{(NMe_2)CHMe}$(SiMe_3)C_6H_4$]Cr$(CO)_3$ (**1c**) were prepared by the published methods.[7,8] Bis[chloro{(*R*)-(dimethylamino-κN)-phenyl-κC^1}palladium] was prepared by the method of Otsuka.[26] Styrene was purchased from Fluka Co. and distilled from CaH_2 under argon. The ethylene used had a purity of >99.5%. [(η^3-C_4H_7)Pd(cod)]BF_4 was prepared by a literature procedure.[27] Catalytic experiments under pressure were carried out in 75 mL stainless steel autoclaves equipped with a magnetic stirring bar.

[η^6-(*R*)-(CHClMe)C_6H_5]Cr$(CO)_3$ (2). A stirred solution of **1a** (5.00 g, 17.5 mmol) in 350 mL of Et_2O was treated dropwise with ethyl chloroformate (2.17 g, 20.0 mmol) at −40 °C. The solution was stirred overnight without cooling, filtered, and then evaporated. The residue was recrystallized from methylene chloride/hexane at −30 °C to give **2** as yellow needles (4.52 g, 16.3 mmol, 93%). Mp: 49−50 °C. $[\alpha]_D$: −41.2° (*c* 1.49 in $CHCl_3$). IR ($CHCl_3$): ν_{CO} 1969, 1894 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 4.59 (dm, 1H, Ar *H*), 4.51 (dm, 1H, Ar *H*), 4.33−4.23 (m, 3H, Ar *H*), 4.11 (q, 1H, J = 6.8 Hz, C*H*ClCH$_3$), 1.31 (d, 3H, J = 6.8 Hz, CHClC*H*$_3$). ^{13}C NMR (50 MHz, C_6D_6): δ 232.72 (*C*O), 110.98 (*ipso* Ar *C*), 93.63 (Ar *C*), 92.40 (Ar *C*), 91.33 (Ar *C*), 90.98 (Ar *C*), 90.07 (Ar *C*), 56.73 (*C*HClCH$_3$), 23.71 (CHCl*C*H$_3$). Anal. Calcd for $C_{11}H_9ClCrO_3$: H, 3.28; C, 47.76. Found: H, 3.22; C, 47.65. MS: *m/z* 276 (19%, M$^{\bullet+}$), 240 (20%, M$^{\bullet+}$ − HCl), 192 (10%, M$^{\bullet+}$ − [3 × CO]), 156 (179%, M$^{\bullet+}$ − [3 × CO] − [HCl]), 105 (100%, M$^{\bullet+}$ − [Cr$(CO)_3$] − [Cl]), 52 (83%, Cr).

(*R*)-α-Ferrocenylethyl Chloride. A stirred solution of (α-ferrocenylethyl)dimethylamine (0.90 g, 3.50 mmol) in 70 mL of Et_2O was treated dropwise with 1-chloroethyl chloroformate (0.50 g, 3.99 mmol) at −40 °C. The resulting solution was stirred overnight without cooling, filtered, and then evaporated. The residue was recrystallized from Et_2O/hexane at −30 °C to give 0.47 g (1.89 mmol, 54%) of (*R*)-α-ferrocenylethyl chloride as orange crystals. ^{1}H NMR (500 MHz, C_6D_6): δ 4.71 (q, 1H, J = 6.7 Hz, C*H*ClCH$_3$), 4.07 (q, 1H, J = 1.5 Hz, Cp *H*), 3.99 (q, 1H, J = 1.5 Hz, Cp *H*), 3.90 (s, 5H, Cp *H*), 3.89 (d, 2H, J = 1.8 Hz, Cp *H*), 1.59 (d, 3H, J = 6.7 Hz, CHClC*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 91.02 (*ipso* Cp *C*), 69.16 (5C, Cp *C*), 68.73 (Cp *C*), 68.42 (Cp *C*), 68.35 (Cp *C*), 66.05 (Cp *C*), 56.53 (*C*HClCH$_3$), 25.28 (CHCl*C*H$_3$).

(*S*)-(1-Chloroethyl)benzene. To a solution of (*R*)-(α-phenylethyl)dimethylamine (5.00 g, 33.50 mmol) in 50 mL of THF was added ethyl chloroformate (4.14 g, 38.19 mmol) at 0 °C. The reaction mixture was warmed to room temperature and refluxed for 1 h, and the solvent was removed. The residue was dissolved in Et_2O and filtered. The solution was evaporated and the residue distilled to give a mixture of styrene, carbamate ester, and (*S*)-1-chloroethylbenzene.[28]

[η^6-(*R*)-{CH(PPh_2)Me}C_6H_5]Cr$(CO)_3$ (5). (a) Diphenylphosphine (0.63 mL, 3.61 mmol) in THF (90 mL) was treated dropwise with *n*-BuLi (1.6 M in hexane, 2.26 mL, 3.61 mmol) at −78 °C. After the mixture was stirred at −78 °C for 1 h, a solution of **2** (1.00 g, 3.61 mmol) in THF (5 mL) was added dropwise. The reaction mixture was warmed overnight, and the solvent was removed. The residue was dissolved in Et_2O and the solution filtered. The solution was evaporated and the residue chromatographed on silica gel (elution with ethyl acetate). Pure product **5** was isolated as yellow needles by crystallization from ethyl acetate/hexane at room temperature (0.94 g, 2.20 mmol, 61%).

