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Expanding the Range of "Daniphos"-Type P∩P- and P∩N-Ligands: Synthesis and Structural Characterisation of New [(η⁶-arene)Cr(CO)₃] Complexes

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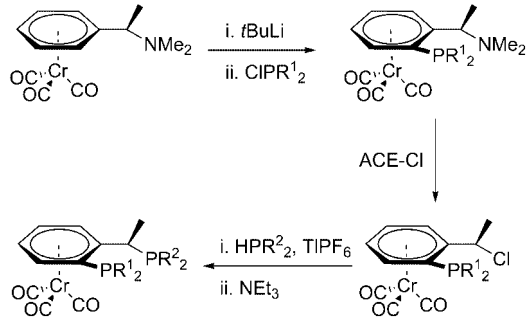
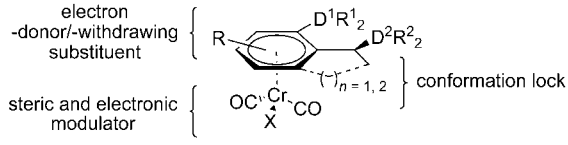
New P∩P- and P∩N-ligands have been synthesised whose core structure is an [(η⁶-arene)Cr(CO)₃] unit. These new ligands, which extend the range of "Daniphos" ligands, are endowed with central and planar chirality and have been prepared through a stereoselective synthetic strategy from optically pure benzylamines bearing a second substituent on the arene other than the benzyldimethylamino group. Because the two faces of unsymmetrically 1,2- and 1,3-disubstituted benzylamine are diastereotopic, which means that diastereomeric complexes arise upon coordination of the Cr(CO)₃ fragment to either of these two faces, the synthetic plan has been adjusted by exploiting the trimethylsilyl group as a temporary steric modulator in order to access both complexes with high diastereoselectivity.

Introduction

"Daniphos" ligands are a class of ligands suitable for application in catalysis whose core structure is an [(η⁶-arene)Cr(CO)₃] unit. A stereoselective synthetic strategy developed recently in our laboratories has provided these ligands with a modular and tunable character (Scheme 1).[1] Daniphos ligands are usually prepared from commercially available optically pure benzylamines and are characterised by the presence of a stereogenic plane and a stereocentre. Planar chirality is introduced by means of a diastereoselective directed orthometallation (DOM) assisted by the benzylic amino group and subsequent electrophilic substitution on the arene ring. Central chirality is preserved by the stereoselective replacement of the dimethylamino group for a chloride by treatment with chloroethyl chloroformate (ACE-Cl) and subsequent stereoselective nucleophilic substitution of the chloro substituent for a different nucleophile. A library of ligands, which comprises mono- and bidentate P∩N and P∩P ligands, has been prepared following this approach.[1–3] The steric and/or electronic properties of these ligands can be easily tuned by varying the R^1/R^2 substituents on the donor atoms D or by reducing their conformational flexibility by tethering the donor atoms to an annelated framework[3e] (Scheme 2). These ligands have been tested in a number of enantioselective homogeneous catalytic processes such as hydrogenation,[3] hydroamination,[3a] allylic sulfonation,[3a] hydrovinylation,[1b] transfer hydrogenation[4] and, more recently, nucleophilic asymmetric ring opening (ARO) of oxabenzonorbornadienes.[5]



Scheme 1. General synthetic strategy for the preparation of "Daniphos"-like diphosphanes. ACE-Cl = 1-chloroethyl chloroformate.



Scheme 2. Accessibility of a modular ligand architecture based on [(η⁶-arene)Cr(CO)₃] complexes.

As shown in Scheme 2, a further possibility for altering the basic structure of Daniphos ligands is to introduce a substituent R onto the arene ring. Such substituents might be important in modulating the electronic properties of the donor atoms D and, depending on their location on the arene, also their steric properties. Such substituents can be introduced at the stage of complexation of the arene to the

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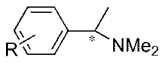
$Cr(CO)_3$ moiety as a range of chiral amines related to 1-phenylethylamine that already bear the R substituent are commercially available. In this paper we detail the synthesis of these complexes and explore the influence of the R group on the outcome of some steps of our established synthetic strategy. The X-ray structures of some intermediates and some of the target ligands are also provided, which, in cases of uncertainty, serve to define the stereochemical outcome of a reaction.

Results and Discussion

The amines used to prepare the "Daniphos" ligands reported in this paper are shown in Figure 1. The corresponding primary benzylamines were reductively methylated with formaldehyde and formic acid following the Eschweiler–Clarke procedure.[6] Protection of the amino group prior to complexation to the $Cr(CO)_3$ moiety is necessary in order to reduce its coordinating ability towards chromium as this might lead to incomplete complex formation. The diphosphanes P∩P were prepared from the *para*-substituted benzylamines (*S*)-**1**, (*S*)-**2**, (*R*)-**3** and (*R*)-**6** while the bidentate P∩N ligands were prepared from *ortho*- and *meta*-methoxy-substituted benzylamines (*S*)-**4** and (*S*)-**5**.

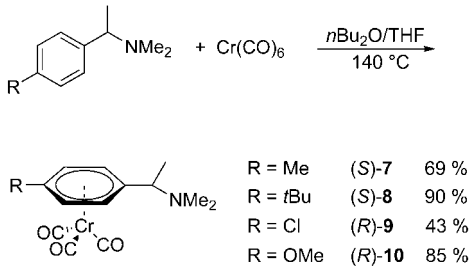


R = 4-Me	(*S*)-**1**
R = 4-*t*Bu	(*S*)-**2**
R = 4-Cl	(*R*)-**3**
R = 2-OMe	(*S*)-**4**
R = 3-OMe	(*S*)-**5**
R = 4-OMe	(*R*)-**6**

Figure 1. Phenylethylamines which have been complexed to the $Cr(CO)_3$ moiety to synthesise the "Daniphos" ligands reported in this paper.

Preparation of Daniphos Diphosphanes P∩P

The coordination of amines (*S*)-**1**, (*S*)-**2**, (*R*)-**3** and (*R*)-**6** was accomplished by thermolysis with $Cr(CO)_6$ (Scheme 3). The reactions weren carried out under the conditions reported by Mahaffy and Pauson.[7] The protected benzylamine and $Cr(CO)_6$ were heated (temperature of the oil bath: 140 °C) in an 8:1 mixture of di-*n*-butyl ether and tetrahydrofuran until the evolution of CO ceased or onset of decomposition was observed. The best yield was obtained with the *para*-*tert*-butyl-substituted benzylamine (*S*)-**2**. It is known that π-electron-withdrawing groups (e.g. CHO or COOH) slow down complexation and are best protected before complexation, while electron-donating arene substituents accelerate complexation.[8a,8b] Complexation of (*R*)-**3** to the $Cr(CO)_3$ moiety gave a modest 43% yield of the expected complex. In this case, decomposition during the reaction, as indicated by formation of a grey-green precipitate, was difficult to avoid. This appears to be progressive and the reaction had to be stopped. The poor yield might also be due to reductive dehalogenation.[9]



R = Me	(*S*)-**7**	69 %
R = *t*Bu	(*S*)-**8**	90 %
R = Cl	(*R*)-**9**	43 %
R = OMe	(*R*)-**10**	85 %

Scheme 3. Yields obtained in the complexation of protected *para*-substituted benzylamines with $Cr(CO)_6$.

DOM of complexes (*S*)-**7**, (*S*)-**8**, (*R*)-**9** and (*R*)-**10** was carried out according to a general procedure consisting of treatment with *t*BuLi in diethyl ether at –78 °C for 1.5 h, subsequent quenching with $ClPPh_2$, and warming to room temperature overnight. The relative amounts of products formed were calculated based on integration of the corresponding ^{31}P NMR signals in the spectra of crude reaction mixtures in all cases. The diastereomeric excesses reported in the schemes were calculated in a similar manner. Products of very high purity were obtained by flash chromatography.

