Optically Active Transition-Metal Complexes. 10.[1] Bifunctional Arene−Chromium−Tricarbonyl Complexes Derived from (*R*)-Phenylethanamine: Easily Accessible Planar-Chiral Diphosphines and Their Application in Enantioselective Hydrogenation, Hydroamination, and Allylic Sulfonation

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(*R*)-[{α-(Dimethylamino)ethyl}-η^6-benzene]Cr(CO)$_3$ is stereoselectively substituted in the ortho-position with PPh_2, $P(O)Ph_2$, and CO_2R groups. After exchange of the amino group for a chloro substituent with chloroformic esters, a variety of phosphorus, nitrogen, and oxygen nucleophiles can be diastereoselectively introduced into the α-position to generate bifunctional chelating ligands. The addition of cyanide is not fully diastereospecific. The diphosphines, structurally similar to the well-known "Josiphos"-ferrocenes, are good catalysts for rhodium-catalyzed enantioselective hydrogenation, iridium-catalyzed hydroamination, and palladium-catalyzed allylic sulfonation.

Introduction

Chiral chelating diphosphines derived from ferrocene constitute a unique class of ligands for asymmetric catalysis.[2] A particular class of these diphosphines (the "Josiphos"-type ligands),[3] incorporating both central and planar chirality, have been successfully employed in a number of different catalytic applications with high enantioselectivities. Two industrial processes at Novartis and Lonza utilize these ligands and constitute possibly the most successful commercial applications of enantioselective transition-metal catalysis to date.[2b,c] The unique synthetic approach to these compounds[3] allows considerable scope for independently varying the substituents at both phosphorus centers, thereby offering an almost "combinatorial" approach to the fine-tuning of ligand properties.[2c]

Very limited attempts have been made to similarly use half-sandwich organometallic units, among them benzene tricarbonyl chromium complexes.[4] (*R*)-[{α-(Dimethylamino)ethyl}-η^6-benzene]tricarbonylchromium (**1**) is readily made from the commercially available optically active precursor (*R*)-phenylethanamine without the need for resolution, as in the analogous ferrocene compound. It had also been shown that it was possible to introduce planar chirality into this complex by diastereoselective metalation and electrophilic substitution into the ortho-position of the arene ring.[5] In this manner, P∧N bifunctional ligands could be synthesized, which were good catalysts for asymmetric allylic alkylation and cross-coupling reactions.[4b]

The methodology developed by Togni[3] for enantioselective nucleophilic displacement of the amino group in the α-position of ferrocenes, however, does not apply to

(1) Part 9: Englert, U.; Härter, R.; Vasen, D.; Salzer, A.; Eggeling, E. B.; Vogt, D.; *Organometallics* **1999**, *18*, 4390.

(2) For recent reviews, see: (a) Hayashi, T. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; p 105. (b) Togni, A. *Angew. Chem.* **1996**, *108*, 1581; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1475. (c) Togni, A. *Chimia* **1996**, *50*, 86.

(3) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.

(4) For a recent review, see: Bolm, C.; Muniz, K. *Chem. Soc. Rev.* **1999**, *28*, 51. (b) Uemura, M.; Miyake, R.; Nishimura, H. *Tetrahedron: Asymmetry* **1992**, *3*, 213. (c) Hayashi, Y.; Sakai, H.; Kaneta, M.; Uemura, M. *J. Organomet. Chem.* **1995**, *503*, 143.

(5) (a) Davies, S. G.; Blagg, J.; Goodfellow, C. L.; Sutton, K. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, *35*, 1805. (b) Heppert, J. A.; Aubé, J.; Thomas-Miller, M. E. Milligan, M. L.; Takusagawa, F. *Organometallics* **1990**, *9*, 727.

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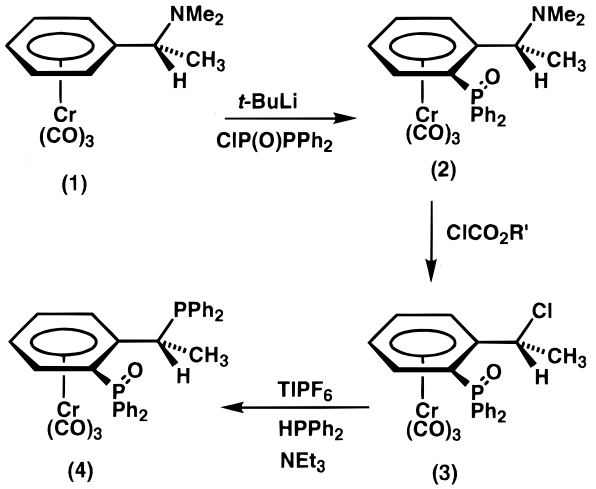
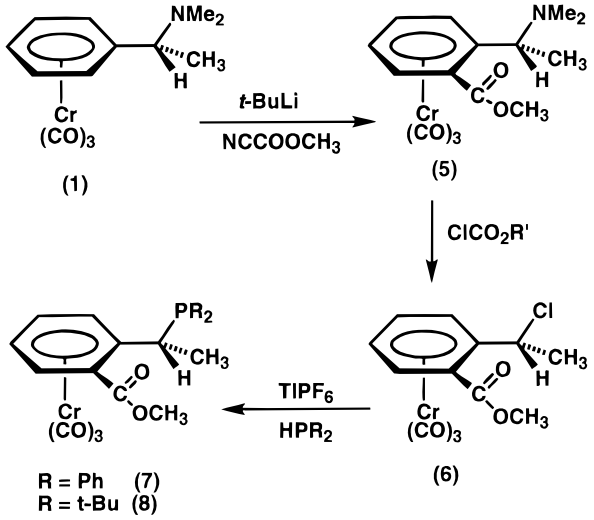
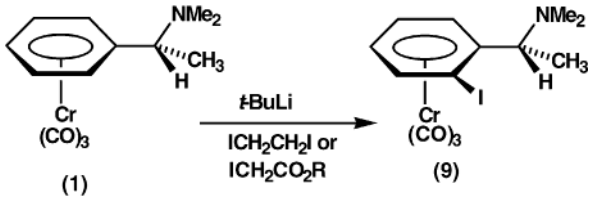
Scheme 1



Scheme 2



Scheme 3



chromium arene complexes. We have therefore recently developed a new strategy for the substitution of the dimethylamino group for a chloro substituent in **1** with subsequent nucleophilic displacement of the chloro substituent for a variety of P, N, and O nucleophiles.[1,6] Both reactions proceed with complete retention of configuration. The α-chiral organometallic monophosphines thus synthesized were successfully employed in the hydrovinylation reaction of styrene to 3-phenyl-1-butene with high enantiomeric excess.[1]

It now remained to show that the same method could be employed for the synthesis of a large variety of bifunctional C_1-symmetrical diphosphines or other didentate ligands and that these were versatile ligands for homogeneous catalysis of a scope similar to the "Josiphos"-ferrocenes.

Results and Discussion

Synthesis of Bifunctional Complexes. The diastereoselective metalation of **1** and subsequent electrophilic addition into the ortho-position had been successfully demonstrated in the case of the PPh_2 or the $SiMe_3$ group.[4b,5] For the construction of hemilabile ligands, it seemed important to also introduce substituents with oxo groups, such as phosphineoxides or esters. We therefore performed a similar reaction on **1** with *t*-BuLi and $ClP(O)Ph_2$. This allowed the clean preparation of (*pR*,*R*)-[1-{α-(dimethylamino)ethyl}-2-(diphenylphosphinyl)-η^6-benzene]Cr(CO)$_3$ (**2**) in good yield (75%). We were also successful in replacing the amino group for a chloro substituent in **2**, using the same reagents as before to generate (*pR*,*R*)-[1-(α-chloroethyl)-2-(diphenylphosphinyl)-η^6-benzene]Cr(CO)$_3$ (**3**) and then to replace the chloro substituent with diphenylphosphine in the presence of $TlPF_6$ to give (*pR*,*R*)-[1-{α-(diphenylphosphanyl)-ethyl}-2-(diphenylphosphinyl)-η^6-benzene]Cr(CO)$_3$ (**4**) in 56% yield (Scheme 1). This clearly established that it should be possible to generate a large number of bifunctional ligands by this procedure, as the introduction of a bulky polar substituent did not inhibit the reactivity at the α-carbon of the side chain. The substituent exchange in the α-position proceeded with complete diastereoselectivity, as before,[1] as otherwise diastereomers would have been generated.