(b) To compound **2** (0.59 g, 2.13 mmol) in 40 mL of acetone was added diphenylphosphine (0.45 mL, 2.56 mmol) and NH_4PF_6 (0.42 g, 2.56 mmol) at room temperature. The resulting mixture was stirred overnight, treated with NEt_3 (5 mL), filtered, and then evaporated. The residue was purified by chromatography on silica gel (elution with dichloromethane) and recrystallized from ethyl acetate/hexane at room temperature to give **5** as yellow crystals (0.41 g, 0.95 mmol, 45%). Mp: 150 °C. UV: 317 nm^{-1}. IR ($CHCl_3$): ν_{max} 1968, 1894 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 7.37−6.87 (m, 10H, Ar *H*(Ph)), 4.65 (brd, 1H, *ortho* Ar *H*), 4.38 (trd, 1H, J = 6.4 Hz, J = 1.2 Hz, Ar *H*), 4.32 (trtr, 1H, J = 6.3 Hz, Ar *H*), 4.21 (brd, 1H, *ortho* Ar *H*), 4.11 (trd, 1H, J = 6.3 Hz, J = 1.2 Hz, Ar *H*), 2.96 (dq, 1H, J = 7.0 Hz, J_{PH} = 3.7 Hz, C*H*(PPh_2)CH$_3$), 1.30 (dd, 3H, J_{PH} = 13.7 Hz, J = 7.0 Hz, CH(PPh_2)C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 233.78 (*C*O), 136.29 (d, J_{CP} = 17.7 Hz, *ipso* Ar *C*(Ph)), 135.70 (d, J_{CP} = 17.7 Hz, *ipso* Ar *C*(Ph)), 134.25−128.87 (10C, Ar *C*(Ph)), 115.34 (d, J_{CP} = 14.7 Hz, *ipso*

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Ar *C*), 95.83 (Ar *C*), 92.13 (Ar *C*), 91.88 (Ar *C*), 91.77 (d, J_{CP} = 5.5 Hz, Ar *C*), 90.86 (Ar *C*), 37.34 (d, J_{CP} = 17.7 Hz, *C*H(PPh$_2$)-CH$_3$), 17.38 (d, J_{CP} = 18.9 Hz, CH(PPh$_2$)*C*H$_3$). ^{31}P NMR (202 MHz, C_6D_6): δ +10.39. Anal. Calcd for $C_{23}H_{19}CrO_3P$: H, 4.49; C, 64.79. Found: H, 4.49; C, 64.83. $[\alpha]_D^{\text{room temp}}$: −17.8° (*c* 1.23 in $CHCl_3$).

Determination of the Enantiomeric Purity of 5. To a solution of **5** in $CDCl_3$ was added a solution of bis[chloro{(*R*)-(dimethylamino-κN)phenyl-κC^1}palladium] in $CDCl_3$. The NMR spectrum was measured after 5 min. ^{31}P NMR (81 MHz, $CDCl_3$): δ +49.44 (*R*,*R* complex). racemic **5**: ^{31}P NMR (81 MHz, $CDCl_3$) δ +50.16 (*S*,*R* complex), + 49.44 (*R*,*R* complex).

[η^6-(*R*)-{CH(PCy$_2$)Me}C$_6$H$_5$]Cr(CO)$_3$ (8). To compound **2** (0.59 g, 2.13 mmol) in 40 mL of acetone was added dicyclohexylphosphine (0.52 mL, 2.56 mmol) and NH_4PF_6 (0.42 g, 2.56 mmol) at room temperature. Workup was carried out as for **5**. After removal of the solvent, 0.88 g of **8** was isolated as a light yellow powder (2.01 mmol, 94%). It is possible to crystallize the complex from ethyl acetate/hexane at −30 °C to give light-yellow crystals. IR ($CHCl_3$): ν_{max} 1968, 1895 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 4.86 (d, 1H, J = 6.7 Hz, Ar *H*), 4.65 (d, 1H, J = 6.4 Hz, Ar *H*), 4.50 (tr, 2H, J = 6.3 Hz, Ar *H*), 4.38 (tr, 1H, J = 6.3 Hz, Ar *H*), 2.62 (q, 1H, J = 7.0 Hz, C*H*(PCy$_2$)-CH$_3$), 1.66−1.46 (br m, 10H, Cy *H*), 1.32 (br tr, 2H, Cy *H*), 1.25 (dd, 3H, J_{HP} = 9.3 Hz, J = 7.0 Hz, CH(PCy$_2$)C*H*$_3$), 1.18−1.00 (m, 10H, Cy *H*). ^{13}C NMR (125 MHz, C_6D_6): δ 233.80 (*C*O), 118.55 (d, J_{CP} = 12.6 Hz, *ipso* Ar *C*), 95.01 (d, J_{CP} = 7.2 Hz, Ar *C*), 92.24 (Ar *C*), 92.15 (Ar *C*), 91.40 (Ar *C*), 90.77 (d, J_{CP} = 3.9 Hz, Ar *C*), 33.06 (d, $^1J_{CP}$ = 20.3 Hz, Cy *C*), 32.41 (d, $^1J_{CP}$ = 19.2 Hz, *C*H(PCy$_2$)CH$_3$), 32.22 (d, $^1J_{CP}$ = 15.5 Hz, Cy *C*), 31.68 (d, J_{CP} = 14.2 Hz, Cy *C*), 31.29 (d, J_{CP} = 14.8 Hz, Cy *C*), 31.11 (d, J_{CP} = 13.1 Hz, Cy *C*), 30.68 (d, J_{CP} = 10.4 Hz, Cy *C*), 27.81 (d, J_{CP} = 9.8 Hz, Cy *C*), 27.67 (Cy *C*), 27.60 (Cy *C*), 27.56 (d, J_{CP} = 9.9 Hz, Cy *C*), 26.63 (d, 2C, J_{CP} = 3.3 Hz, Cy *C*), 16.73 (d, J_{CP} = 10.9 Hz, CH(PCy$_2$)*C*H$_3$). ^{31}P NMR (81 MHz, C_6D_6): δ +24.99. Anal. Calcd for $C_{23}H_{31}CrO_3P$: H, 7.13; C, 63.00. Found: H, 7.30; C, 63.17. $[\alpha]_D^{\text{room temp}}$: −22° (*c* 1.03 in $CHCl_3$).