Coordination of the $Cr(CO)_3$ group to the arene enhances the kinetic acidity of the ring C–H bonds due to the strong electron-withdrawing character of the $Cr(CO)_3$ moiety,[8c] therefore direct lithiation of the arene ring occurs more easily than that of the parent chromium-free arene. Because of the presence of a heteroatom-containing functionality, lithiation can be extremely selective towards the *ortho* position due to specific coordination of the base through its lithium counterion.[10]

The two hydrogen atoms *ortho* to the ethylamino group in complexes (*S*)-**7**, (*S*)-**8**, (*R*)-**9** and (*R*)-**10** are diastereotopic because of the α-stereogenic centre, which means that preferential replacement of either of them gives rise to unequal amounts of two molecules endowed with the same central chirality but opposite planar chirality.[11] When the related complex [{(*R*)-*N*,*N*-dimethyl-1-phenylethylamine}$Cr(CO)_3$] is treated with *tert*-butyllithium in diethyl ether at –78 °C, the ortholithiated species derived from preferential abstraction of the H_S proton is formed with 96% diastereoselectivity (Figure 2).[12] The origin of this high diastereoselectivity stems from a preferential average solution-state conformation in which both the α-methyl and α-dimethylamino groups lie above the plane of the arene ring, opposite the bulky $Cr(CO)_3$ unit (Figure 2, a). This "sensible" spatial arrangement has been inferred by deuterium-labelling and difference NOE ^1H NMR experiments. According to these data, it can be expected that the *ortho*-directing dimethylamino group preferentially directs a precoordinated lithium base towards the closest H_S proton (Figure 2, b). Removal of the H_R proton would force the benzylic methyl group below the plane of the arene, thereby causing an unfavourable steric interaction with the tricarbonylchromium unit. The absolute configuration of the α-stereogenic centre dictates the relative planar chirality, thus

indicating that the sense of asymmetric induction is determined in the deprotonation step. The greater discrimination between the two diastereotopic hydrogens achieved with a sterically more demanding base such as *t*BuLi is consistent with this assumption. In fact, although high *ortho* diastereoselectivity has been demonstrated with both *n*BuLi and *t*BuLi, only the latter allows for complete transfer of side-chain chirality on to the arene ring.

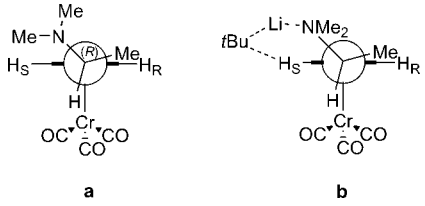
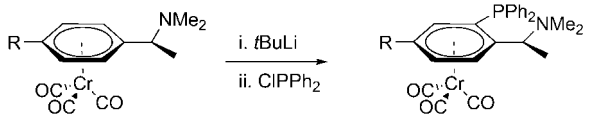


Figure 2. (a) Average solution-state conformation of the benzylic side chain of [{(*R*)-*N*,*N*-dimethyl-1-phenylethylamine}$Cr(CO)_3$] as inferred from NOEDS. (b) Newman projection of the possible directed orthometallation intermediate along the C_α–C_{ipso} bond.

Uemura and Hayashi prepared the first ever reported P,N ligand of the "Daniphos" type by diastereoselective lithiation of [{(*R*)-*N*,*N*-dimethyl-1-phenylethylamine}$Cr(CO)_3$] and subsequent reaction with chlorodiphenylphosphane.[13]

DOM of (*S*)-**7** and (*S*)-**8** proceeds with high diastereoselectivity to give the expected products (*S*,*R*p)-**11** and (*S*,*R*p)-**12**, respectively (Scheme 4). No competitive α-proton abstraction was observed in the *ortho* functionalisation of (*S*)-**7** either from the dimethylaminoethyl group or from



R = Me (*S*)-**7** (*S*,*R*p)-**11** *de* = 92% (90%)

R = *t*Bu (*S*)-**8** (*S*,*R*p)-**12** *de* > 99% (78%)

Scheme 4. Products obtained in the *ortho*-functionalisation of (*S*)-**7** and (*S*)-**8**.

the *para*-substituted methyl group − α-proton abstraction from [(η^6-arene)$Cr(CO)_3$] complexes is in fact the thermodynamically favoured process and the high yield of ring-substituted products clearly demonstrates that proton abstraction by *tert*-butyllithium is kinetically controlled.[14]

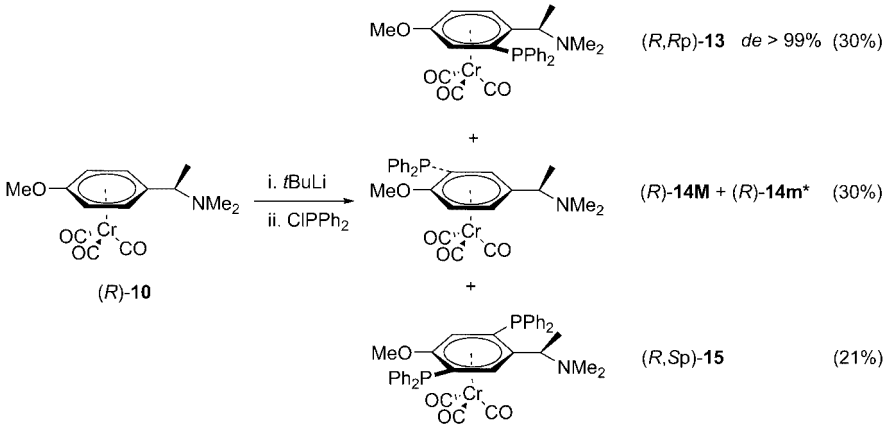
ortho-Functionalisation of [{η^6-(*R*)-1-(4-methoxyphenyl)-*N*,*N*-dimethylethylamine}$Cr(CO)_3$] [(*R*)-**10**] according to the procedure described above affords a mixture of products due to the presence of two coordinating substituents (Scheme 5).

A very useful study has demonstrated that the substituent effects on regioselectivity in the deprotonation of free arenes are distinctly different from those found for [$Cr(CO)_3$]-complexed arenes.[15] A series of *para*-disubstituted arenes were complexed and deprotonated, and the ratio of the two possible products in each case allowed a reactivity series to be generated. The following ratio of *ortho*-directing abilities of functional groups was deduced:

$F > CONHR > NHCOR > CH_2NR_2 \approx OMe >> CH_2OMe$

According to this study, when lithiation is performed at –78 °C with *s*BuLi for 1.5 h and is followed by electrophilic quenching with Me_3SiCl, the relative kinetic acidity of a ring proton takes precedence over simple base coordination by a heteroatom in the substituent group as the principal factor in determining the site of metallation in disubstituted arene complexes. The chromium complex of *p*-methoxy-*N*,*N*-dimethylbenzylamine provides a comparison of the directing effect of the OMe and CH_2NMe_2 groups. In this case, the two effects, namely OMe-induced labilisation of the *ortho* proton by electron withdrawal and CH_2NMe_2 coordination of the incoming base, are almost exactly balanced. In line with this result, D*O*M of (*R*)-**10** produces similar amounts of products in which lithiation has occurred *ortho* to the benzylic amino group and *ortho* to the methoxy group.

The products reported in Scheme 5 were separated by means of flash chromatography, although (*R*)-**14M** (the more abundant isomer) and (*R*)-**14m** (the less abundant iso-



Scheme 5. Products obtained in the *ortho*-functionalisation of (*R*)-**10**. Yields of isolated products are reported in parentheses. * This notation indicates the two regioisomeric products bearing a diphenylphosphanyl group *ortho* to the OMe substituent; the absolute configurations, however, could not be assigned.

Table 1. Products obtained in the *ortho*-functionalisation of (*R*)-**10** along with diagnostic chemical shifts.

Complex	Relative amounts[a] [%]	Yield[b] [%]	$\delta_{^1H}$ [ppm] (mult) C*H*(Me)NMe$_2$	$\delta_{^{31}P}$ [ppm] PPh$_2$ *ortho* to CH(Me)NMe$_2$	OMe
(*R*)-**10**	–	–	2.96 (q)	–	–
(*R*,*R*p)-**13**	32	30	4.41 (m)	–14.22	–
(*R*)-**14M**	26	30[c]	2.69 (q)	–	–18.57
(*R*)-**14m**	10		2.86 (q)	–	–17.92
(*R*,*S*p)-**15**	32	30	4.22 (m)	–14.23	–17.69

[a] Ratio of products based on peak integration in the ^{31}P NMR spectrum of the crude reaction mixture. [b] Yield of product isolated after flash chromatography. [c] The two regioisomeric products could not be separated by flash chromatography and were isolated as a single fraction.

mer), which are the two regioisomeric products bearing a diphenylphosphanyl group *ortho* to the -OMe substituent, could not be separated and were collected as a single fraction.