As other potential hemilabile ligands we envisaged γ-phosphino esters, and we therefore reacted (*pR*,*R*)-[1-{α-(dimethylamino)ethyl}-2-lithio-η^6-benzene]Cr(CO)$_3$, generated in situ, with ethyl chloroformate. This also gave reasonable yields (51%) of the substitution product, but, as expected, the side reaction of the amino group with the chloroformate, which we utilize for the replacement of the amino group, is in competition with electrophilic attack. As an alternative reagent for the introduction of the COOR group, we then used methyl cyanoformate ("Mander's reagent"), which gave yellow crystals of of (*pS*,*R*)-[1-{α-(dimethylamino)ethyl}-2-(methyloxycarbonyl)-η^6-benzene]Cr(CO)$_3$ (**5**). Subsequent steps as before generated the chloride (**6**) and then the phosphanyl derivative with PPh_2 (**7**) and P(*t*-Bu)$_2$ (**8**) (Scheme 2).

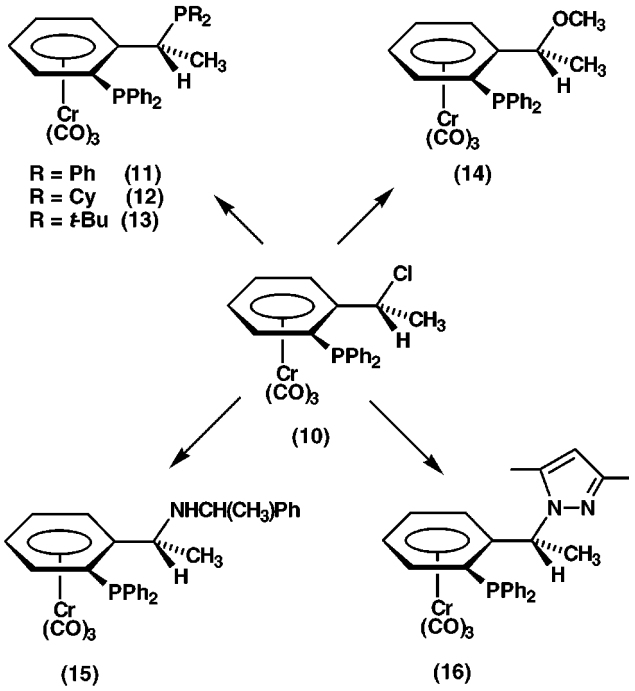
We were also able to introduce a halide substituent into the ortho-position by reaction of the lithio intermediate with either methyl iodoacetate or diiodoethane. The previously known (*pS*,*R*)-[2-(α-*N*,*N*-dimethylaminoethyl)-1-iodo-η^6-benzene]Cr(CO)$_3$ (**9**)[7] was formed in up to 68% yield in this reaction and may serve in the future as a very useful starting material for further ortho-substituted derivatives (Scheme 3).

The major aim of our research was of course the synthesis of chelating diphosphines. Uemura had already prepared two derivatives, but through a somewhat elaborate route via chromium complexes derived from expensive (*S*)-phenylethanol.[4c] Our method seems to be superior, as it has considerably greater scope (vide

(6) Englert, U.; Salzer, A.; Vasen, D. *Tetrahedron: Asymmetry* **1998**, *9*, 1867.

(7) Christian, P. W. N.; Gibsin, S. E.; Gil, R.; Jones, P. C. V.; Marcos, C. F.; Prechtl, F.; Wierzchleyski, A. T. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 195.

Scheme 4



infra) and higher overall yields, starting from commercially available, cheap (*R*)-phenylethanamine. After metalation and electrophilic introduction of the PPh_2 moiety into the ortho-position, the amino group was replaced for a chloro substituent to give compound **10**, which was easily dehalogenated with $TlPF_6$ in the presence of a secondary phosphine to give compounds **11**, **12**, and **13** with PPh_2, PCy_2, and $P(t\text{-}Bu)_2$ in α-position in good yields (Scheme 4).[8] The synthesis of **10** required the reagent 1-chloroethyl chloroformate (ACE-Cl),[9] which is more reactive than the simple ethyl chloroformate.

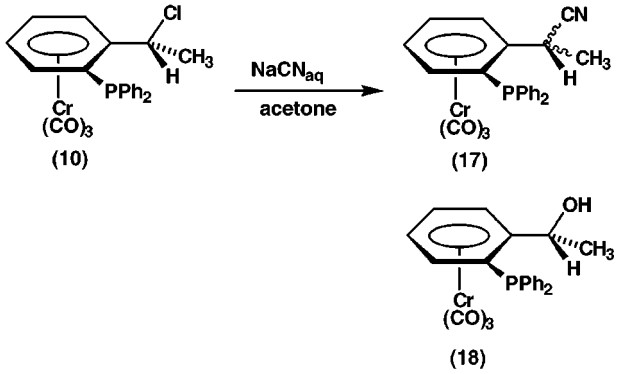
In addition, as previously demonstrated,[1] the mild conditions required for the diastereoselective introduction of nucleophiles into the α-position also allow the exchange of Cl in **10** for O, N, and C functional groups. Treatment of **10** with benzene/methanol led to the almost quantitative formation of the phosphinoether **14** (another potential hemilabile ligand), while treatment with (*R*)-phenylethanamine introduced a secondary amino function into the α-position of **15**. 3,5-Dimethylpyrazole reacted likewise, giving the bifunctional P∧N ligand **16** (Scheme 4). The latter compound, in analogy with similar ferrocene derivatives, should be a good ligand for enantioselective hydroboration,[10] which is currently under investigation.

As a last example, we treated **10** with NaCN in a mixture of acetone/water to give low yields of the cyano derivative **17** together with the alcohol **18**. While the alcohol is formed as a single diastereomer, the introduction of the cyano group is not fully diastereoselective, as observed before[1], but the major diastereomer is formed with a de of 82% (Scheme 5).

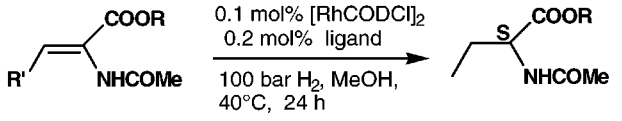
*These results show that the synthesis of bifunctional optically active ligands of symmetry C_1 starting from compound **1** is easily done in three reaction steps, allowing an almost "combinatorial" approach to a large variety of chelating planar-chiral ligands.*

(8) Because of the rather long systematic names for these compounds, we, in our laboratories, refer to compound **12** as "Daniphos".
(9) Cooley, J. H.; Evain, E. J. *Synthesis* **1989**, 1.
(10) Schnider, A.; Hintermann, L.; Togni, A. *Angew. Chem.* **1995**, *107*, 996; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 931.

Scheme 5

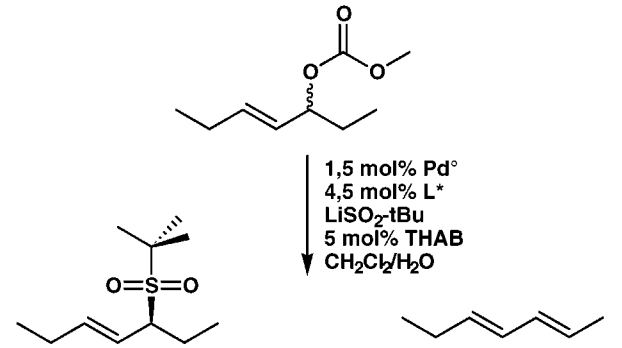


Scheme 6



11 80%y, 66% ee (R = H, R' = Ph)
12 100%y, 78% ee (R = H, R' = Ph)
12 100%y, >95% ee (R = Me, R' = Me)
13 100%y, 3% ee (R = H, R' = Ph)

Scheme 7

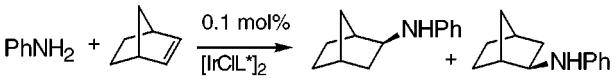


L*	A/B	yield, %	ee, %
11	73/27	100	57 (3*S*)
12	15/85	100	14 (3*S*)
13	100/0	100	11 (3*S*)

Homogeneous Catalysis. Compounds **11** and **12**, as the *S*-enantiomers, had already been prepared by Uemura and proved to be good catalysts for the enantioselective allylic alkylation.[4c] We were able to show that the diphosphines **11**−**13**, like the corresponding ferrocene derivatives, could be used in asymmetric rhodium-catalyzed hydrogenation, Scheme 6, palladium-catalyzed allylic sulfonation, Scheme 7, and iridium-catalyzed hydroamination reactions, Scheme 8.

Thus, reaction of methyl acetamidoacrylate, under 100 bar of hydrogen pressure in methanol and 40 °C, in the presence of 0.2% of catalyst, formed in situ from $[CODRhCl]_2$ and the "Daniphos"[8] ligand (**12**), afforded a quantitative yield of the hydrogenation product in >95% ee. This result compares well with those obtained from the best C_2-symmetrical ligands found in the

Scheme 8



L*	T, °C	F⁻/Ir	yield, % (TOF, h^{-1})	ee, %
21	60	40	26.8 (2.5)	13.3 (2S)
22	60	40	1.1 (0.1)	64.0 (2S)
18	60	40	trace	51.1 (2S)
19	60	40	trace	70.3 (2S)

literature[11] as well as with Togni's Josiphos ligand (88% ee).[3] On the other hand, when acetamidocinnamic acid was used as a substrate, a significantly lower enantioselectivity of 78% was observed. This again parallels the results from the Josiphos ligand (84%), although the results are not directly comparable, as reactions with the chromium ligands were performed under different conditions, e.g., a lower catalyst concentration (0.2 vs 1%).