Enantiomeric Purity of 8. To a solution of **8** in $CDCl_3$ was added a solution of bis[chloro{(*R*)-(dimethylamino-κN)-phenyl-κC^1}palladium] in $CDCl_3$. The NMR spectrum was measured as soon as possible. ^{31}P NMR (81 MHz, $CDCl_3$): δ +53.25 (*R*,*R* complex). racemic **8**: ^{31}P NMR (81 MHz, $CDCl_3$) δ +53.25 (*R*,*R* complex), +51.42 (*S*,*R* complex).

[η^6-(*R*)-{CHP^{t}Bu$_2$Me}C$_6$H$_5$]Cr(CO)$_3$ (9). To compound **2** (0.28 g, 1.00 mmol) in 40 mL of acetone was added di-*tert*-butylphosphine (0.22 mL, 1.20 mmol) and NH_4PF_6 (0.20 g, 1.20 mmol) at room temperature. Workup was carried out as for **5**. After removal of the solvent, 0.30 g of **9** was isolated as a light yellow powder (0.78 mmol, 78%). The complex can be crystallized from ethyl acetate/hexane at −30 °C. IR ($CHCl_3$): ν_{max} 1966, 1892 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 5.18 (dd, 1H, J = 7.0 Hz, J = 1.1 Hz, Ar *H*), 4.60−4.57 (m, 1H, Ar *H*), 4.53 (trd, 1H, J = 6.4 Hz, J = 1.2 Hz, Ar *H*), 4.34 (trtr, 1H, J = 6.1 Hz, J = 1.1 Hz, Ar *H*), 2.80 (qd, 1H, J = 7.3 Hz, J_{HP} = 2.8 Hz, C*H*(P^{t}Bu$_2$)CH$_3$), 1.36 (dd, 3H, J = 7.6 Hz, J_{HP} = 3.4 Hz, CH(P^{t}Bu$_2$)C*H*$_3$), 1.09 (d, 9H, J_{HP} = 11.0 Hz, C(C*H*$_3$)), 0.96 (d, 9H, J_{HP} = 11.0 Hz, C(C*H*$_3$)). ^{13}C NMR (125 MHz, C_6D_6): δ 233.96 (*C*O), 120.04 (d, J_{CP} = 25.8 Hz, *ipso* Ar *C*), 96.40 (d, J_{CP} = 16.5 Hz, Ar *C*), 93.30 (Ar *C*), 92.40 (Ar *C*), 90.63 (Ar *C*), 90.39 (d, J_{CP} = 2.7 Hz, Ar *C*), 35.17 (d, $^1J_{CP}$ = 34.5 Hz, *C*H-(P^{t}Bu$_2$)CH$_3$), 34.52 (d, $^1J_{CP}$ = 32.3 Hz, *C*(CH$_3$)), 33.14 (d, $^1J_{CP}$ = 26.9 Hz, *C*(CH$_3$)), 30.99 (d, J_{CP} = 14.2 Hz, C(*C*H$_3$)), 30.54 (d, J_{CP} = 13.2 Hz, C(*C*H$_3$)), 14.56 (d, J_{CP} = 2.2 Hz, CH(P^{t}Bu$_2$)-*C*H$_3$). ^{31}P NMR (81 MHz, C_6D_6): δ +61.38. Anal. Calcd for $C_{19}H_{27}CrO_3P$: H, 7.04; C, 59.06. Found: H, 7.38; C, 59.08. $[\alpha]_D^{\text{room temp}}$: −136° (*c* 0.76 in $CHCl_3$).