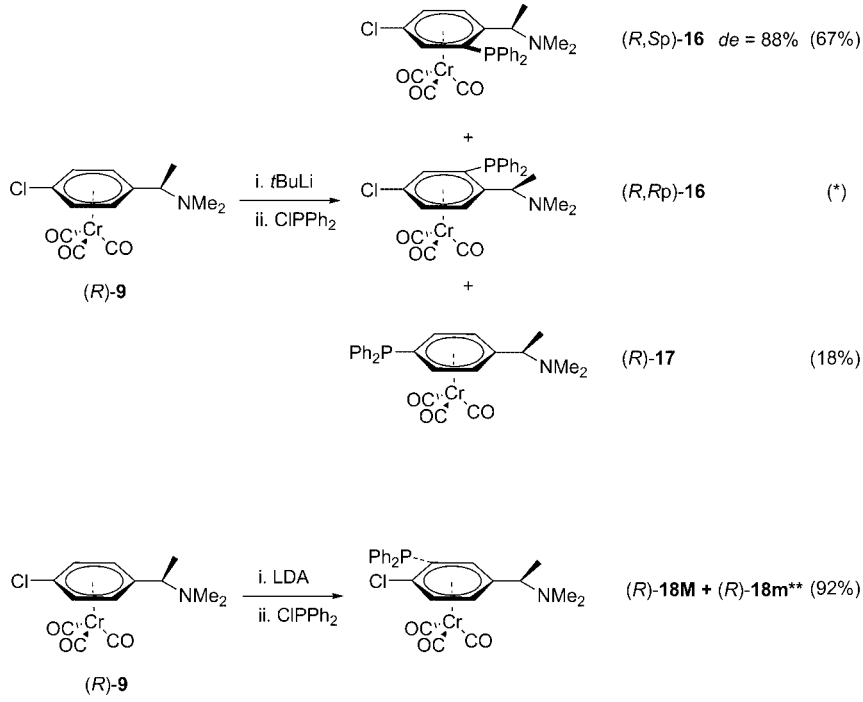
The identity of the products was assigned based on the mass, ^1H and ^{31}P NMR, and 2D NMR spectra (Table 1). The location of the diphenylphosphanyl group *ortho* to the dimethylethylamino group was easily inferred from the ^1H NMR spectrum due to the phosphorus-hydrogen coupling, which further splits the signal of the α-hydrogen compared to the corresponding signal in complex (*R*)-**10**. Furthermore, this resonance is shifted nearly 2 ppm to lower field due to the proximity of the phenyl groups and their "ring current" effect. This is observed both in the spectrum of the desired (*R*,*R*p)-**13** [its diastereomeric product (*R*,*S*p)-**13** could not be detected in the ^1H NMR spectrum of the crude reaction mixture] and in the spectrum of disubstituted (*R*,*S*p)-**15**. The chemical shift of the α-hydrogen signal is nearly unchanged and no H-P coupling is detected in the spectrum of (*R*)-**14M** or (*R*)-**14m**, which were identified as the species in which lithiation has occurred *ortho* to the OMe group. The two regioisomers are formed in a 72:28 ratio, thereby suggesting a possible influence of the remote stereogenic centre; the absolute planar chirality was not assigned.

Formation of complex (*R*,*S*p)-**15** might proceed via a dianion stabilized by the strongly electron-withdrawing Cr(CO)$_3$ moiety, which could mean that the mono-lithiated arene ring is sufficiently acidic to allow a second deprotonation or the second deprotonation is faster than the first one.[16] Unfortunately, to the best of our knowledge, there is no reliable structural and spectroscopic information on lithiated [(η^6-arene)Cr(CO)$_3$] complexes which would make it possible to determine whether the electronic effect of Li as a substituent does or does not deactivate the aromatic ring towards further H-abstraction. The existence of an intermediate polycarbanion has been postulated recently in a detailed investigation of multiple substitution of [(η^6-arene)Cr(CO)$_3$] complexes.[17] The treatment of representative complexes such as [{η^6-1-(*tert*-butyl-sulfonyl)-benzene}Cr(CO)$_3$], [(η^6-anisole)Cr(CO)$_3$] and [(η^6-*N*,*N*-dimethylbenzylamine)Cr(CO)$_3$] with three equivalents of 2,2,6,6-tetramethylpiperidyllithium (LiTMP), followed by electrophilic quenching with Me$_3$SiCl, provided a series of di- and trisilylated complexes. Deuteration studies using lithium diisopropylamide (LDA) as the base and deuteroacetic acid as the electrophile led to the observation of a trideuterated species presumably derived from a trianionic species formed during the reaction. Alternatively, complex (*R*,*S*p)-**15** might arise from successive deprotonation/trapping/deprotonation processes enabled by the unreacted *t*BuLi. This would imply that electrophilic trapping of the base itself is rather slower than deprotonation of the arene complex, although the isolation of *t*BuPPh$_2$ as a by-product in some cases suggests that this might not be the case.

The stereochemistry of complex (*R*,*S*p)-**15** was tentatively assigned based on the most stable charge arrangement of the intermediate dianion considering that both the dimethylethylamino group and the methoxy group favour the formation of the corresponding *ortho* anion and that the dimethylethylamino group stereoselectively promotes abstraction of the pro-S_P *ortho* H atom.

Lithiation of [{η^6-(*R*)-1-(4-chlorophenyl)-*N*,*N*-dimethylethylamine}Cr(CO)$_3$] [(*R*)-**9**] with *t*BuLi followed by treatment of the lithiated species with ClPPh$_2$ afforded the expected *ortho*-functionalised diastereomeric complexes (*R*,*S*p)-**16** and (*R*,*R*p)-**16** and the product of metal/halogen exchange [(*R*)-**17**; Scheme 6]. According to the ^{31}P NMR spectrum of the crude reaction mixture, the relative ratio of (*R*,*S*p)-**16** and (*R*,*R*p)-**16** is 94:6, which corresponds to an 88% diastereoselectivity of the ortholithiation reaction (Table 2). Pure (*R*,*S*p)-**16** was obtained by flash chromatography. A second fraction contained (*R*,*R*p)-**16** as the main product. Attempts to further purify this complex failed, however, and its structure was assigned based on its ^1H NMR spectrum, where the diagnostic H-P coupling and shift of the -C*H*(Me)NMe$_2$ signal to lower field are observed. Although directed orthometallation is predominant, competitive chloride/lithium exchange leads to the formation of complex (*R*)-**17**. Interestingly, no lithiation *ortho* to the chloro substituent was detected.

Because lithium amides enable metallation to be achieved in preference to metal/halogen exchange,[18a] lithiation of (*R*)-**9** was repeated with LDA under otherwise identical conditions. However, only the two diastereoisomers corresponding to lithiation *ortho* to the chloro substituent were detected in a nearly 1:1 ratio (Scheme 6). The steric bulk of the base most likely prevents coordination by the ethyldimethylamino group and the electron-withdrawing effect of the chloro substituent prevails in dictating the regiochemis-



Scheme 6. Products obtained in the *ortho*-functionalisation of (*R*)-**9**. Yields of isolated products are reported in parentheses. * See Table 2. ** This notation indicates the two regioisomeric products bearing a diphenylphosphanyl group *ortho* to the Cl substituent whose absolute configuration could not be assigned.

Table 2. Products obtained in the *ortho*-functionalisation of (*R*)-**9** along with diagnostic chemical shifts.

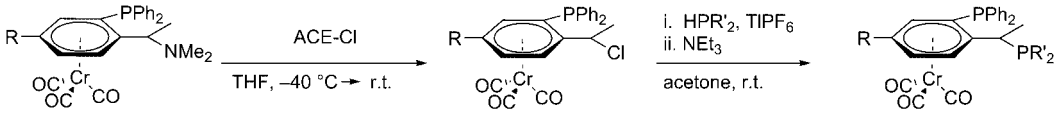
Complex	Rel. amounts[a] [%]	Yield[b] [%]	δ_{1H} [ppm] (mult.) C*H*(Me)NMe$_2$	δ_{31P} [ppm]
(*R*)-**9**	–	–	2.88 (q)	
(*R*,*S*p)-**16**	77	67	4.39 (m)	–14.41
(*R*,*R*p)-**16**	5	[c]	3.57 (m)	–17.53
(*R*)-**17**	18	18	3.25 (q)	–7.83
(*R*)-**18M**	54	92[d]	2.64 (q)	–12.06
(*R*)-**18m**	46		2.75 (q)	–11.83

[a] Relative amounts of products based on peak integration in the ^{31}P NMR spectrum of the crude reaction mixture. [b] Yield of product isolated after flash chromatography. [c] The collected fraction was not clean and contained some (*R*,*S*p)-**16** and (*R*)-**17**. [d] The two diastereomeric products (*R*)-**18M** and (*R*)-**18m** could not be separated by flash chromatography and were isolated as a single fraction (see text).

try of deprotonation.[18b] These complexes could not be separated by flash chromatography and the regiochemistry of lithiation was assigned based on the ^{1}H NMR spectrum of the mixture of the two diastereoisomers. The two compounds, the absolute planar chirality of which could not be defined, are labelled as the major [(*R*)-**18M**] and minor [(*R*)-**18m**] diastereoisomers in Table 2.

After the first phosphorus donor has been introduced into the *ortho* position, a second one has to be appropriately placed in the benzylic position for subsequent metal chelation. This was achieved in two steps, both of which are highly stereoconservative (Scheme 7). The first step involves transformation of the phosphanylamino complex into a chlorobenzyl derivative by treatment of the former with an excess of 1-chloroethyl chloroformate (ACE-Cl). This procedure, which has been developed in our laboratory,[1a] relies on the ability of chloroformates to promote the mild debenzylation of tertiary amines.[19] Replacement of the dimethylamino group by chloride takes place with retention of configuration and no evidence of epimerisation was observed. All the desired α-chloro derivatives were obtained in good yields after purification by flash chromatography except the *para*-chloro one [(*R*,*S*p)-**22**], which readily decomposes while adsorbed on silica gel. The reported yield of (*R*,*S*p)-**22** therefore refers to the crude product after the removal of excess ACE-Cl and carbamate by-product.