Ligand **11** gave 66% ee after 24 h (80% conversion), while **13** showed complete conversion, but almost no enantioselectivity (3% ee) (Scheme 6).

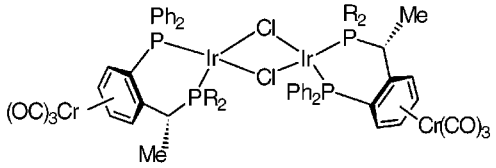
To obtain a more complete picture of the catalytic activity of **11**−**13** in hydrogenation, we need to run more experiments with other substrates. A fine-tuning of catalyst selectivity should also be possible by using other PR_2 groups in both positions. This is currently in progress.

Ligands **11**−**13** were also successfully employed in the palladium-catalyzed substitution reaction of allylic acetates with sulfur nucleophiles.[12] Thus, reaction of racemic 3-acetoxyhept-4-ene with lithium *tert*-butylsulfinate in the presence of 1.5 mol % of Pd_2dba_3 and 4.5 mol % of the ligands gave complete conversion in all cases, but with marked differences in the product selectivity (Scheme 7).

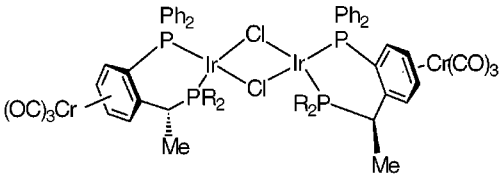
The highest ee with 57% was obtained with **11**, but here again, there should be considerable scope for improvement by variation of the steric and electronic properties of the two ligand functions. The higher ee values obtained by Uemura in the allylic alkylation with these ligands are probably due to the use of the 1,3-diphenyl-3-acetoxypropene, a precursor that is known to give good enantioselectivities in this reaction.

A third reaction we investigated was the intermolecular enantioselective olefin hydroamination, which was recently pioneered by one uf us.[13] Ferrocene ligands such as Josiphos had been shown to give good enantioselectivities in this reaction. We now wish to report a comparison study of the analogous iron and chromium complexes in the same catalysis. After isolation of the dimeric iridium complexes **19** and **20** as an inseparable mixture of cis/trans isomers (Chart 1), the reactions were performed as described before without solvent and

Chart 1



trans-**19** (R = Cy) **20** (R = t-Bu)



cis-**19** (R = Cy) **20** (R = t-Bu)

with a catalyst concentration of 0.1 mol % of Ir (Scheme 8). The same reactions under identical conditions were performed with the iridium complexes of Josiphos[13] **21** and its *tert*-butyl derivative **22**. A common reaction time of 96 h was adopted.

Only the Josiphos catalyst showed reasonable turnover (2.5 for **21**), but with considerable loss of enantioselectivity compared to our previous study conducted with higher catalyst concentration and at lower temperatures.[13] Good ee values were obtained with the P(*tert*-butyl)$_2$ derivative **22**, which had not been tested before (64% ee). With the chromium ligands, only small amounts of the hydroamination product were isolated. Nevertheless, these ligands showed a higher enantiomeric excess compared to the analogous Josiphos-type ligands (Scheme 8), the P(*tert*-butyl)$_2$ derivative **20** being better than the PCy_2 compound **19**. A reason for the low activity may be the thermal instability of the chromium catalyst, but possibly also competing side reactions, such as hydroarylation of aniline with norbornene, as an as yet unidentified product is also detected.

The enantioselective hydroamination reaction, as seen from these results and our previous experiments,[13] is extremely sensitive to small variations in the reaction parameters, such as temperature and concentration of the added "naked" fluoride anion.

The hemilabile ligands **7** and **8** were also tested in the hydrovinylation reaction, where they were active, but did not reach the efficiency of the previously investigated compounds of the chromium series.[1] Other potential applications of these ligands are currently under investigation.

Conclusions

We have found a very general route to optically active bifunctional arene complexes of chromium, which offer a considerable potential as hemilabile or didentate ligands in homogeneous catalysis. The chromium diphosphines of the Daniphos-type closely match the corresponding Josiphos ferrocenyl ligands in enantioselectivity in a number of catalytic applications. At the current stage, we cannot conclusively argue the respective merits of the two systems. It is interesting to note for each of the three catalytic reactions investigated a different ligand gave the highest ee values. As yet, we have no structural data on metal complexes of the

(11) (a) Koenig, K. E. In *Asymmetric Syntheses*; Morrison, J. D., Ed.; Academic Press: Orlando, 1985; Vol. 5, p 71. (b) Burk, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 8518.

(12) Gais, H. J.; Eichelmann, H.; Spalthoff, N.; Gerhards, F.; Frank, M.; Raabe, G. *Tetrahedron: Asymmetry* **1998**, 235.

(13) Dorta, R.; Egli, P.; Zürcher, F. Togni, A. *J. Am. Chem. Soc.* **1997**, *119*, 10857. Bieler, N. H. Egli, P.; Dorta, R.; Togni, A.; Eyer, M. EP 0 909 762 A2, 1999.

diphosphines **11**−**13** to compare the bite angles with the corresponding ferrocene derivatives, although the angle between two ortho-substituents on an arene ring (60°) is expected to be substantially smaller than in a corresponding cyclopentadienyl ring (72°).

A major advantage of the chromium complexes is their ready availability in optically active form without any need for resolution. This also applies to other functional derivatives. In contrast to the cyclopentadienyl ring, arenes have an almost unlimited potential for controlled substitutional variation, accessible through standard organic reaction protocols.

We are currently extending our studies to other transition-metal-catalyzed reactions, such as hydroboration, hydrosilylation, and hydrogenation of ketones and imines. We are also increasing the range of diphosphines to include other substituents to be able to fine-tune ligand properties for each catalytic application.

Experimental Section

All reactions were performed under nitrogen using Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. 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 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. Compounds (*R*)-[{(NMe_2)CHMe}C_6H_5]Cr$(CO)_3$ (**1**) and (*pR,R*)-[{(NMe_2)CHMe}-$C_6H_4PPh_2$]Cr$(CO)_3$ were prepared by the published methods.[4b]

General Method A. *t*-BuLi (1.14 equiv, 1.7 M solution in hexane) was added dropwise at − 80 °C to a solution of the unsubstituted complex **1** (1 equiv) in dry Et_2O. The solution was stirred at this temperature for 1 h, and the resulting yellow precipitate was dissolved with THF. The electrophile (1.14 equiv) was then added slowly. After warming to ambient temperature, the solid was filtered off, and the solvent was evaporated.

General Method B. A stirred solution of the chromium complex (1 equiv) in dry THF was treated dropwise with 1-chloroethyl chloroformate (4 equiv) at −40 °C. The solution was stirred overnight without cooling and evaporated, and the residue was redissolved in Et_2O, filtered, and then evaporated to dryness under high vacuum.

General Method C. To the chromium complex (1 equiv) in dry acetone (20 mL/mmol chromium complex) were added 1 equiv of the nucleophile and $TlPF_6$ (1 equiv) at ambient temperature. The resulting mixture was stirred overnight, treated with NEt_3, filtered, and then evaporated.

[η^6-*(pR,R)*{(NMe_2)CHMe}$C_6H_4P(O)Ph_2$]Cr$(CO)_3$ (2). 2 was produced from **1** (5.00 g, 17.53 mmol), *t*-BuLi (11.75 mL, 19.98 mmol, 1.7 M solution in hexane), and chlorodiphenylphosphinoxide (4.73 g, 19.98 mmol), according to general method A. The substance was purified by chromatography on silica [Et_2O] and recrystallized from Et_2O/hexane at −30 °C to give 6.34 g (13.06 mmol, 75%) of **2**. IR ($CHCl_3$): ν_{max} 1981, 1917 (CO) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6): δ 7.85−7.80 (m, 2H, ar-*H*(P(O)Ph_2)), 7.56−7.63 (m, 2H, ar-*H*(P(O)Ph_2)), 7.06−7.08 (m, 6H, ar-*H*(P(O)Ph_2)), 5.32 (q, 1H, J = 6.5 Hz, NMe_2C*H*Me), 4.81 (tr, 1H, J = 6.5 Hz, ar-*H*), 4.70 (dd, 1H, J_{HP} = 10 Hz, J = 6 Hz, ar-*H*), 4.43 (dbrd, 1H, J = 6.5 Hz, ar-*H*), 4.09 (tr, 1H, J = 6 Hz, ar-*H*), 1.58 (s, 6H, N*Me*$_2$), 0.73 (d, 3H, J = 6.5 Hz, NMe_2CH*Me*). ^{13}C NMR (75 MHz, C_6D_6): δ 231 (*C*O), 135.20 (d, $^1J_{CP}$ = 111.5 Hz, ar-ipso*C*(P(O)Ph_2)), 134.38 (d, $^1J_{CP}$ = 104.5 Hz, ar-ipso*C*(P(O)Ph_2)), 133.07−127.78 (10C, ar-*C*(P(O)Ph_2)), 119.66 (d, J_{CP} = 6 Hz, ar-ipso*C*), 100.30 (d, J_{CP} = 13 Hz, ar-*C*), 96.04 (d, J_{CP} = 101 Hz, ar-ipso*C*), 94.36 (ar-*C*), 87.33 (d, J_{CP} = 10 Hz, ar-*C*), 86.54 (d, J_{CP} = 6.5 Hz, ar-*C*), 55.99 (NMe_2*C*HMe), 38.49 (N*Me*$_2$), 5.68 (NMe_2CH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ +26.75. Anal. Calcd for $C_{25}H_{24}CrNO_4P$: H, 4.98; C, 61.86; N, 2.89. Found: H, 5.08; C, 61.65; N, 2.89.