[η^6-(*R*)-{((C$_6$H$_5$(Me)CH)NH)(Me)CH}C$_6$H$_5$]Cr(CO)$_3$ (10). To compound **2** (1.50 g, 5.42 mmol) in 30 mL of dichloromethane was added (*R*)-α-phenylethylamine (0.79 g, 6.51 mmol) and $AgBF_4$ (1.27 g, 6.51 mmol) at room temperature. The resulting mixture was stirred overnight, treated with NEt_3 (5 mL), filtered, and then evaporated. The residue was purified by chromatography on silica gel (elution with ethyl ether/hexane 1:4). After removal of the solvent, 1.08 g (2.99 mmol, 55%) of **10** was isolated as a yellow oil which crystallized on cooling to 5 °C. IR ($CHCl_3$): ν_{max} 1970, 1897 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 7.22−7.09 (m, 5H, Ar *H*(Ph$_{uncompl}$)), 5.13 (d, 1H, J = 6.4 Hz, Ar *H*), 4.69 (d, 1H, J = 5.8 Hz, Ar *H*), 4.55 (tr m, 1H, Ar *H*), 4.42−4.38 (m, 2H, Ar *H*), 3.75 (br m, 1H, C*H*(NHR)CH$_3$), 3.05 (q, 1H, J = 6.4 Hz, C*H*(NHR$_{uncompl}$)-CH$_3$), 1.20 (d, 3H, J = 6.4 Hz, CH(NHR$_{uncompl}$)C*H*$_3$), 1.02 (br m, 1H, N*H*), 0.91 (d, 1H, J = 6.7 Hz, CH(NHR)C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 233.71 (*C*O), 146.18 (*ipso* Ar *C*(Ph$_{uncompl}$)), 128.71 (2C, Ar *C*(Ph$_{uncompl}$)), 127.14 (Ar *C*(Ph$_{uncompl}$)), 126.54 (Ar *C*(Ph$_{uncompl}$)), 116.69 (*ipso* Ar *C*), 94.11 (Ar *C*), 94.04 (Ar *C*), 93.42 (Ar *C*), 91.02 (Ar *C*), 90.59 (Ar *C*), 55.83 (*C*H(NHR)-CH$_3$), 53.26 (*C*H(NHR$_{uncompl}$)CH$_3$), 24.98 (CH(NHR)*C*H$_3$), 24.52 (CH(NHR$_{uncompl}$)*C*H$_3$). Anal. Calcd for $C_{19}H_{19}CrNO_3$: H, 5.30; C, 63.10; N, 3.88. Found: H, 5.33; C, 62.74; N, 3.54. $[\alpha]_D^{\text{room temp}}$: +36° (*c* 0.95 in $CHCl_3$).

[η^6-(*R*)-{CH(OMe)Me}C$_6$H$_5$]Cr(CO)$_3$ (11). Compound **2** (0.81 g, 2.93 mmol) was dissolved in 40 mL of methanol, and the mixture was stirred at room temperature for 2 h. Evaporation of the solvent affords 0.80 g of the desired compound (2.93 mmol, 100%). IR ($CHCl_3$): ν_{max} 1964, 1886 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 4.98 (d, 1H, J = 6.4 Hz, Ar H), 4.50 (d, 1H, J = 6.1 Hz, Ar H), 4.45−4.36 (m, 3H, Ar H), 3.50 (q, 1H, J = 6.4 Hz, C*H*(OCH$_3$)CH$_3$), 3.10 (s, 3H, OC*H*$_3$), 1.04 (d, 3H, J = 6.4 Hz, CH(OCH$_3$)C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 233.42 (*C*O), 113.86 (*ipso* Ar *C*), 92.17 (Ar C), 91.70 (Ar C), 91.64 (Ar C), 91.25 (Ar C), 90.61 (Ar C), 76.72 (*C*H(OCH$_3$)-CH$_3$), 56.93 (OCH$_3$), 22.28 (CH(OCH$_3$)*C*H$_3$). $[\alpha]_D^{\text{room temp}}$: +55° (*c* 0.99 in $CHCl_3$).

[η^6-(*R*)-{CH(OH)Me}C$_6$H$_5$]Cr(CO)$_3$ (13). Compound **2** (1.00 g, 3.61 mmol) was dissolved in a mixture of 50 mL of acetone and 14 mL of water at room temperature. The resulting solution was stirred for 12 h and the solvent evaporated. The residue was separated from byproducts by chromatography on silica gel with dichloromethane. The hydroxy complex can be eluted with Et_2O. After removal of the solvent, 0.46 g of **13** was isolated as a yellow oil (1.78 mmol, 49%). IR ($CHCl_3$): ν_{max} 1972, 1899 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 5.08 (d, 1H, J = 6.1 Hz, Ar *H*), 4.57 (tr, 1H, J = 6.4 Hz, Ar *H*), 4.51 (d, 2H, J = 3.4 Hz, Ar *H*), 4.46−4.43 (m, 1H, Ar *H*), 4.03 (q, 1H, J = 6.4 Hz, C*H*(OH)CH$_3$), 1.85 (s, 1H, O*H*), 1.07 (d, 3H, J = 6.4 Hz, CH(OH)C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 233.64 (*C*O), 117.49 (*ipso* Ar *C*), 92.79 (Ar *C*), 92.55 (Ar *C*), 92.13 (Ar *C*), 90.87 (Ar *C*), 89.95 (Ar *C*), 67.86 (*C*H(OH)CH$_3$), 25.07 (CH-(OH)*C*H$_3$). $[\alpha]_D^{\text{room temp}}$: −9° (*c* 1.58 in $CHCl_3$).