The new C_1-symmetric diphosphane ligands were finally prepared by treatment of the corresponding benzyl chloride complexes with a slight excess of a secondary phosphane (HPR′$_2$) in acetone at room temperature in the presence of $TlPF_6$, which acts as a chloride scavenger by precipitation of highly insoluble TlCl. The ^{31}P NMR spectra of all ligands display two doublets − one for each non-equivalent phosphorus atom − whose splitting is due to coupling to the other phosphorus atom in the molecule (Table 3). Large low-field shifts are observed upon changing the substituent on the α-phosphorus atom from phenyl to cyclohexyl and, to a larger extent, to *tert*-butyl. This downfield shift with increasing steric bulk at phosphorus can be explained by a concomitant change in the hybridisation at phosphorus.[20] However, within the same set of diphosphanes having the



R = Me	(*S*,*R*p)-**11**	R = Me	(*S*,*R*p)-**19**	86%	R = Me	R' = Ph	(*S*,*R*p)-**23a**	64%
						R' = Cy	(*S*,*R*p)-**23b**	63%
						R' = *t*Bu	(*S*,*R*p)-**23c**	62%
R = *t*Bu	(*S*,*R*p)-**12**	R = *t*Bu	(*S*,*R*p)-**20**	80%	R = *t*Bu	R' = Cy	(*S*,*R*p)-**24**	61%
R = OMe	(*R*,*R*p)-**13**	R = OMe	(*R*,*R*p)-**21**	85%	R = OMe	R' = Ph	(*R*,*R*p)-**25a**	88%
						R' = Cy	(*R*,*R*p)-**25b**	77%
						R' = *t*Bu	(*R*,*R*p)-**25c**	78%
R = Cl	(*R*,*S*p)-**16**	R = Cl	(*R*,*S*p)-**22**	90%*	R = Cl	R' = Ph	(*R*,*S*p)-**26a**	28%
						R' = Cy	(*R*,*S*p)-**26b**	36%
						R' = *t*Bu	(*R*,*S*p)-**26c**	31%

Scheme 7. Yields of isolated products (* yield of crude product) obtained from the nucleophilic replacement of the dimethylamino group by chloride and of diphosphanes prepared by replacement of benzyl chloride with a secondary phosphane HPR'_2. Both reactions take place with retention of configuration.

same substituents on the phosphorus donors, replacing a hydrogen on the arene directly complexed to chromium with either a methoxy, methyl, *tert*-butyl or chloro substituent does not bring about any meaningful change in the properties of the phosphorus donors, as measured by the corresponding chemical shifts. This means that the influence of the $Cr(CO)_3$ moiety on the electron richness of the arene, either as an aryl substituent on the phosphorus directly attached to the arene or a benzyl substituent on the α-phosphorus, is too strong and levels out any electronic contribution due to substituents on the arene.

Table 3. ^{31}P NMR spectroscopic data for the diphosphanes reported in this paper.

Ligand	R	R′	$\delta_{^{31}P}$ [ppm][a] *o*-PPh_2	$\delta_{^{31}P}$ [ppm] α-PR′	$J_{P,P}$ [Hz]
(*R*,*S*p)-**27a**[b]	H	Ph	–18.74	10.12	26.5
(*S*,*R*p)-**23a**	Me		–17.56	8.47	18.3
(*R*,*R*p)-**25a**	OMe		–17.99	5.02	11.0
(*R*,*S*p)-**26a**	Cl		–18.93	7.33	18.3
(*R*,*S*p)-**27b**[b]	H	Cy	–19.95	16.66	46.7
(*S*,*R*p)-**23b**	Me		–18.71	15.85	38.3
(*S*,*R*p)-**24**	*t*Bu		–20.83	15.73	46.7
(*R*,*R*p)-**25b**	OMe		–17.48	15.49	26.0
(*R*,*S*p)-**26b**	Cl		–20.17	15.20	39.3
(*R*,*S*p)-**27c**[b]	H	*t*Bu	–20.19	50.49	68.0
(*S*,*R*p)-**23c**	Me		–19.79	49.33	61.7
(*R*,*R*p)-**25c**	OMe		–18.58	48.07	54.3
(*R*,*S*p)-**26c**	Cl		–21.06	48.78	63.2

[a] NMR spectra recorded in C_6D_6. [b] These data, which are provided for comparison, have been taken from ref.[3a].

The diphosphanes are characterised by large four-bond phosphorus-phosphorus coupling constants whose values increase from 11–26 Hz in PPh_2/PPh_2 diphosphanes to 54–68 Hz in $PPh_2/PtBu_2$ ones. A similar trend has been reported for the analogous ferrocene-based ligands.[21] The two phosphorus donors are bound to an allylic fragment (P–C_o=C_{ipso}–C_α–P) and π-systems usually lead to unexpectedly large long-range couplings.[22] The large value of the $^4J_{P,P}$ coupling might stem from "through-space" nuclear spin-spin coupling made possible by partial overlap of the two phosphorus lone pairs.[23a] The steric crowding provided by the substituents on phosphorus locks the molecule in a preferred time-average conformation in solution which, by keeping the substituents on the *ortho*- and α-donors far apart, brings the lone pairs into close proximity. The X-ray structure of ligand (*S*,*R*p)-**23b** supports this hypothesis (Figure 3).[24a] The larger values observed for the derivatives bearing bulky cyclohexyl and *tert*-butyl groups compared to those which only possess phenyl substituents might reflect the further restricted conformational freedom caused by the former substituents, although formal hybridisation of the coupled nuclei and the electronegativity of their substituents also play a role.[22,23b]

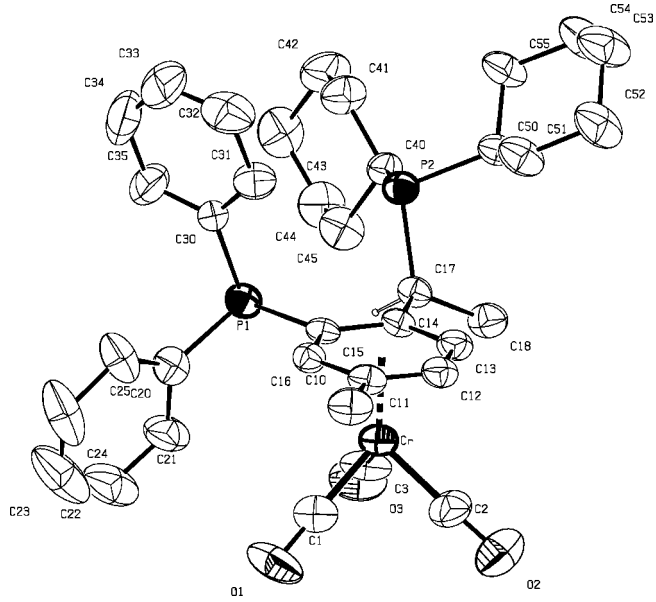


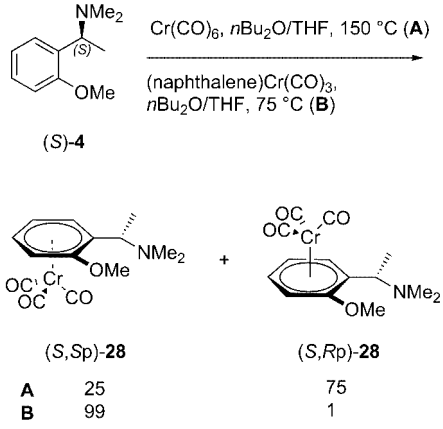
Figure 3. Displacement ellipsoids plot (PLATON) of (*S*,*R*p)-**23b**. Ellipsoids are shown at the 30% probability level. The H-atom attached to the stereogenic centre is shown with arbitrary radius; other H-atoms have been omitted for clarity.

The diphosphanes were tested in a variety of hydrogenations in comparison with the complexes without R substituents. Some of the results of these studies have already been published elsewhere.[3c] In most reactions there was a general trend in that the more electron-rich *para*-substituted ligands gave better *ee* values in enantioselective hydrogenations.

Synthesis of Daniphos N∩P Ligands

The two faces of unsymmetrically 1,2- and 1,3-disubstituted benzylamine (*S*)-**4** and (*S*)-**5**, respectively, are diastereotopic, which means that diastereomeric complexes arise upon coordination of the $Cr(CO)_3$ fragment to either of these two faces.[25]

When complexation of (*S*)-**4** is carried out under harsh conditions [$Cr(CO)_6$, nBu_2O/thf, 150 °C] the isomer (*S*,*R*p)-**28** is preferentially formed with a diastereoselectivity of 50% (Scheme 8). An excellent diastereoselectivity in favour of the other diastereoisomer (*S*,*S*p)-**28** is achieved when complexation is carried out using Kündig's reagent [(naphthalene)$Cr(CO)_3$]. The latter is a good starting material for the mild synthesis of other [(arene)$Cr(CO)_3$] compounds by $Cr(CO)_3$ fragment transfer.[26] The absolute configuration of complex (*S*,*S*p)-**28** was confirmed by X-ray crystallographic analysis (Figure 4).