[η^6-*(pR,R)*{ClCHMe}$C_6H_4P(O)Ph_2$]Cr$(CO)_3$ (3). 3 was produced from compound **2** (2.95 g, 6.08 mmol) and 1-chloroethyl chloroformate (3.48 g, 24.31 mmol), according to general method B. The residue was dissolved in ethyl acetate and filtered over silica. **3** can be isolated as yellow crystals from ethyl acetate at − 30 °C (2.24 g, 4.70 mmol, 77%). IR ($CHCl_3$): ν_{max} 1986, 1925 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 7.82−7.74 (m, 4H, ar-*H*(P(O)Ph_2)), 7.07−7.04 (m, 6H, ar-*H*(P(O)Ph_2)), 6.91 (q, 1H, J = 7.0 Hz, ClC*H*Me), 4.60 (md, 1H, ar-*H*), 4.56 (tr, 1H, J = 6.5 Hz, ar-*H*), 4.51 (dbrd, 1H, J_{HP} = 10.0 Hz, J = 6.5 Hz, ar-*H*), 4.02 (tr, 1H, J = 6 Hz, ar-*H*), 1.44 (d, 3H, J = 6.5 Hz, ClCH*Me*). ^{13}C NMR (125 MHz, C_6D_6): δ 231.09 (*C*O), 132.63 (d, $^1J_{CP}$ = 105.5 Hz, ar-ipso*C*(P(O)Ph_2)), 132.15 (d, $^1J_{CP}$ = 109 Hz, ar-ipso*C*(P(O)Ph_2)), 132.89−128.65 (10C, ar-*C*(P(O)-Ph_2)), 116.88 (d, J_{CP} = 6.5 Hz, ar-ipso*C*), 97.28 (d, J_{CP} = 11.5 Hz, ar-*C*), 95.16 (d, J_{CP} = 94.4 Hz, ar-ipso*C*), 94.14 (ar-*C*), 88.26 (d, J_{CP} = 9.5 Hz, ar-*C*), 87.48 (d, J_{CP} = 6.5 Hz, ar-*C*), 53.19 (Cl*C*HMe), 23.24 (ClCH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ +28.76. Anal. Calcd for $C_{23}H_{18}ClCrO_4P$: H, 3.81; C, 57.94. Found: H, 3.87; C, 57.88.

[η^6-*(pR,R)*{(PPh_2)CHMe}$C_6H_4P(O)Ph_2$]Cr$(CO)_3$ (4). 4 was produced from **3** (0.96 g, 2.01 mmol), diphenylphosphine (0.39 mL, 2.21 mmol), and $TlPF_6$ (0.70 g, 2.01 mmol), according to general method C. Complex **4** was purified by washing with Et_2O. More product can be obtained by chromatography of the ether solution over silica [Et_2O/hexane, 2:1]. Yield: 0.70 g (1.12 mmol, 56%). IR ($CHCl_3$): ν_{max} 1980, 1917 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 7.97−7.92 (m, 2H, ar-*H*(P(O)Ph_2) or ar-*H*(PPh_2)), 7.87−7.82 (m, 2H, ar-*H*(P(O)Ph_2) or ar-*H*(PPh_2)), 7.45 (trm, 2H, ar-*H*(P(O)Ph_2) or ar-*H*(PPh_2)), 7.20−7.17 (trm, 2H, ar-*H*(P(O)Ph_2) or ar-*H*(PPh_2)), 7.12−6.91 (m, 12H, ar-*H*(P(O)Ph_2) or ar-*H*(PPh_2)), 6.01 (q, 1H, J = 7.0 Hz, PPh_2C*H*Me), 4.76 (ddd, 1H, J_{HP} = 10 Hz, J = 6 Hz, J = 1 Hz, ar-*H*), 4.50 (trm, 1H, ar-*H*), 4.05−4.00 (m, 2H, ar-*H*), 1.23 (dd, 3H, J = 7.0 Hz, J = 4.5 Hz, PPh_2CH*Me*). ^{13}C NMR (125 MHz, C_6D_6): δ 231.70 (*C*O), 137.08 (d, J_{CP} = 19 Hz, ar-ipso*C*(PPh_2)), 136.59−127.51 (20C, ar-*C*(P(O)Ph_2) and ar-*C*(PPh_2)), 133.95 (d, $^1J_{CP}$ = 19 Hz, ar-ipso*C*(PPh_2)), 133.42 (d, $^1J_{CP}$ = 102.5 Hz, ar-ipso*C*(P(O)Ph_2)), 133.29 (d, $^1J_{CP}$ = 105.5 Hz, ar-ipso*C*(P(O)-Ph_2)), 123.10 (d, $^2J_{CP}$ = 24 Hz, ar-ipso*C*), 98.00 (d, $^3J_{CP}$ = 13 Hz, ar-*C*), 95.03 (d, $^1J_{CP}$ = 93 Hz, ar-ipso*C*), 94.20 (ar-*C*), 88.09 (dd, $^3J_{CP}$ = 6 Hz, $^3J_{CP}$ = 6.0 Hz, ar-*C*), 87.60 (d, $^2J_{CP}$ = 9.5 Hz, ar-*C*), 31.61 (d, $^1J_{CP}$ = 23.5 Hz, PPh_2C*H*Me)), 14.94 (PPh_2-CH*Me*)). ^{31}P NMR (81 MHz, C_6D_6): δ +28.92 (*P*(O)Ph_2), +12.13 (*P*Ph_2). Anal. Calcd for $C_{35}H_{28}CrO_4P_2$: H, 4.50; C, 67.09. Found: H, 4.53; C, 66.97.

[η^6-*(pR,R)*{(NMe_2)CHMe}C_6H_4COOMe]Cr$(CO)_3$ (5). 5 was produced from **1** (1.50 g, 5.26 mmol), *t*-BuLi (3.53 mL, 5.99 mmol), and methyl cyanoformate (0.48 mL, 5.99 mmol), according to general method A. The residue was purified by chromatography on alumina [ethyl acetate/hexane, 1:4] and crystallized from Et_2O/hexane at −30 °C to give 0.81 g (2.36 mmol, 45%) of **5** as yellow crystals. IR ($CHCl_3$): ν_{max} 978, 1909 (CO), 1721 (COOMe) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 5.41 (d, 1H, J = 6.5 Hz, ar-*H*), 4.59 (tr, 1H, J = 6.5 Hz, ar-*H*), 4.56 (q, 1H, J = 7 Hz, NMe_2C*H*Me), 4.53 (d, 1H, J = 6.5 Hz, ar-*H*), 4.30 (tr, 1H, J = 6.5 Hz, ar-*H*), 3.38 (s, 3H, COO*Me*), 1.85 (s, 6H, N*Me*$_2$), 0.83 (d, 3H, J = 7 Hz, NMe_2CH*Me*). ^{13}C NMR (125 MHz, C_6D_6): δ 232.10 (*C*O), 166.54 (*C*OOMe), 116.52 (ar-ipso*C*), 97.67 (ar-ipso*C*), 94.77, 93.02, 89.11, 88.39 (ar-*C*),

56.20 (NMe_2CHMe), 52.37 (COO*Me*), 39.80 (NMe_2), 30.22 (NMe_2CH*Me*). Anal. Calcd for $C_{15}H_{17}CrNO_5$: H, 4.08; C, 52.48; N, 4.99. Found: H, 3.95; C, 52.18; N, 5.07.