[η^6-{CH(CN)Me}C$_6$H$_5$]Cr(CO)$_3$ (15a,b). Compound **2** (2.00 g, 7.23 mmol) was dissolved in a mixture of 120 mL of acetone and 12 mL of degassed water; NaCN was added (0.43 g, 8.68 mmol), and the resulting solution was stirred for 12 h at room temperature. After evaporation of the solvent under high vacuum, the residue was taken up in ethyl acetate and the resulting suspension was filtered. The crude product was purified by crystallization from ethyl acetate/hexane at −30 °C to give 1.45 g (5.43 mmol, 75%) of the nitrile **15a**,**b**. IR ($CHCl_3$): ν_{max} 1980, 1910 (CO), 2248 (CN) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 4.63 (d tr, 1H, J = 6.4 Hz, J = 1.2 Hz, Ar *H*), 4.31 (trd, 1H, J = 6.1 Hz, J = 1.5 Hz, Ar *H*), 4.27 (trd, 1H, J = 6.1 Hz, J = 1.5 Hz, Ar *H*), 4.24 (trtr, 1H, J = 6.1 Hz, J = 1.2 Hz, Ar *H*), 4.13 (d tr, 1H, J = 6.4 Hz, J = 1.5 Hz, Ar *H*), 2.57 (q, 1H, J = 7.3 Hz, C*H*(CN)CH$_3$), 0.80 (d, 1H, J = 7.3 Hz, CH(CN)C*H*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 232.14 (*C*O), 119.45 (*C*N), 107.01 (*ipso* Ar *C*), 91.77 (Ar *C*), 91.58 (Ar *C*), 91.31 (Ar *C*), 90.72 (Ar *C*), 90.40 (Ar *C*), 30.11 (*C*H(CN)CH$_3$), 20.07 (CH(CN)*C*H$_3$). Anal. Calcd for $C_{12}H_9CrNO_3$: H, 3.40; C, 53.94; N, 5.24. Found: H, 3.34; C, 53.74; N, 4.91.

[η^6-{CH(COOMe)Me}C$_6$H$_5$]Cr(CO)$_3$ (17). 15a,**b** (0.33 g, 1.23 mmol) was dissolved in 100 mL of methanol and treated for 4 h with hydrogen chloride gas. To isolate pure product,

the solvent was removed under vacuum and the crude mixture was purified twice using chromatographic techniques, first with ethyl acetate as eluent, followed by Et_2O/hexane (3:1). This afforded the desired product as a yellow oil (0.15 g, 0.50 mmol, 41%). IR ($CHCl_3$): ν_{max} 1973, 1901 (CO), 1736 (COOMe) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 4.95 (d, 1H, $J = 7.0$ Hz, Ar *H*), 4.60 (d, 1H, $J = 5.8$ Hz, Ar *H*), 4.38 (br tr, 1H, Ar *H*), 4.32 (br tr, 2H, Ar *H*), 3.29 (s, 3H, OCH_3), 2.97 (q, 1H, $J = 7.3$ Hz, $CH(COOCH_3)CH_3$), 1.15 (d, 3H, $J = 7.3$ Hz, $CH(COOCH_3)CH_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 233.04 (*C*O), 172.72 (*C*OOCH$_3$), 110.08 (*ipso* Ar *C*), 94.25 (Ar *C*), 92.74 (Ar *C*), 92.60 (Ar *C*), 91.25 (Ar *C*), 91.23 (Ar *C*), 51.77 (OCH_3), 43.78 (*C*H(COOCH$_3$)CH$_3$), 17.92 (CH(COOCH$_3$)*C*H$_3$). Anal. Calcd for $C_{13}H_{12}CrO_5$: H, 4.03; C, 52.01. Found: H, 4.25; C, 52.70.

[η^6-(*R,S*)-*o*-(CHClMe)(Me)C_6H_4]Cr(CO)$_3$ (3). A stirred solution of **1b** (1.85 g, 6.18 mmol) in 120 mL of Et_2O was treated dropwise with ethyl chloroformate (0.77 g, 7.05 mmol) at −40 °C. The reaction mixture was stirred overnight without cooling and then filtered and evaporated. The residue was recrystallized from Et_2O/hexane at −30 °C to give 1.70 g (5.85 mmol, 95%) of **3** as yellow crystals. Dec pt: ∼95 °C**.** IR ($CHCl_3$): ν_{max} 1971, 1898 (CO) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 4.81 (d, 1H, $J = 6.1$ Hz, Ar *H*), 4.50−4.43 (m, 2H, Ar *H*, H-4), 4.18 (br tr, 1H, Ar *H*), 4.11 (d, 1H, $J = 5.8$ Hz, Ar *H*), 1.72 (s, 3H, *o*-CH_3), 1.41 (d, 3H, $J = 6.4$ Hz, CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 232.95 (*C*O), 109.30 (*ipso* Ar *C*), 108.32 (*ipso* Ar *C*), 94.25 (Ar *C*), 92.77 (Ar *C*), 91.16 (Ar *C*), 89.06 (Ar *C*), 53.76 (*C*HClCH$_3$), 22.52 (CHCl*C*H$_3$), 17.89 (*o*-*C*H$_3$). Anal. Calcd for $C_{12}H_{11}ClCrO_3$: H, 3.81; C, 49.59. Found: H, 3.78; C, 49.24. $[\alpha]_D^{room\ temp}$: +52.13° (*c* 1.36 in $CHCl_3$).