Scheme 8. Relative amounts of diastereomeric complexes obtained in the complexation of (*S*)-**4** under thermodynamic (A) and kinetic (B) conditions.

These results can be explained on the basis of the preferred average conformation adopted by (*S*)-**4** in solution at room temperature (Figure 5a), which was inferred by difference NOE/^{1}H NMR experiments. Thus, a much greater NOE enhancement of the α-CH_3 signal is observed compared to the α-H signal upon irradiation of the *ortho*-hydrogen, thus suggesting that, in order to minimize non-bonding interactions between the α-substituents and the *ortho* OMe group, the dimethylamino group is preferentially located below the pro-*R*p face of the arene. Under thermodynamic conditions, the $Cr(CO)_3$ fragment coordinates to the less crowded pro-S_P face of the arene; under milder conditions, it is delivered to the pro-*R*p face due to temporary coordination by the amino group.

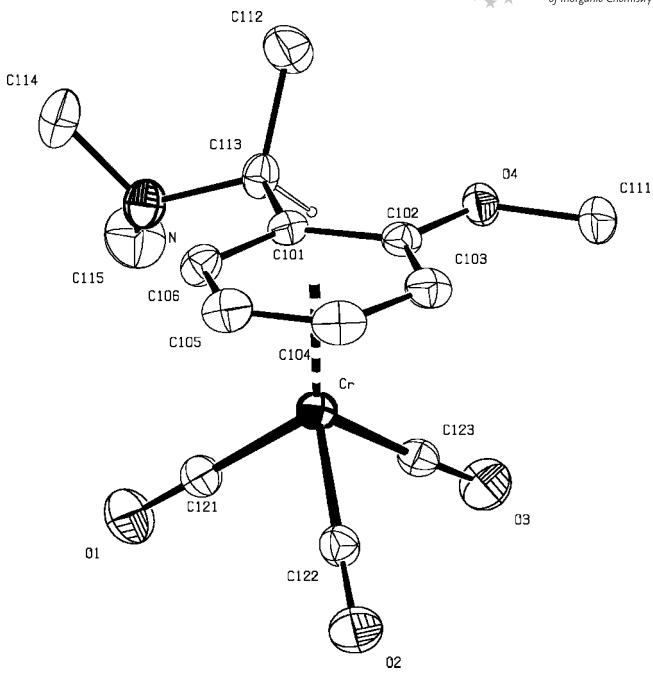


Figure 4. Displacement ellipsoids plot (PLATON) of (*S*,*S*p)-**28**. Ellipsoids are shown at the 30% probability level. The H-atom attached to the stereogenic centre is shown with arbitrary radius; other H-atoms have been omitted for clarity.

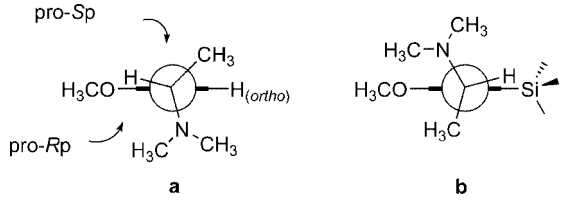
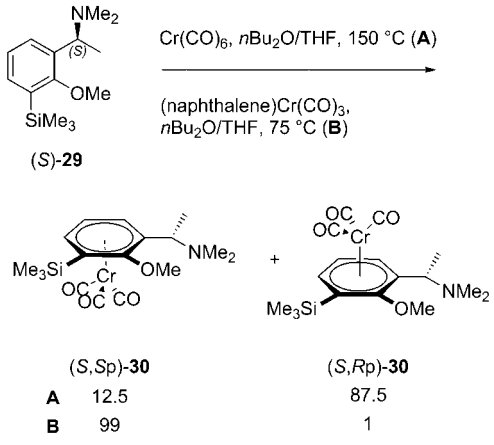


Figure 5. (a) Preferred average conformation adopted by (*S*)-**4** in solution at room temperature as inferred by difference NOE/^{1}H NMR experiments. (b) Preferred conformation in the presence of a bulky $–SiMe_3$ group in the *ortho* position.

Because flash chromatography and fractional crystallisation failed to provide the (*S*,*R*p)-**28** isomer in acceptable yield and purity, an alternative synthetic strategy was devised in order to obtain it as a single diastereoisomer. This strategy is based on the direct complexation of a benzylamine derivative in which a sterically bulky and easily removable trimethylsilyl group has been temporarily introduced at the *ortho* position of the 1-*N*,*N*-dimethylaminoethyl group in (*S*)-**4**.[27] The presence of this group should restrict rotation of the benzylic group at high temperature and favour a conformation which, while limiting interaction of the α-Me with the $SiMe_3$ group, preferentially confines the dimethylamino group to the "upper" face, thus enhancing the diastereoselectivity of the complexation (Figure 5b). However, treatment of (*S*)-**4** with *t*BuLi at –50 °C followed by quenching with $ClSiMe_3$ afforded benzylamine (*S*)-**29** in which lithiation has taken place at the most acidic site of the molecule *ortho* to the methoxy group, instead.[10b,28]

As shown in Scheme 9, the presence of an $SiMe_3$ group improves the diastereoselectivity of the complexation which, however, is still not satisfactory in the (*S*,*R*p)-**30** isomer, the absolute configuration of which was unambiguously assigned based on an X-ray crystallographic analysis (Figure 6).



Scheme 9. Relative amounts of diastereomeric complexes obtained in the complexation of (*S*)-**29** under thermodynamic (A) and kinetic (B) conditions.

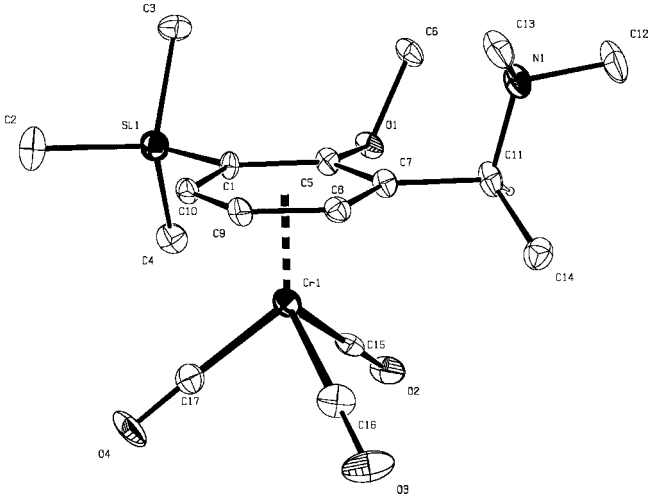
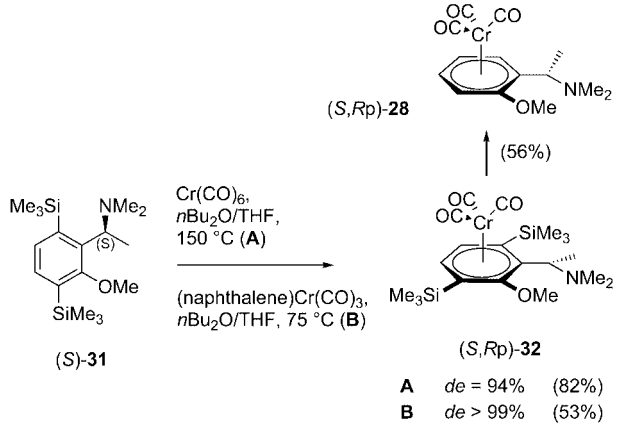


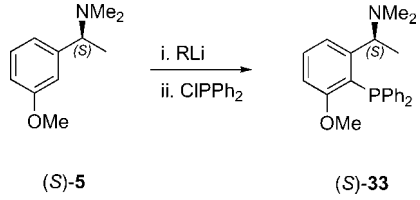
Figure 6. Displacement ellipsoids plot (PLATON) of one independent molecule of (*S*,*R*p)-**30**. Ellipsoids are shown at the 30% probability level. The H-atom attached to the stereogenic centre is shown with arbitrary radius; other H-atoms have been omitted for clarity.

Complexation of (*S*)-**31**, in which a second $SiMe_3$ group has been introduced *ortho* to the benzylamino group by lithiation and subsequent electrophilic quenching of (*S*)-**29** with $ClSiMe_3$, turned out to be highly selective for the desired isomer (*S*,*R*p)-**32** (Scheme 10).[24b] Notably, the (*S*,*R*p) isomer is formed preferentially even under the rigorous conditions of the thermal complexation due to hampered rotation of the amino group around the benzylic bond. The $SiMe_3$ groups are easily removed by treatment with Bu_4NF, thereby opening a stereoselective route to (*S*,*R*p)-**28**.



Scheme 10. Stereoselective route to (*S*,*R*p)-**28**.