[η^6-*(pR,R)*{ClCHMe}C_6H_4COOMe]Cr(CO)$_3$ (6). 6 was produced from **5** (1.46 g, 4.25 mmol) and 1-chloroethyl chloroformate (1.22 g, 8.50 mmol), according to general method B. To purify **6**, it was chromatographed on silica [ethyl acetate/hexane, 4:1] to give 0.64 g (1.91 mmol, 45%). IR ($CHCl_3$): ν_{max} 1985, 1917 (CO), 1725 (COOMe) cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 6.26 (q, 1H, J = 6.5 Hz, ClC*H*Me), 5.47 (d, 1H, J = 6.5 Hz, ar-*H*), 4.72 (d, 1H, J = 6.5 Hz, ar-*H*), 4.57 (tr, 1H, J = 6.5 Hz, ar-*H*), 4.37 (tr, 1H, J = 6.5 Hz, ar-*H*), 3.33 (s, 3H, COO*Me*), 1.46 (d, 3H, J = 7 Hz, ClCH*Me*). ^{13}C NMR (50 MHz, C_6D_6): δ 231.04 (*C*O), 165.57 (*C*OOMe), 113.41 (ar-ipso*C*), 94.39, 93.38 (ar-*C*), 91.11 (ar-ipso*C*), 90.00, 88.11 (ar-*C*), 52.91 (COO*Me*), 52.56 (ClCHMe), 22.51 (ClCH*Me*). Anal. Calcd for $C_{13}H_{11}ClCrO_5$: H, 3.31; C, 46.65. Found: H, 3.41; C, 45.70.

[η^6-*(pR,R)*{(PPh$_2$)CHMe}C_6H_4COOMe]Cr(CO)$_3$ (7). 7 was produced from **6** (0.48 g, 1.4 mmol), diphenylphosphine (0.27 g, 1.5 mmol), and $TlPF_6$ (0.50 g, 1.4 mmol) according to general method C. The substance was purified by chromatography on alumina [ethyl acetate/Et_2O, 1:4]. Yield: 0.38 g (0.78 mmol, 56%). IR ($CHCl_3$): ν_{max} 1979, 1912 (CO), 1720 (COOMe) cm^{-1}, ^1H NMR (500 MHz, C_6D_6): δ 7.53 (trm, 4H, ar-*H*(PPh$_2$)), 7.14−7.10 (m, 4H, ar-*H*(PPh$_2$)), 6.93−6.85 (m, 2H, ar-*H*(PPh$_2$)), 5.51 (dd, 1H, J = 7 Hz, J = 1 Hz, ar-*H*), 5.37−5.32 (m, 1H, PPh$_2$C*H*Me), 4.68 (trd, 1H, J = 6.5 Hz, J = 1 Hz, ar-*H*), 4.62 (d, 1H, J = 6.5 Hz, ar-*H*), 4.35 (trm, 1H, ar-*H*), 3.15 (s, 3H, COO*Me*), 1.32 (dd, J_{HP} = 12 Hz, J = 7 Hz, PPh$_2$CH*Me*). ^{13}C NMR (125 MHz, C_6D_6): δ 232.00 (*C*O), 165.94 (*C*OOMe), 136.31 (d, J_{CP} = 19.2, ar-ipso*C*(PPh$_2$)), 134.87 (d, J_{CP} = 18.1, ar-ipso*C*(PPh$_2$)), 134.87−128.07 (ar-*C*(PPh$_2$)), 119.70 (d, J_{CP} = 17.0 Hz, ar-ipso*C*), 94.12 (d, 2C, J_{CP} = 17 Hz, ar-*C*), 91.69 (d, J_{CP} = 3.5 Hz, ar-ipso*C*), 89.72 (d, J_{CP} = 6 Hz, ar-*C*), 88.95 (ar-*C*), 52.02 (COO*Me*), 30.93 (d, J_{CP} = 18 Hz, PPh$_2$*C*HMe), 16.64 (d, J_{CP} = 16 Hz, PPh$_2$CH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ +17.84. Anal. Calcd for $C_{25}H_{21}CrO_5P$: H, 4.37; C, 61.99. Found: H, 4.47; C, 61.70.

[η^6-*(pR,R)*{(P*t*-Bu$_2$)CHMe}C_6H_4COOMe]Cr(CO)$_3$ (8). 8 was produced from **6** (1.76 g, 5.3 mmol), di-*tert*-butylphosphine (1.07 g, 5.8 mmol), and $TlPF_6$ (1.85 g, 5.3 mmol), according to general method C. The substance was purified by chromatography on alumina [Et_2O/hexane, 1:4] to give 0.94 g (2.11 mmol, 40%) of **8.** IR ($CHCl_3$): ν_{max} 1976, 1910 (CO), 1721 (COOMe) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 5.59 (brd, 1H, J = 7 Hz, ar-*H*), 4.66−4.65 (m, 2H, ar-*H*), 4.48 (qd, 1H, J = 7.5 Hz, J_{HP} = 2.1 Hz, P*t*-Bu$_2$C*H*Me), 4.27 (trm, 1H, ar-*H*), 3.40 (s, 3H, COO*Me*), 1.46 (dd, 3H, J = 7.5 Hz, J_{HP} = 3.5 Hz, P*t*-Bu$_2$CH*Me*), 1.19 (d, 9H, J_{HP} = 11 Hz, C*Me*$_3$), 0.90 (d, 9H, J_{HP} = 11 Hz, C*Me*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 232.24 (*C*O), 166.45 (*C*OOMe), 123.08 (d, J_{CP} = 20 Hz, ar-ipso*C*), 95.61 (d, J_{CP} = 9.5 Hz, ar-ipso*C*), 95.03, 93.43 (ar-*C*), 88.74 (d, J_{CP} = 2 Hz, ar-*C*), 88.23 (ar-*C*), 52.47 (COO*Me*), 34.90 (d, J_{CP} = 32.5 Hz, *C*Me$_3$), 33.69 (d, J_{CP} = 29.5 Hz, *C*Me$_3$), 32.23 (P*t*-Bu$_2$*C*HMe), 31.97 (d, J_{CP} = 14 Hz, C*Me*$_3$), 31.21 (d, J_{CP} = 13 Hz, C*Me*$_3$), 14.62 (P*t*-Bu$_2$CH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ +64.10.

[η^6-*(pR,R)*{ClCHMe}C_6H_4PPh$_2$]Cr(CO)$_3$ (10). 10 was produced from [η^6-*(pR,R)*{(NMe$_2$)CHMe}C_6H_4PPh$_2$]Cr(CO)$_3$ (1.00 g, 2.13 mmol) and 1-chloroethyl chloroformate (0.67 g, 4.69 mmol), according to general method B. The substance was purified by crystallization from ethyl acetate/hexane at −30 °C followed by chromatography on silica [ethyl acetate/hexane, 2:1]. Yield: 0.88 g (1.91 mmol, 90%). IR ($CHCl_3$): ν_{max} 1970, 1902 (CO) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 7.51 (brtr, 2H, ar-*H*(PPh$_2$)), 7.33 (trm, 2H, ar-*H*(PPh$_2$)), 7.14−7.04 (m, 6H, ar-*H*(PPh$_2$)), 5.94 (dq, 1H, J = 9.5 Hz, J = 6.5 Hz, ClC*H*Me), 4.66 (d, 1H, J = 6.5 Hz, ar-*H*), 4.62 (dd, 1H, J = 3 Hz, J = 6.5 Hz, ar-*H*), 4.51 (tr, 1H, J = 6.4 Hz, ar-*H*), 4.22 (tr, 1H, J = 6.5 Hz, ar-*H*), 1.43 (d, 3H, J = 6.5 Hz, ClCH*Me*). ^{13}C NMR (125 MHz, C_6D_6): δ 232.23 (*C*O), 135.98 (d, $^1J_{CP}$ = 8 Hz, ar-ipso*C*(PPh$_2$)), 134.95 (d, $^1J_{CP}$ = 12.5 Hz, ar-ipso*C*(PPh$_2$)), 135.03−128.73 (10C, ar-*C*(PPh$_2$)), 117.35 (d, $^1J_{CP}$ = 22 Hz, ar-ipso*C*), 103.92 (d, $^1J_{CP}$ = 25 Hz, ar-ipso*C*), 97.72 (d, J_{CP} = 2.5 Hz, ar-*C*), 93.87, 90.85 (ar-*C*), 87.99 (d, J_{CP} = 3 Hz, ar-*C*), 54.50 (d, $^4J_{CP}$ = 29 Hz, ClCHMe), 23.00 (ClCH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ −16.88. Anal. Calcd for $C_{23}H_{18}ClCrO_3P$: H, 3.94; C, 59.95. Found: H, 4.05; C, 60.16.