[η^6-(*R,S*)-*o*-{CH(PPh$_2$)Me}(Me)C_6H_4]Cr(CO)$_3$ (6). Diphenylphosphine (0.80 mL, 4.58 mmol) in THF (100 mL) was cooled to −78 °C and treated dropwise with *n*-BuLi (1.6 M in hexane, 2.86 mL, 4.58 mmol). After the mixture was stirred at −78 °C for 1 h, a solution of **3** (1.00 g, 3.61 mmol) in THF (5 mL) was added dropwise. Workup was carried out as described for **5**, and chromatography on silica gel (Et_2O/hexane 1:4) gave 0.95 g (2.32 mmol, 51%) of **6** as a yellow powder. It is possible to crystallize complex **6** at room temperature from ethyl acetate/hexane. IR ($CHCl_3$): ν_{max} 1964, 1891 (CO) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 7.37 (trm, 2H, Ar *H*(Ph)), 7.12 (trm, 3H, Ar *H*(Ph)), 6.95 (trm, 2H, Ar *H*(Ph)), 6.90 (trm, 1H, Ar *H*(Ph)), 6.83 (trm, 2H, Ar *H*(Ph)), 4.98 (d, 1H, $J = 6.4$ Hz, Ar *H*), 4.62 (dtr, 1H, $J = 6.1$ Hz, $J = 0.9$ Hz, Ar *H*), 4.35 (dtr, 1H, $J = 6.4$ Hz, $J = 1.2$ Hz, Ar *H*), 4.18 (dd, 1H, $J = 6.4$ Hz, $J = 0.9$ Hz, Ar *H*)), 3.35 (dq, 1H, $J = 7.0$ Hz, $^2J_{HP} = 4.3$ Hz, C*H*(PPh$_2$)CH$_3$), 1.42 (s, 3H, *o*-CH_3), 1.32 (dd, 3H, $^3J_{HP} = 12.2$ Hz, $J = 7.0$ Hz, CH(PPh$_2$)CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 234.10 (*C*O), 136.55 (d, $J_{CP} = 18.1$ Hz, *ipso* Ar *C*(Ph)), 134.59 (d, $J_{CP} = 17.5$ Hz, *ipso* Ar *C*(Ph)), 134.64−128.27 (10C, Ar *C*(Ph)), 114.28 (d, $^2J_{CP} = 15.9$ Hz, *ipso* Ar *C*), 110.13 (d, $^3J_{CP} = 2.2$ Hz, *ipso* Ar *C*), 94.17 (Ar *C*), 94.17 (d, $J_{CP} = 8.8$ Hz, Ar *C*), 91.76 (Ar *C*), 89.15 (Ar *C*), 32.17 (d, $J_{CP} = 18.1$ Hz, *C*H(PPh$_2$)CH$_3$), 18.86 (d, $J_{CP} = 2.2$ Hz, *o*-*C*H$_3$), 18.63 (d, $J_{CP} = 16.5$ Hz, CH(PPh$_2$)*C*H$_3$). ^{31}P NMR (81 MHz, C_6D_6): δ +10.41. Anal. Calcd for $C_{24}H_{21}CrO_3P$: H, 4.81; C, 65.45. Found: H, 5.16; C, 65.68.

[η^6-(*R,S*)-*o*-{CH(OMe)Me}(Me)C_6H_4]Cr(CO)$_3$ (12). Compound **3** (0.16 g, 0.55 mmol) was dissolved in 10 mL of methanol, and the solution was stirred at room temperature for 2 h. Evaporation of the solvent gave 0.16 g of the desired complex **12** (0.55 mmol, 100%). IR ($CHCl_3$): ν_{max} 1968, 1893 (CO) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 5.13 (dd, 1H, $J = 6.6$ Hz, $J = 1.0$ Hz, Ar *H*), 4.65 (trd, 1H, $J = 6.4$ Hz, $J = 1.2$ Hz, Ar *H*), 4.34−4.26 (md, 2H, $J = 6.4$, $J = 1.2$ Hz, Ar *H*), 3.81 (q, 1H, $J = 6.4$ Hz, C*H*(OCH$_3$)CH$_3$), 2.87 (s, 3H, OCH_3), 1.76 (s, 3H, *o*-CH_3), 1.23 (d, 3H, $J = 6.4$ Hz, CH(OCH$_3$)CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 232.02 (*C*O), 109.05 (*ipso* Ar *C*), 108.65 (*ipso* Ar *C*)), 93.51 (Ar *C*), 92.39 (Ar *C*), 90.66 (Ar *C*), 86.77 (Ar *C*), 72.46 (*C*H(OCH$_3$)CH$_3$), 54.18 (OCH_3), 18.15 (CH(OCH_3)CH$_3$), 16.79 (*o*-*C*H$_3$). Anal. Calcd for $C_{13}H_{14}CrO_4$: H, 4.93; C, 54.55. Found: H, 4.98; C, 54.60.

[η^6-(*R,S*)-*o*-{CH(OH)Me}(Me)C_6H_4]Cr(CO)$_3$ (14). Compound **3** (1.09 g, 3.75 mmol) was dissolved in a mixture of 60 mL of acetone and 41 mL of water at room temperature. Reaction and workup was carried out as for **13**. After removal of the solvent, 0.46 g of **14** was isolated as a yellow solid (0.93 mmol, 91%). IR ($CHCl_3$): ν_{max} 1969, 1895 (CO) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 5.05 (d, 1H, $J = 6.4$ Hz, Ar *H*), 4.71 (tr, 1H, $J = 6.1$ Hz, Ar *H*), 4.42 (tr, 1H, $J = 6.1$ Hz, Ar *H*), 4.36 (d, 1H, $J = 6.1$ Hz, Ar *H*), 4.23 (br q, 1H, C*H*(OH)CH$_3$), 1.87 (s, 3H, *o*-CH_3), 1.61 (br s, 1H, O*H*), 1.18 (d, 3H, $J = 6.4$ Hz, CH(OH)CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 233.77 (*C*O), 112.27 (*ipso* Ar *C*), 109.98 (*ipso* Ar *C*), 94.85 (Ar *C*), 93.29 (2C, Ar *C*), 88.97 (Ar *C*), 66.09 (*C*H(OH)CH$_3$), 22.34 (CH(OH)*C*H$_3$), 18.20 (*o*-*C*H$_3$). Anal. Calcd for $C_{12}H_{12}CrO_4$: H, 4.44; C, 52.95. Found: H, 4.57; C, 53.05.