Complexation of the *meta*-substituted benzylamine (*S*)-**5** to the $Cr(CO)_3$ moiety gives rise to equal amounts of the two possible diastereomers whatever the method of complexation. The same approach used for (*S*)-**4** was therefore applied to (*S*)-**5** by introduction of an $SiMe_3$ group as steric modulator. According to a previous report, metallation of the related compound *m*-methoxy-*N*,*N*-dimethylbenzylamine occurs exclusively at the position mutually *ortho* to both the methoxy and the amine side chain.[27] This was explained by assuming that the combined *ortho*-directing effects of both coordinating substituents and inductive electron withdrawal by the methoxy group serve to stabilize metallation at the position mutually *ortho* to these two substituents. In the case of (*S*)-**5**, optimisation of the metallation conditions was carried out using $ClPPh_2$ as electrophile since this compound allows an easy monitoring of the reaction course by ^{31}P NMR spectroscopy (Scheme 11). Table 4 summarises the relative amounts of products formed when lithiation was carried out using different RLi reagents under different reaction conditions.



Scheme 11. Lithiation and subsequent electrophilic quenching of (*S*)-**5**.

Treatment of (*S*)-**5** with *t*BuLi at –78 °C for 4 h in Et_2O and subsequent quenching of the Li salt formed with $ClPPh_2$ did not provide the expected product (*S*)-**33** (Table 4, entry 5) – $tBuPPh_2$ and unreacted (*S*)-**5** were isolated instead. The bulkiness of the tBu^- anion might hamper its access to the *ortho* position between the two coordinating groups in (*S*)-**5**. However, the use of *n*BuLi both at –78 °C and –50 °C (Table 4, entries 1 and 2, respectively) was also unsuccessful. Formation of (*S*)-**33** was observed when either *s*BuLi or *t*BuLi were used at –50 °C (Table 4, entries 3 and 6, respectively). A further temperature increase up to room temperature favoured formation of a side

Table 4. Relative amounts of products formed in the lithiation of (*S*)-**5** and subsequent quenching with $ClPPh_2$.

Entry	RLi	*T* [°C]	Deprotonation time [h]	Products[a] (relative amounts)		
				$RPPh_2$	(*S*)-**33**	other product
1	*n*BuLi	–78	4	1	n.d.[b]	n.d.
2		–50	4	10	n.d.	1
3	*s*BuLi	–50	4	5	1	0.5
4		room temp.	4	n.d.	1	3.5
5	***t*BuLi**	–78	4	1	n.d.	n.d.
6		–50	4	3	3	1
7[c]		**–50**	**24**	n.d.	1	n.d.
8		room temp.	4	n.d.	1	1

[a] The ratio of the three products was calculated based on integration of the areas of the corresponding ^{31}P NMR signals of the crude reaction mixture: (*S*)-**33**: δ_{31P} = –24 ppm; *n*BuPPh$_2$: δ_{31P} = –17.8 ppm; *s*BuPPh$_2$: δ_{31P} = –0.8 ppm; *t*BuPPh$_2$: δ_{31P} = 16.8 ppm; other unidentified product: δ_{31P} = 115 ppm. [b] n.d. = non detected. [c] The best reaction conditions are printed in bold.

product (δ_{31P} = 115 ppm) which, unfortunately, could not be identified (Table 4, entries 4 and 8, respectively). The best selectivity and yield for the desired *ortho*-substituted product (*S*)-**33** were achieved by carrying out the metallation with *t*BuLi at –50 °C for 24 h (Table 4, entry 7). The identity of this product was unambiguously assigned by X-ray crystallographic analysis (Figure 7).

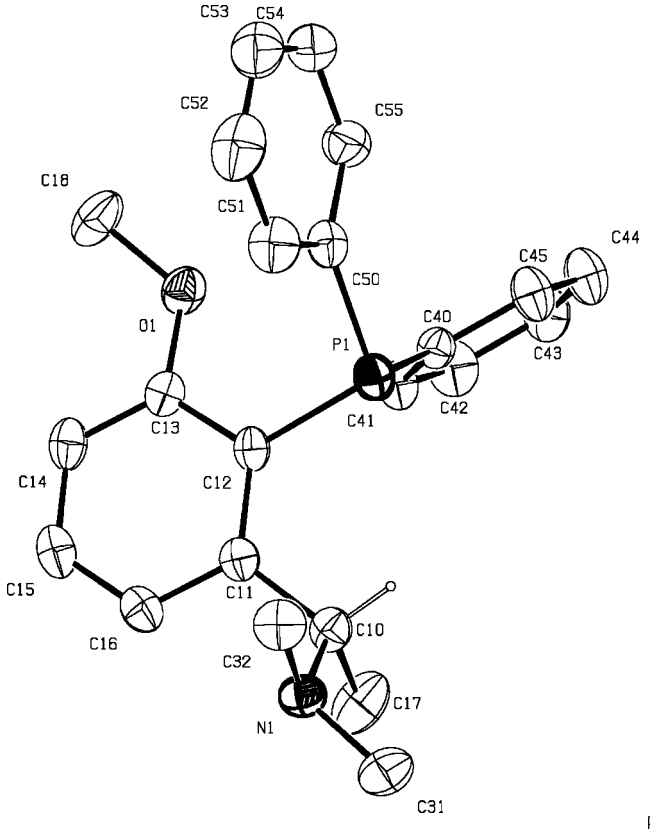
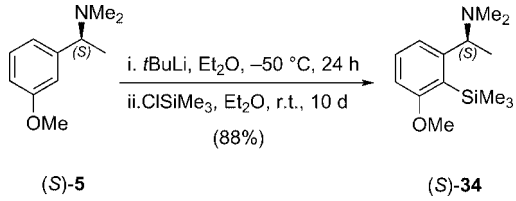


Figure 7. Displacement ellipsoids plot (PLATON) of one independent molecule of (*S*)-**33**. Ellipsoids are shown at the 30% probability level. The H-atom attached to the stereogenic centre is shown with arbitrary radius; other H-atoms have been omitted for clarity.

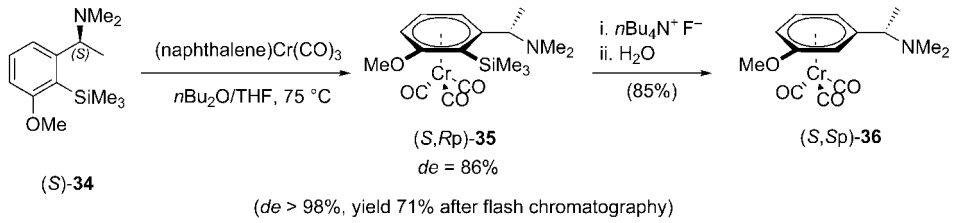
The optimised conditions were applied to the preparation of (*S*)-**34** (Scheme 12), although a large excess of $ClSiMe_3$ had to be used and the electrophilic trapping following metallation required ten days at room temperature.



Scheme 12. Synthesis of (*S*)-**34**.

Complexation of (*S*)-**34** to $Cr(CO)_3$ was carried out using Kündig's reagent under mild conditions (Scheme 13). The diastereoselectivity was 86% in favour of the (*S*,*R*p)-**35** isomer, as established from the NMR spectra of the crude reaction mixture. This complex could be obtained as a single diastereoisomer after flash chromatography [the other diastereoisomer (*S*,*S*p)-**35** was not isolated]. Desilylation of (*S*,*R*p)-**35** afforded complex (*S*,*S*p)-**36**, the absolute configuration of which was confirmed by X-ray crystallographic analysis (Figure 8).

(*S*,*S*p)-**37** was obtained by treatment of complex (*S*,*S*p)-**28** with *t*BuLi at –78 °C for four hours and then with $ClPPh_2$ (Scheme 14). The site of ortholithiation was confirmed by an X-ray crystallographic analysis (Figure 9). The NMR spectrum of the crude reaction mixture did not show the formation of other regioisomers. This result is surprising because the OMe group and the CH_2NMe_2 group have a similar *ortho*-directing ability in [(η^6-arene)$Cr(CO)_3$] complexes.[15c] Lithiation of the diastereomeric complex (*S*,*R*p)-**28** with opposite planar chirality under analogous conditions failed and was also unsuccessful at higher temperatures or when using the less bulky base *n*BuLi. Directed orthometallation adjacent to the OMe group might be expected in (*S*,*R*p)-**28**, as is the case for (*S*,*S*p)-**28**, whereas lithiation adjacent to the $CH(Me)NMe_2$ group is hampered due to steric reasons. Removal of the *ortho* proton by a lithium base pre-coordinated by the amino group would



Scheme 13. Stereoselective route to (*S*,*S*p)-**36**.