[η^6-*(pR,R)*{(PPh$_2$)CHMe}C_6H_4PPh$_2$)Cr(CO)$_3$ (11). 11 was produced from **10** (1.11 g, 2.41 mmol), diphenylphosphine (0.46 mL, 2.65 mmol), and $TlPF_6$ (0.84 g, 2.41 mmol), according to general method C. The complex was purified by chromatography on silica [methylene chloride]. Yield: 1.15 g (1.88 mmol, 78%). Crystallization of this complex is possible from methylene chloride/hexane at −30 °C. IR ($CHCl_3$): ν_{max} 1969, 1900 (CO) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 7.67 (trm, ortho- or α-ar-*H*(PPh$_2$)), 7.43 (trm, ortho- or α-ar-*H*(PPh$_2$)), 7.24−6.95 (m, ortho- or α-ar-*H*(PPh$_2$)), 5.03−4.96 (m, 2H, ar-*H* and PPh$_2$C*H*Me), 4.50 (tr, 1H, J = 6.5 Hz, ar-*H*), 4.22 (trd, 1H, J = 6.5 Hz, J = 0.9 Hz, ar-*H*), 4.11 (ddtr, 1H, J = 6.5, J_{HP} = 3.5 Hz, J = 0.5 Hz, ar-*H*), 1.28 (dd, 3H, J = 6.5 Hz, J_{HP} = 4.5 Hz, PPh$_2$CH*Me*). ^{13}C NMR (125 MHz, C_6D_6): δ 232.84 (*C*O), 136.80 (d, J_{CP} = 19 Hz, ortho- or α-ar-ipso*C*(PPh$_2$)), 136.49 (d, J_{CP} = 22 Hz, ortho- or α-ar-ipso*C*(PPh$_2$)), 136.30−128.29 (ortho- and α-ar-*C*(PPh$_2$)), 123.34 (dd, J_{CP} = 22 Hz, J_{CP} = 22 Hz, ar-ipso*C*), 103.89 (dd, J_{CP} = 19.2 Hz, J_{CP} = 3.5 Hz, ar-ipso*C*), 99.31, 94.11, 89.70 (ar-*C*), 88.75 (dd, J_{CP} = 4 Hz, J_{CP} = 4 Hz, ar-*C*), 33.78 (dd, J_{CP} = 24.5 Hz, J_{CP} = 24.5 Hz, PPh$_2$*C*HMe), 15.02 (PPh$_2$-CH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ +10.12 (d, J_{PP} = 25.5 Hz, α-*P*Ph$_2$), −18.74 (d, J_{PP} = 27.5 Hz, ortho-*P*Ph$_2$).

[η^6-*(pR,R)*{(PCy$_2$)CHMe}C_6H_4PPh$_2$]Cr(CO)$_3$ (12). 12 was produced from **10** (1.10 g, 2.39 mmol), dicyclohexylphosphine (0.55 mL, 2.72 mmol), and $TlPF_6$ (0.83 g, 2.39 mmol), according to general method C. The product was purified by chromatography on silica [methylene chloride]. Yield: 0.76 g (1.22 mmol, 51%). IR ($CHCl_3$): ν_{max} 1975, 1905 (CO) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 7.64 (brtr, 2H, ar-*H*(PPh$_2$)), 7.39 (tr, 2H, J = 7.5 Hz, ar-*H*(PPh$_2$)), 7.13−7.04 (m, 6H, ar-*H*(PPh$_2$)), 5.08 (d, 1H, J = 6.5 Hz, ar-*H*), 4.72 (tr, 1H, J = 6.5 Hz, ar-*H*), 4.58 (dd, 1H, J = 6 Hz, J_{HP} = 3.5 Hz, ar-*H*), 4.31 (trd, 1H, J = 7.5 Hz, J_{HP} = 7.5 Hz, PCy$_2$C*H*Me), 4.21 (tr, 1H, J = 6.5 Hz, ar-*H*), 1.82−1.40 (m, 11H, *Cy*$_2$), 1.33 (dd, 3H, J = 7 Hz, J_{CP} = 3.5 Hz, PCy$_2$CH*Me*), 1.19−1.00 (m, 11H, P*Cy*$_2$). ^{13}C NMR (125 MHz, C_6D_6): δ 232.93 (*C*O), 138.66 (dd, J_{CP} = 6.5 Hz, J_{CP} = 3 Hz, ar-ipso*C*(PPh$_2$)), 137.88 (dd, J_{CP} = 14.5 Hz, J_{CP} = 4.5 Hz, ar-ipso*C*(PPh$_2$)), 135.45−127.91 (10C, ar-*C*(PPh$_2$)), 126.50 (dd, J_{CP} = 22.5 Hz, J_{CP} = 19 Hz, ar-ipso*C*), 103.32 (dd, J_{CP} = 24 Hz, J_{CP} = 3 Hz, ar-ipso*C*), 100.89, 94.73, 89.12 (ar-*C*), 87.69 (d, J_{CP} = 3.5 Hz, ar-*C*), 33.81 (d, J_{CP} = 23.5 Hz, *Cy*), 33.50 (d, $^1J_{CP}$ = 21.5 Hz, *Cy*), 32.19 (d, J_{CP} = 26.5 Hz, J_{CP} = 21 Hz, PCy$_2$*C*HMe), 31.74 (d, J_{CP} = 19 Hz, *Cy*), 31.68 (dd, $^1J_{CP}$ = 25 Hz, J_{CP} = 2 Hz, *Cy*), 30.36 (d, J_{CP} = 5.5 Hz, *Cy*), 30.03 (d, J_{CP} = 10 Hz, J_{CP} = 1.5 Hz, *Cy*), 27.99 (d, J_{CP} = 13 Hz, *Cy*), 27.79 (d, J_{CP} = 5.5 Hz, *Cy*), 27.46 (d, J_{CP} = 7.5 Hz, *Cy*), 26.99 (d, J_{CP} = 11.5 Hz, *Cy*), 26.64 (2C, *Cy*), 14.37 (PCy$_2$CH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ +16.66 (d, J_{PP} = 47.5 Hz, *P*Cy$_2$), −19.95 (d, J_{PP} = 46 Hz, *P*Ph$_2$).

[η^6-*(R,R)*{(P*t*-Bu$_2$)CHMe}C_6H_4PPh$_2$]Cr(CO)$_3$ (13). 13 was produced from **10** (1.11 g, 2.41 mmol), di-*tert*-butylphosphine (0.39 mL, 2.65 mmol), and $TlPF_6$ (0.84 g, 2.41 mmol), according to general method C. The product was purified by chromatography on silica [methylene chloride]. Yield: 0.78 g (1.38 mmol, 56%). IR ($CHCl_3$): ν_{max} 1983, 1924 (CO) cm^{-1}. ^1H NMR (500 MHz, C_6D_6): δ 7.63 (trm, 2H, ar-*H*(PPh$_2$)), 7.37 (trm, 2H, ar-*H*(PPh$_2$)), 7.15 (m, 6H, ar-*H*(PPh$_2$)), 5.16 (trd, 1H, J = 6 Hz, J = 1 Hz, ar-*H*), 4.71 (tr, 1H, J = 6.5 Hz, ar-*H*), 4.55 (dd, 1H, J = 6.5 Hz, J_{HP} = 3.5 Hz, ar-*H*), 4.47 (dqd, 1H, J = 7 Hz, J_{HP} = 7 Hz, J_{HP} = 1 Hz, P*t*-Bu$_2$C*H*Me), 4.23 (trd, 1H, J = 6 Hz, J = 1 Hz, ar-*H*), 1.51 (dd, 3H, J = 7 Hz, J_{HP} = 2.5 Hz, P*t*-Bu$_2$-CH*Me*), 1.21 (d, 9H, J_{HP} = 10.5 Hz, C*Me*$_3$), 0.86 (d, 9H, J_{HP} = 11 Hz, C*Me*$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ 233.00 (*C*O), 139.57 (dd, J_{CP} = 5 Hz, J_{CP} = 4.5 Hz, ar-ipso*C*(PPh$_2$)), 138.36 (dd, J_{CP} = 15.5 Hz, J_{CP} = 9 Hz, ar-ipso*C*(PPh$_2$)), 135.59−128.19

(10C, ar-*C*(PPh_2)), 127.09 (dd, J_{CP} = 22 Hz, J_{CP} = 20 Hz, ar-ipso*C*), 103.57 (dd, J_{CP} = 25 Hz, J_{CP} = 3.5 Hz, ar-ipso*C*), 101.69 (d, J_{CP} = 2.7 Hz, ar-*C*), 94.69 (ar-*C*), 89.15 (d, J_{CP} = 2 Hz, ar-*C*), 88.68 (dd, J_{CP} = 3.5 Hz, J_{CP} = 2.5 Hz, ar-*C*), 35.21 (dd, J_{CP} = 38 Hz, J_{CP} = 15.5 Hz, P*t*-Bu_2*C*HMe), 35.09 (dd, J_{CP} = 35.5 Hz, J_{CP} = 3.5 Hz, *C*Me_3), 34.56 (d, J_{CP} = 32 Hz, *C*Me_3), 32.16 (d, J_{CP} = 14 Hz, C*Me*$_3$), 31.57 (dd, J_{CP} = 13 Hz, J_{CP} = 4 Hz, C*Me*$_3$), 15.09 (P*t*-Bu_2CH*Me*)). ^{31}P NMR (81 MHz, C_6D_6): δ +50.49 (d, J_{PP} = 68 Hz, *P*(*t*-Bu)$_2$), −20.19 (d, J_{PP} = 68 Hz, *P*Ph_2). Anal. Calcd for $C_{31}H_{36}CrO_3P_2$: H, 6.36; C, 65.26. Found: H, 6.51; C, 64.59.