[η^6-*o*-{CH(CN)Me}(Me)C_6H_4]Cr(CO)$_3$ (16a,b). Compound **3** (1.05 g, 3.61 mmol) was dissolved in a mixture of 50 mL of acetone and 5 mL of degassed water; NaCN was added (0.21 g, 4.33 mmol). Further reaction and workup was carried out as for **15a**,**b**. The crude product was purified by chromatography (Et_2O/hexane 1:1), which also allowed separation of the two diastereomers. The first diastereomer was **(p*S,R*)-16a**, which crystallized as yellow needles from Et_2O/hexane at −30 °C (0.26 g, 0.92 mmol, 26%). The second diastereomer was **(p*S,S*)-16b**, which crystallized as orange needles from Et_2O at −30 °C (0.27 g, 0.96 mmol, 27%). (p*S,R*)-**16a**: IR ($CHCl_3$) ν_{max} 1974, 1904 (CO), 2243 (CN) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 4.54 (dd, 1H, $J = 6.7$ Hz, $J = 0.9$ Hz, Ar *H*), 4.41 (trd, 1H, $J = 6.4$ Hz, $J = 1.2$ Hz, Ar *H*), 4.14 (dd, 1H, $J = 6.4$ Hz, $J = 1.2$ Hz, Ar *H*), 4.09 (dd, 1H, $J = 6.4$ Hz, $J = 0.9$ Hz, Ar *H*), 2.85 (q, 1H, $J = 7.0$ Hz, C*H*(CN)CH$_3$), 1.59 (s, 3H, *o*-CH_3), 0.95 (d, 3H, $J = 7.0$ Hz, CH(CN)CH_3); ^{13}C NMR (125 MHz, C_6D_6) δ 232.66 (*C*O), 119.60 (*C*N), 108.46 (*ipso* Ar *C*), 104.82 (*ipso* Ar *C*), 93.92 (Ar *C*), 92.69 (Ar *C*), 91.73 (Ar *C*), 88 (Ar *C*), 26.08 (*C*H(CN)CH$_3$), 18.08 (CH(CN)*C*H$_3$), 16.91 (*o*-*C*H$_3$); $[\alpha]_D^{room\ temp}$ +20° (*c* 0.71 in $CHCl_3$). (*S,S*)-**16a**: IR ($CHCl_3$) ν_{max} 1976, 1907 (CO), 2249 (CN) cm^{-1}; ^1H NMR (500 MHz, C_6D_6) δ 5.18 (dd, 1H, $J = 6.4$ Hz, $J = 0.9$ Hz, Ar *H*), 4.46 (trd, 1H, $J = 6.4$ Hz, $J = 1.2$ Hz, Ar *H*), 4.35 (trd, 1H, $J = 6.4$ Hz, $J = 1.2$ Hz, Ar *H*), 4.16 (dd, 1H, $J = 6.4$ Hz, $J = 0.9$ Hz, Ar *H*), 2.95 (q, 1H, $J = 7.3$ Hz, C*H*(CN)CH$_3$), 1.37 (s, 3H, *o*-CH_3), 0.76 (d, 3H, $J = 7.3$ Hz, CH(CN)CH_3); ^{13}C NMR (125 MHz, C_6D_6) δ 332.54 (*C*O), 119.37 (*C*N), 106.08 (*ipso* Ar *C*), 105.17 (*ipso* Ar *C*), 93.09 (Ar *C*), 92.85 (Ar *C*), 91.62 (Ar *C*), 89.95 (Ar *C*), 28.90 (*C*H(CN)CH$_3$), 20.95 (CH(CN)CH$_3$), 17.46 (*o*-*C*H$_3$); $[\alpha]_D^{room\ temp}$ +253° (*c* 0.71 in $CHCl_3$). Anal. Calcd for $C_{13}H_{11}CrNO_3$: H, 3.94; C, 55.52; N, 4.98. Found: H, 4.08; C, 55.04; N, 4.84.

[η^6-(*R,R*)-*o*-(CHClMe)(SiMe$_3$)C_6H_4]Cr(CO)$_3$ (4). A stirred solution of **1c** (3.18 g, 8.90 mmol) in 200 mL of Et_2O was treated dropwise with 1-chloroethyl chloroformate (5.09 g, 35.60 mmol) at −40 °C. The resulting solution was stirred overnight without cooling, filtered, and then evaporated. The residue was recrystallized from hexane at −30 °C to give 2.46 g (7.05 mmol, 79%) of **4** as yellow crystals. IR ($CHCl_3$): ν_{max} 1971, 1900 (CO) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 4.87 (q, 1H, $J = 6.7$ Hz, C*H*ClCH$_3$), 4.78 (d, 1H, $J = 6.1$ Hz, Ar *H*), 4.65 (d, 1H, $J = 3.1$ Hz, Ar *H*), 4.35 (m, 2H, Ar *H*), 1.49 (d, 3H, $J = 6.7$ Hz, CHClCH_3), 0.23 (s, 9H, Si(CH_3)$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 233.09 (*C*O), 117.19 (*ipso* Ar *C*), 99.85 (*ipso* Ar *C*), 99.10 (Ar *C*), 94.29 (Ar *C*), 91.39 (Ar *C*), 88.85 (Ar *C*), 56.85 (*C*HClCH$_3$), 23.10 (CHCl*C*H$_3$), 0.60 (Si(*C*H$_3$)$_3$). Anal. Calcd for $C_{14}H_{17}ClCrO_3Si$: H, 4.92; C, 48.21. Found: H, 4.97; C, 48.29.