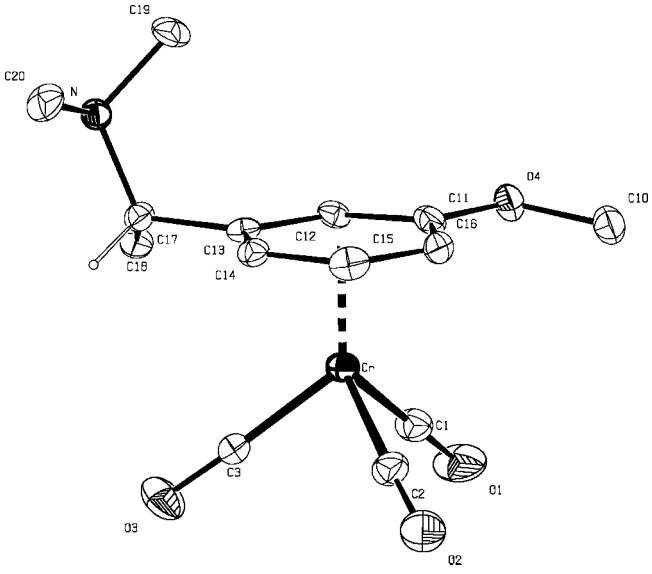


Figure 8. Displacement ellipsoids plot (PLATON) of (*S*,*S*p)-**36**. Ellipsoids are shown at the 30% probability level. The H-atom attached to the stereogenic centre is shown with arbitrary radius; other H-atoms have been omitted for clarity.

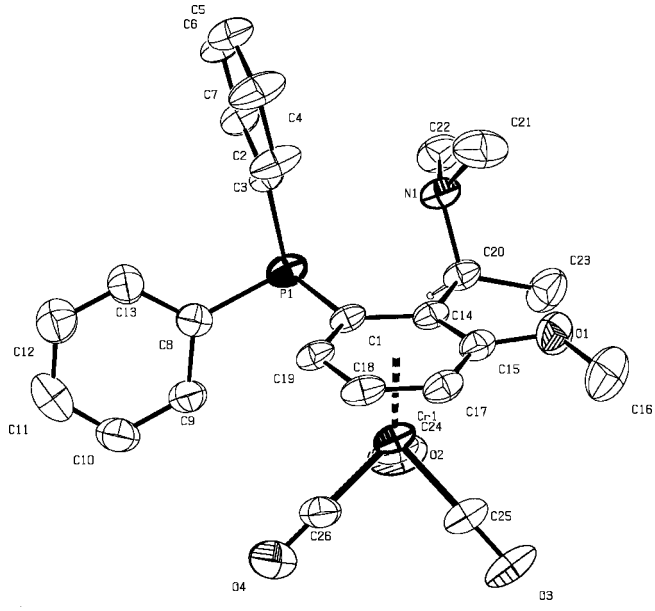
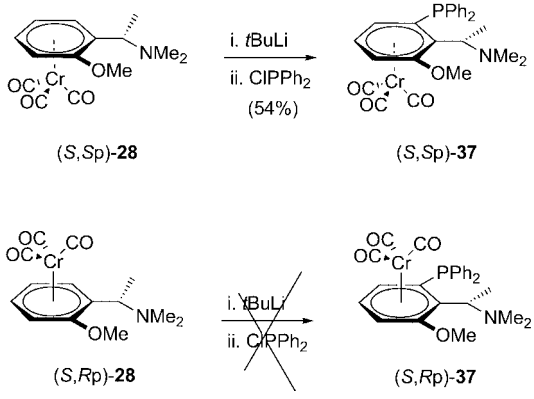


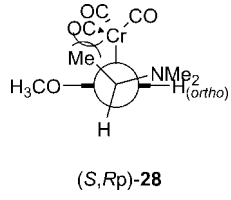
Figure 9. Displacement ellipsoids plot (PLATON) of (*S*,*S*p)-**37**. Ellipsoids are shown at the 30% probability level. The H-atom attached to the stereogenic centre is shown with arbitrary radius; other H-atoms have been omitted for clarity.

force the benzylic methyl group below the plane of the arene, thereby causing unfavourable steric interaction with the $Cr(CO)_3$ unit (Figure 10).



Scheme 14. Lithiation of diastereomeric complexes (*S*,*S*p)-**28** and (*S*,*R*p)-**28** and subsequent electrophilic quenching with $ClPPh_2$. The latter complex fails to react (see text for experimental conditions).

The inertness of (*S*,*R*p)-**28** towards *ortho*-functionalisation was advantageously exploited to separate the diastereomeric mixture of (*S*,*S*p)-**28** and (*S*,*R*p)-**28** obtained in



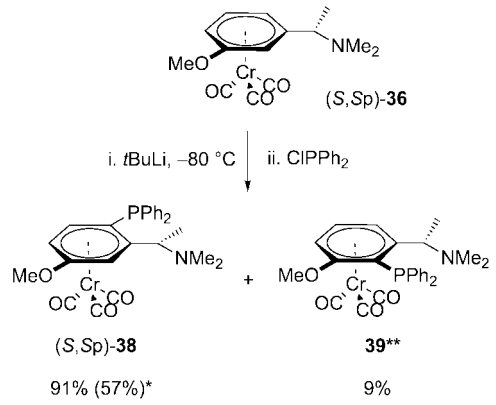
(*S*,*R*p)-**28**

Figure 10. Conformation of (*S*,*R*p)-**28** required for ortholithiation assisted by the benzylic dimethylamino group.

the thermal complexation of (*S*)-**4** with $Cr(CO)_6$. Thus, after treatment of this mixture with *t*BuLi and $ClPPh_2$, (*S*,*S*p)-**37** and unreacted (*S*,*R*p)-**28** were easily separated and purified by flash chromatography.

When complex (*S*,*S*p)-**36** was treated with *t*BuLi and then with $ClPPh_2$, the ^{31}P NMR spectrum of the crude reaction mixture indicated the formation of two products in a 10:1 ratio, as established from the areas of the corresponding NMR signals [81 MHz, $CDCl_3$; (*S*,*S*p)-**38**: δ = –16.74 ppm; **39**: δ = –12.67 ppm; Scheme 15]. An X-ray crystallographic analysis of the major product (*S*,*S*p)-**38**

indicated that lithiation had occurred *ortho* to the benzylic amino group and *para* to the methoxy group (Figure 11). The minor product **39** could not be isolated in a pure form.



Scheme 15. Lithiation of (*S*,*S*p)-**36** and subsequent electrophilic quenching with $ClPPh_2$. * Yield of isolated products. ** The structure of complex **39** is only a proposal.

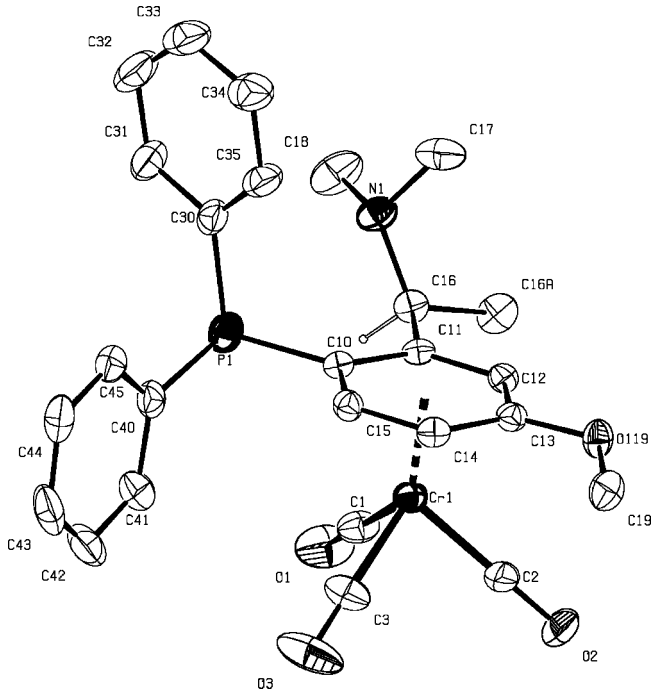
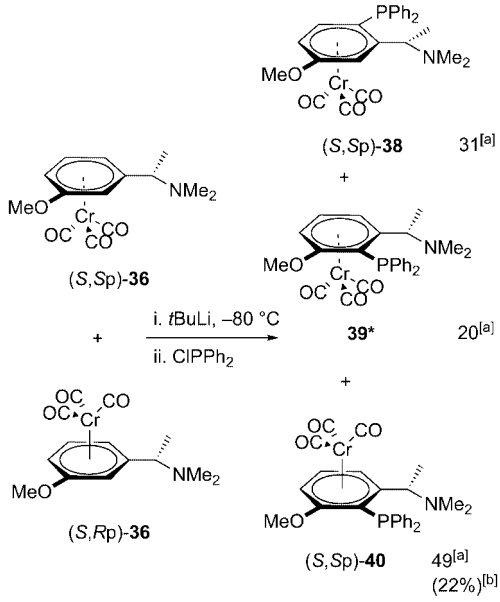


Figure 11. Displacement ellipsoids plot (PLATON) of one independent molecule of (*S*,*S*p)-**38**. Ellipsoids are shown at the 30% probability level. The H-atom attached to the stereogenic centre is shown with arbitrary radius; other H-atoms have been omitted for clarity.