[η^6-*(pR,R)*{(OMe)CHMe}$C_6H_4PPh_2$]Cr(CO)$_3$ (14). 10 (0.96 g, 2.08 mmol, 1 equiv) was dissolved at ambient temperature in benzene (30 mL) and treated with methanol (30 mL) for 4 h. After evaporation of the solvent, complex **14** was crystallized from benzene/Et_2O at 10 °C. Yield: 0.88 g (1.93 mmol, 93%). IR ($CHCl_3$): ν_{max} 1972, 1901 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 7.58−6.99 (m, 10H, ar-*H*(PPh_2)), 4.96 (qd, 1H, J = 6.5 Hz, J_{HP} = 6.5 Hz, OMeC*H*Me), 4.80 (ddd, 1H, J = 6.5 Hz, J = 3 Hz, J = 1 Hz, ar-*H*), 4.65 (dtr, 1H, J = 6.5 Hz, J = 1.5 Hz, ar-*H*), 4.54 (tr, 1H, J = 6.5 Hz, ar-*H*), 4.23 (trd, 1H, J = 6.5 Hz, J = 1 Hz, ar-*H*), 2.62 (s, 3H, H-6), 1.21 (d, 3H, J = 6.5 Hz, OMeCH*Me*). ^{13}C NMR (125 MHz, C_6D_6): δ 232.58 (d, J_{CP} = 1.5 Hz, *C*O), 136.77 (d, J_{CP} = 9.5 Hz, ar-ipso*C*(PPh_2)), 135.05 (d, J_{CP} = 13 Hz, ar-ipso*C*(PPh_2)), 135.12−128.35 (ar-*C*(PPh_2)), 117.99 (d, J_{CP} = 21 Hz, ar-ipso*C*), 104.85 (d, J_{CP} = 24 Hz, ar-ipso*C*), 97.46 (d, J_{CP} = 3 Hz, ar-*C*), 93.18 (ar-*C*), 91.02 (d, J_{CP} = 1.5 Hz, ar-*C*), 89.16 (d, J_{CP} = 4.5 Hz, ar-*C*), 74.76 (d, J_{CP} = 19 Hz, OMe*C*HMe), 55.22 (d, J_{CP} = 1.5 Hz, O*Me*), 16.73 (OMeCH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ −13.49. Anal. Calcd for $C_{24}H_{21}CrO_4P$: H, 4.64; C, 63.16. Found: H, 4.65; C, 63.11.

[η^6-*(pR,R,R)*{(PhCH(CH$_3$)NHCH(CH$_3$)}$PPh_2C_6H_4$]Cr(CO)$_3$ (15). 15 was produced from **10** (1.21 g, 2.63 mmol), (*R*)-phenylethanamine (1.67 mL, 13.13 mmol, 5.0 equiv), and $TlPF_6$ (1.01 g, 2.89 mmol, 1.1 equiv), according to general method C. The complex was purified by chromatography on silica [Et_2O/hexane, 1:1]. Yield: 0.86 g (1.58 mmol, 60%). IR ($CHCl_3$): ν_{max} 1971, 1900 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 7.51 (trm, 2H, ar-*H*(PPh_2)) or ar-*H*($Ph_{uncompl}$)), 7.26 (trm, 2H, ar-*H*(PPh_2)) or ar-*H*($Ph_{uncompl}$)), 7.13−7.03 (m, 9H, ar-*H*(PPh_2)) or ar-*H*($Ph_{uncompl}$)), 6.76−6.72 (m, 2H, ar-*H*(PPh_2)) or ar-*H*($Ph_{uncompl}$)), 4.80−4.75 (m, 2H, ar-*H* and C*H*(NHPh)Me), 4.69 (dtr, 1H, J = 6.5 Hz, J = 1.5 Hz, ar-*H*), 4.66 (trm, 1H, ar-*H*), 4.31 (trm, 1H, ar-*H*), 4.31 (trm, 1H, ar-*H*), 3.54 (q, 1H, J = 6.5 Hz, C*H*(NHPh$_{uncompl}$)Me), 1.11 (d, 3H, J = 6.5 Hz, CH(NHPh$_{uncompl}$)*Me*), 0.87 (d, 3H, J = 6.5 Hz, CH(NHPh)*Me*), 0.62 (brs, 1H, N*H*). ^{13}C NMR (125 MHz, C_6D_6): δ 232.79 (d, J_{CP} = 1.5 Hz, *C*O), 147 (ar-ipso-*C*($Ph_{uncompl}$)), 137.58 (d, J_{CP} = 10.5 Hz, ar-ipso*C*(PPh_2)), 135.62 (d, J_{CP} = 14.5 Hz, ar-ipso*C*(PPh_2)), 135.10−126.75 (15C, ar-*C*(PPh_2)) and ar-*C*($Ph_{uncompl}$)), 122.26 (d, J_{CP} = 21.5 Hz, ar-ipso*C*), 104.08 (d, J_{CP} = 23 Hz, ar-ipso*C*), 98.07 (d, J_{CP} = 3 Hz, ar-*C*), 93.80, 90.73 (ar-*C*), 89.30 (d, J_{CP} = 4 Hz, ar-*C*). 56.74 (*C*H(NHPh$_{uncompl}$)Me), 51.58 (d, J_{CP} = 21.5 Hz, C*H*(NHPh)Me), 22.57 (CH(NHPh$_{uncompl}$)*Me*), 19.07 (CH(NHPh)*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ −16.63. Anal. Calcd for $C_{31}H_{28}CrNO_3P$: H, 5.00; C, 68.38; N, 2.57. Found: H, 5.46; C, 69.13; N, 2.33.

[η^6-*(R,R)*{(3,5-dimethylaminopyrazole)CHMe}C_6H_4-PPh_2)Cr(CO)$_3$ (16). 16 was produced from **10** (1.03 g, 2.24 mmol), 3,5-dimethylpyrazole (0.24 g, 2.46 mmol, 1.1 equiv), and $TlPF_6$ (0.78 g, 2.24 mmol, 1.0 equiv), according to general method C. The substance was purified by chromatography on silica [ethyl acetate/hexane, 1:4] to give dark yellow **16**. Yield: 0.71 g (1.36 mmol, 61%). IR ($CHCl_3$): ν_{max} 1972, 1904 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 7.45 (trm, 2H, ar-*H*(PPh_2)), 7.09 (trm, 2H, ar-*H*(PPh_2)), 7.03 (trm, 1H, ar-*H*(PPh_2)), 6.94−6.83 (m, 5H, ar-*H*(PPh_2)), 6.14 (qd, 1H, J = 7 Hz, J_{HP} = 7 Hz, NC*H*Me), 5.25 (ddd, 1H, J = 6.5 Hz, J = 3 Hz, J = 1 Hz, ar-*H*), 5.01 (s, 1H, pz-C*H*), 4.72 (tr, 1H, J = 6.5 Hz, ar-*H*), 4.63 (dtr, 1H, J = 6.5 Hz, J = 1.5 Hz, ar-*H*), 4.18 (trd, 1H, J = 6.5 Hz, J = 1 Hz, ar-*H*), 1.95 (s, 3H, pz-*Me*), 1.92 (s, 3H, pz-*Me*), 1.38 (d, 3H, J = 6.5 Hz, NCH*Me*). ^{13}C NMR (125 MHz, C_6D_6): δ 232.71 (*C*O), 147.69 (pz-*C*Me), 138.03 (pz-*C*Me), 134.84 (d, J_{CP} = 11.5 Hz, ar-ipso*C*(PPh_2)), 134.50 (d, J_{CP} = 7.5 Hz, ar-ipso*C*(PPh_2)), 135.18−128.26 (10C, ar-*C*(PPh_2)), 116.26 (d, J_{CP} = 22 Hz, ar-ipso*C*), 104.79 (pz-*C*H), 103.08 (d, J_{CP} = 22.5 Hz, ar-ipso*C*), 98.58 (d, J_{CP} = 3 Hz, ar-*C*), 94.70 (ar-*C*), 90.74 (d, J_{CP} = 4 Hz, ar-*C*), 90.53 (ar-*C*), 53.24 (d, J_{CP} = 22.5 Hz, N*C*HMe), 19.22 (pz-*Me*), 13.85 (pz-*Me*), 10.60 (d, J_{CP} = 9 Hz, NCH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ −14.35.