[η^6-(*R,R*)-*o*-{CH(PPh$_2$)Me}(SiMe$_3$)C_6H_4]Cr(CO)$_3$ (7). To compound **4** (1.74 g, 4.99 mmol) in 100 mL of acetone was added diphenylphosphine (1.04 mL, 5.99 mmol) and NH_4PF_6 (1.22 g, 7.49 mmol) at room temperature. The resulting mixture was stirred overnight, treated with NEt_3 (5 mL), filtered, and evaporated. The residue was purified by chro-

matography on silica gel (elution with dichloromethane) and recrystallized from ethyl acetate/hexane at −30 °C to give **7** as yellow crystals (2.10 g, 4.21 mmol, 84%). IR ($CHCl_3$): ν_{max} 1964, 1893 (CO) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 7.26 (tr m, 2H, Ar *H*(Ph)), 7.10 (tr m, 3H, Ar *H*(Ph)), 7.03 (tr m, 2H, Ar *H*(Ph)), 6.97 (dm, 3H, Ar *H*(Ph)), 4.92 (dd, 1H, J = 6.4 Hz, J_{HP} = 1.2 Hz, Ar *H*), 4.66 (trd, 1H, J = 6.4 Hz, J_{HP} = 1.2 Hz, Ar *H*), 4.43 (d, 1H, J = 6.4 Hz, J_{HP} = 0.9 Hz, Ar *H*), 4.36 (br d, 1H, J = 6.7 Hz, Ar *H*), 3.71 (q, 1H, J = 7.0 Hz, C*H*(PPh_2)-CH_3), 1.28 (dd, 3H, J_{HP} = 7.9 Hz, J = 7.0 Hz, CH(PPh_2)C*H*$_3$), 0.30 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 233.92 (*C*O), 136.99 (d, J_{CP} = Hz, *ipso* Ar *C*(Ph)), 133.60 (d, J_{CP} = Hz, *ipso* Ar *C*(Ph)), 136−128.11 (10C, Ar *C*(Ph)), 123.49 (d, J = 19.7 Hz, *ipso* Ar *C*), 100.59 (d, J = 3.9 Hz, *ipso* Ar *C*), 99.64 (Ar *C*), 93.91 (Ar *C*), 91.27 (Ar *C*), 90.96 (d, J = 8.3 Hz, Ar *C*), 35.27 (d, J = 20.9 Hz, CH(PPh_2)*C*H$_3$), 16.36 (d, J = 5.4 Hz, CH(PPh_2)*C*H$_3$), 1.43 (d, J = 3.3 Hz, Si(*C*H$_3$)$_3$). ^{31}P NMR (81 MHz, C_6D_6): δ +14.72. Anal. Calcd for $C_{26}H_{27}CrO_3PSi$: H, 5.46; C, 62.64. Found: H, 5.48; C, 62.58.

Hydrovinylation Reaction. A solution of 1.00 equiv of the phosphorus ligand (0.05 mmol) in CH_2Cl_2 was added to a solution of 0.05 mmol of [(η^3-C_4H_7)Pd(cod)]BF_4[22] in CH_2Cl_2. After it was stirred for 60 min at 0 °C, the resulting solution was used for catalysis.

The cold catalyst solution (0.05 mmol of [(η^3-C_4H_7)Pd(P*)]-BF_4 in 20 mL of CH_2Cl_2) was transferred into a 75 mL stainless steel autoclave via a syringe with a stainless steel cannula. The autoclave was cooled in an ice bath. Chilled styrene (4 mL, 34.8 mmol) was added, and the autoclave was pressurized with ethylene (30 bar initial pressure). After the reaction, the autoclave was slowly vented and the reaction mixture separated from the catalyst and higher oligomers by flash chromatography over basic alumina. Products were analyzed by GC and the enantiomeric excess determined by GC using a capillary column with a chiral stationary phase.[29]

X-ray Structure Determinations of 2, 5, and 16b. Geometry and intensity data were collected on Enraf-Nonius CAD4 diffractometers equipped with graphite monochromators. A summary of crystal data, data collection parameters, and convergence results is compiled in Table 1. Due to the high linear absorption coefficients in the case of **2**, a numerical absorption correction by Gaussian integration[30] was applied before averaging symmetry-equivalent data. The structures of **2** and **5** were solved by direct methods;[31] that of **16b** was solved by Patterson and subsequent Fourier difference syntheses.[32] The models were refined on structure factors with the local version of the SDP program suite.[32] In the full-matrix least-squares refinement, all non-hydrogen atoms were assigned anisotropic displacement parameters. Hydrogen atoms were refined with isotropic displacement parameters in the case of **5** and included as riding on the corresponding carbon atoms (C−H = 0.98 Å, U_{iso}(H) = 1.3[U_{eq}(C)]) in the case of **2** and **16b**. For all structures less satisfactory reliability indices were obtained for the alternative enantiomorphs. In addition, the Flack enantiopol parameters were determined and are compiled in Table 1.[33,34] Further details on the structure determination are available from the Cambridge Crystallographic Data Center: CCDC-120595 (for **2**), CCDC-120596 (for **5**), and CCDC-132995 (for **16b**).

Supporting Information Available: Tables giving crystal data and details of the data collection and structure refinement, atomic coordinates, bond distances and angles, and thermal parameters for **2**, **5**, and **16b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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