[η^6-*(pR,R)*{(CN)CHMe}$C_6H_4PPh_2$]Cr(CO)$_3$ (17). A 1.10 g (2.39 mmol, 1.0 equiv) sample of compound **10** was dissolved in acetone (15 mL/mmol chromium complex) and treated with NaCN (0.35 g, 7.17 mmol, 3.0 equiv) in H_2O (mL/mmol chromium complex) at ambient temperature. The complex was purified by chromatography on silica [methylene chloride/hexane, 9:1]. Yield: 0.20 g (0.44 mmol, 19%). IR ($CHCl_3$): ν_{max} 1980, 1916 (CO), 2247 (CN) cm^{-1}. Main diastereoisomer: ^{1}H NMR (500 MHz, C_6D_6): δ 7.41 (trm, 2H, ar-*H*(PPh_2)), 7.13−7.02 (m, 8H, ar-*H*(PPh_2)), 4.93 (ddd, 1H, J = 6.5 Hz, J = 3.5 Hz, J = 1 Hz, ar-*H*), 4.71−4.64 (m, 2H, ar-*H* and CNC*H*Me), 4.58 (dtr, 1H, J = 6 Hz, J = 1 Hz, ar-*H*), 4.13 (trd, 1H, J = 6.5 Hz, J = 1 Hz, ar-*H*), 0.66 (d, 3H, J = 7 Hz, CNCH*Me*). ^{13}C NMR (125 MHz, C_6D_6): δ 231.44 (*C*O), 135.64 (d, J_{CP} = 8.5 Hz, ar-ipso*C*(PPh_2)), 133.56 (d, J_{CP} = 11 Hz, ar-ipso*C*(PPh_2)), 134.73−128.27 (ar-*C*(PPh_2)), 119.65 (d, J_{CP} = 2 Hz, *C*N), 114.15 (d, J_{CP} = 24 Hz, ar-ipso*C*), 100.58 (d, J_{CP} = 23 Hz, ar-ipso*C*), 97.10 (d, J_{CP} = 2 Hz, ar-*C*), 94.49, 89.46 (ar-*C*), 88.01 (d, J_{CP} = 3.5 Hz, ar-*C*), 29.84 (d, J_{CP} = 30 Hz, CN*C*HMe), 2.02 (CNCH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ −17.74.

18 can be isolated as a side product of this reaction by elution with ethyl acetate. Yield: 0.58 g (1.31 mmol, 55%)**.** IR ($CHCl_3$): ν_{max} 1973, 1904 (CO) cm^{-1}. ^{1}H NMR (500 MHz, C_6D_6): δ 7.51−7.48 (m, 2H, ar-*H*(PPh_2)), 7.28−7.24 (m, 2H, ar-*H*(PPh_2)), 7.16−7.00 (m, 6H, ar-*H*(PPh_2)), 5.40 (dq, 1H, J_{HP} = 11 Hz, J = 6.5 Hz, OHC*H*Me), 4.76 (ddd, 1H, J = 6.5 Hz, J = 3 Hz, J = 1 Hz, ar-*H*), 4.62 (dtr, 1H, J = 6 Hz, J = 1.5 Hz, ar-*H*), 4.56 (tr, 1H, J = 6.5 Hz, ar-*H*), 4.23 (trd, 1H, J = 6.5 Hz, J = 1 Hz, ar-*H*), 1.19 (d, 3H, J = 6.5 Hz, OHCH*Me*). ^{13}C NMR (125 MHz, C_6D_6): δ 232.50 (d, J_{CP} = 1 Hz, *C*O), 136.90 (d, J_{CP} = 10 Hz, ar-ipso*C*(PPh_2)), 134.54 (d, J_{CP} = 13.5 Hz, ar-ipso*C*(PPh_2)), 135.04−128.86 (ar-*C*(PPh_2)), 119.01 (d, J_{CP} = 20 Hz, ar-ipso*C*), 103.94 (d, J_{CP} = 23 Hz, ar-ipso*C*), 97.22 (d, J_{CP} = 2 Hz, ar-*C*), 93.58 (ar-*C*), 90.74 (d, J_{CP} = 1.5 Hz, ar-*C*), 88.75 (d, J_{CP} = 4 Hz, ar-*C*), 66.32 (d, J_{CP} = 21.5 Hz, OH*C*HMe), 21.09 (d, J_{CP} = 1.5 Hz, OHCH*Me*). ^{31}P NMR (81 MHz, C_6D_6): δ −14.92.

Hydrogenation Reactions. A 120 mL glass insert for steel autoclaves was filled under argon with 20 mmol of [CODRhCl]$_2$, 45 mmol of ligand, and 60 mL of degassed methanol. After stirring for 30 min, 20 mmol of acetamidocinnamic acid was added and the autoclave closed. The inert gas was replaced by hydrogen and the pressure set at 100 bar and 40 °C. After a reaction time of 24 h, the reaction mixture was reduced in volume to 30 mL and the precipitate collected and dried. The acid was converted into the methyl ester by treatment with diazomethane and the optical purity (*S*) of the hydrogenation product analyzed by GC (Chirasil-Val, Astec). Methyl acetamidoacrylate was treated similarly, and the hydrogenation product was analyzed via GC (Chiraldex GT-A, Astec).

Allylic Sulfonations. General Procedure. A 25 mL Schlenk tube was filled with 1.5 mol % of $Pd_2(dba)_3$·$CHCl_3$ and 4.5 mol % of the ligand in 5 mL of CH_2Cl_2. The deep red solution lightens in color after a few minutes. After 5 min, the substrate was added. In a second Schlenk tube, 200 mol % of lithium *tert*-butylsulfinate[12] and 5 mol % of tetrahexylammonium bromide were suspended in 5 mL of degassed H_2O and 5 mL of CH_2Cl_2. The sulfinate emulsion was added to the catalyst/substrate mixture at 0 °C and stirred for 150 h at room temperature. Conversion was periodically checked via GC. Enantiomeric excess was determined via GC (LIPODEX-E,

Macherey-Nagel: octakis-(2,6-di-*O*-pentyl-3-*O*-butyryl)-γ-cyclodextrin, 25 m × 0.0.25 mm).

Hydroamination Reactions. [{(η^6-*(pR,R)*{CHPCy$_2$Me}-C$_6$H$_4$PPh$_2$)Cr(CO)$_3$}IrCl]$_2$. Ethene was bubbled through a yellow pentane (3 mL) slurry of [IrCl(cyclooctene)$_2$]$_2$ (34.5 mg, 0.0385 mmol) at 0 °C for 20 min. After evaporation of the solvent, toluene (2 mL) was added to the off-white solid. A toluene solution of **12** (48.0 mg, 0.077 mmol) was added dropwise over 15 min at −80 °C. The solution was slowly allowed to warm to room temperature, ethene being vented from the flask. All volatiles were removed in vacuo, leaving a fine red powder in quantitative yield. ^{31}P{^{1}H} NMR (C_6D_6), AA′XX′ spin system, isomer A: 16.34 and 43.36 ppm (J_{PP} 34.7 Hz); isomer B: 17.31, 54.16 ppm (J_{PP} 30.3 Hz). This cis/trans mixture was used in catalysis without any further purification.

[{(η^6-*(pR,R)*{CHP*t*-Bu$_2$Me}C$_6$H$_4$PPh$_2$)Cr(CO)$_3$}IrCl]$_2$. Same procedure as before was used, from [IrCl(cyclooctene)$_2$]$_2$ (39.2 mg, 0.044 mmol) and **13** (50.0 mg, 0.0875 mmol). ^{31}P-{^{1}H} NMR (C_6D_6), AA′XX′ spin system, isomer A: 13.54 and 71.51 ppm (J_{PP} 29.08 Hz); isomer B: 14.04, 71.78 ppm (J_{PP} 30.7 Hz).

Ir(I)-Catalyzed Addition of Aniline to Norbornene. Typical Procedure. To a solution of [IrCl((*R*)-(*S*)-Josiphos)]$_2$ (cis/trans mixture, 5.0 mg, 0.0029 mmol) and norbornene (575 mg, 6.11 mmol) in aniline (569 mg, 6.11 mmol) was added [N(P(NMe$_2$)$_3$)$_2$]F (0.10 mL, ca. 0.5 M in benzene, ca. 0.05 mmol) via a plastic syringe, affording a yellow-orange clear solution. The reaction mixture was stirred and heated at 60 °C for 96 h. The reaction was quenched by exposure to air, and the product was isolated and purified by chromatography on silica (l = 10 cm, d = 2 cm, ethyl acetate/hexane = 1:10), affording 306.1 mg (26.8%) of a pale yellow oil. The enantiomeric excess was determined by HPLC using a Daicel Chiralcel OJH column and eluting with a hexane/*i*-PrOH mixture (95:5 v/v; 0.5 mL/min; T = 25 °C; retention times: (2*R*)-**5** 18.0 min, (2*S*)-**5** 19.5 min).

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