Because (*S*,*R*p)-**36** was not available in a pure form, the 1:1 diastereomeric mixture of (*S*,*S*p)-**36** and (*S*,*R*p)-**36** was lithiated instead (Scheme 16). A third product [(*S*,*S*p)-**40**] was detected along with (*S*,*S*p)-**38** and **39** in the ^{31}P NMR spectrum of the crude product [(*S*,*S*p)-**40**: $\delta = -10.70$ ppm]. This complex was isolated and its structure confirmed by an X-ray crystallographic analysis (Figure 12). (*S*,*S*p)-**40** is formed from (*S*,*R*p)-**36** by selective abstraction of the proton *ortho* to both substituents on the arene. The relative amounts of (*S*,*S*p)-**38**, **39** and (*S*,*S*p)-**40** depend on the temperature at which lithiation is carried out. Thus, at 0 °C and at room temperature (*S*,*S*p)-**38** is not detected and **39** and (*S*,*S*p)-**40** are formed in equal amounts. This might suggest that **39** is the product derived from (*S*,*S*p)-**36** when the dimethylamino group can overcome restricted rotation



Scheme 16. Products arising from *ortho*-functionalisation of a 1:1 diastereomeric mixture of (*S*,*S*p)-**36** and (*S*,*R*p)-**36**. * The structure of complex **39** is only a proposal. [a] Relative amounts of products as inferred from the ^{31}P NMR spectrum of the crude reaction mixture. [b] Yield after flash chromatography; only this product was isolated.

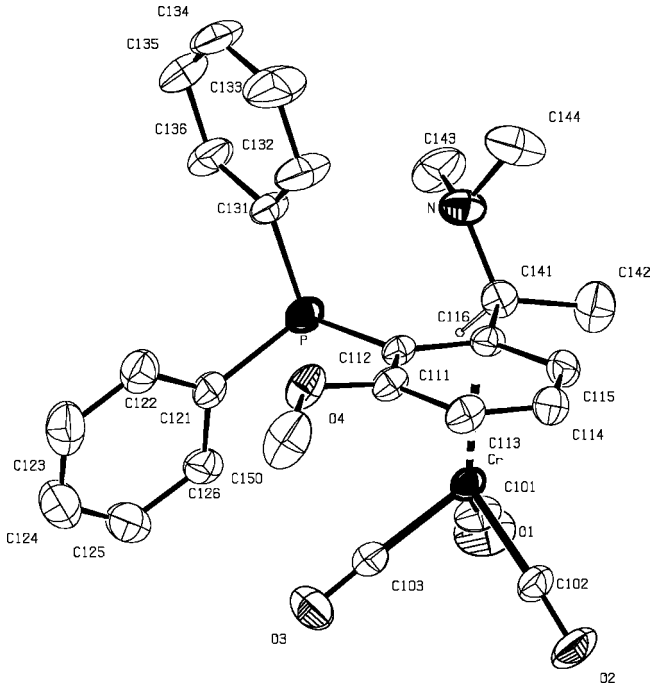


Figure 12. Displacement ellipsoids plot (PLATON) of (*S*,*S*p)-**40**. Ellipsoids are shown at the 30% probability level. The H-atom attached to the stereogenic centre is shown with arbitrary radius; other H-atoms have been omitted for clarity.

around the benzylic bond at higher temperature and the base is delivered to the other *ortho* proton through chelation by both substituents on the arene.

Some of the complexes containing P∩N ligands coordinated to the $Cr(CO)_3$ moiety have been successfully tested by us in asymmetric transfer hydrogenation. The results of these studies have been reported elsewhere.[4]

Conclusions

The range of "Daniphos" ligands has been expanded to include N∩P and P∩P ligands bearing a substituent R on the arene of the [(η^6-arene)$Cr(CO)_3$] unit, which might serve to modulate the steric and electronic properties of the donor atoms. The stereoselective synthetic strategy originally devised for the preparation of this class of ligands has been successfully applied to their preparation. In the case of N∩P ligands derived from 1,2- and 1,3-disubstituted benzylamines, because the two faces of such amines are diastereotopic and diastereomeric complexes arise from the coordination of the $Cr(CO)_3$ fragment to either of the two faces, the synthetic plan has been adjusted by exploiting the trimethylsilyl group as a temporary steric modulator in order to access both complexes with high diastereoselectivity.

Experimental Section

Materials and Methods: All reactions involving air- and moisture-sensitive compounds, and their subsequent workup, were carried out under nitrogen using Schlenk and syringe techniques. Reactions were monitored by analytical TLC using either Merck silica gel 60 F 254 or Merck aluminium oxide F 254 aluminium cards. The chromatograms were visualized with UV light. Solutions of crude reaction mixtures were filtered through a short bed of the filter aid Fluka Celite 535. The solvent was then evaporated. Flash chromatography of the crude products was performed either on silica gel 60 [Merck; particle size: 0.063–0.200; pH 7.0 (0.5)] or aluminium oxide 90 II–III [Merck; particle size: 0.063–0.200; pH 9.0 (0.5)]. Solvents were dried and deoxygenated by standard procedures. NMR spectra were recorded with a Varian Mercury 200 spectrometer operating at 200 (for ^1H), 50 (for ^{13}C) or 81 MHz (for ^{31}P), a Varian Unity 300 spectrometer operating at 300 (for ^1H), 75.5 (for ^{13}C) or 121.5 MHz (for ^{31}P), a Varian Mercury Plus spectrometer operating at 400 (for ^1H), 100.5 (for ^{13}C) or 162 MHz (for ^{31}P), or a Varian Unity 500 spectrometer operating at 500 (for ^1H), 125 (for ^{13}C) or 202 MHz (for ^{31}P) at ambient temperature. Chemical shifts (δ) are given in ppm relative to TMS (^1H, ^{13}C) or 85% H_3PO_4 as external standards (^{31}P). IR spectra were recorded with a Perkin–Elmer FT-IR Model 1720-X spectrometer. Optical rotations were measured in 1-dm cells with a Perkin–Elmer Model 341 polarimeter at ambient temperature. Mass spectra were obtained by electron impact (EI) or chemical ionisation (CI) with isobutane with a Finnigan MAT 95 spectrometer. Elemental analyses were performed with a Carlo Erba Strumentazione Element Analyzer (Model 1106). Generous loans of chiral amines were kindly provided by BASF GmbH. [(η^6-naphthalene)$Cr(CO)_3$]. was prepared according to published procedure.[9,26] All other chemicals were purchased and used without further purification.

General Methods

A. Methylation of Amines: Benzylamines were methylated according to the Eschweiler–Clarke procedure with formic acid and formaldehyde.[6] Formaldehyde (37% aqueous solution, d = 1.090, 3 equiv.) and formic acid (98% aqueous solution, d = 1.220, 5 equiv.) were added dropwise to the amine (1 equiv.) at 0 °C. The solution was heated at 80 °C for the reported time, then cooled and acidified with 10 N HCl. The solution was extracted with diethyl ether and then basified with 50% aqueous NaOH. The basic aqueous phase was extracted three times with diethyl ether and the combined ether extracts were washed with water and dried with $MgSO_4$. Diethyl ether was evaporated and the crude product finally distilled under reduced pressure.

B. Synthesis of [(η^6-Arene)$Cr(CO)_3$] Complexes by Thermolysis with $Cr(CO)_6$: [(η^6-arene)$Cr(CO)_3$] complexes were prepared according to the Pauson–Mahaffy procedure.[7] $Cr(CO)_6$ (1.2 equiv.) and the protected benzylamine (1 equiv.) were refluxed (bath temperature: 140 °C) in an 8:1 di-*n*-butyl ether/thf mixture ([Cr] = 0.36 M) for the reported time. The solution was cooled and filtered through a short pad of Celite on a sintered glass filter, which was then washed with some additional solvent. The solvents were distilled off on a rotary evaporator from a water bath held at 60 °C (an oil pump was required to remove the solvents completely). The crude product was purified by column chromatography and crystallised from suitable solvents.

C. Directed Orthometallation and Functionalisation of [(η^6-arene)-$Cr(CO)_3$] Complexes: The appropriate [(η^6-arene)$Cr(CO)_3$] complex (1 equiv.) was dissolved in dry diethyl ether ([Cr] = 0.05 M). The solution was cooled to –78 °C and *tert*-butyllithium (1.7 M in pentane, 1.14 equiv.) was added dropwise with a syringe. After 1.5 h, chlorodiphenylphosphane (1.14 equiv.) was added dropwise. The reaction mixture was warmed slowly to room temperature overnight and then filtered through a short pad of Celite on a sintered glass filter. The solvent was distilled off on a rotary evaporator and the crude product purified by column chromatography.

D. Replacement of NMe_2 with Cl: The appropriate [(η^6-arene)-$Cr(CO)_3$] complex (1 equiv.) was dissolved in dry thf ([Cr] = 0.05 M). The solution was cooled to –40 °C and 1-chloroethyl chloroformate (d = 1.312, 4 equiv.) was added dropwise. The reaction mixture was warmed up to room temperature overnight. The course of the reaction was monitored by ^{31}P NMR spectroscopy on a small sample of the crude reaction mixture dissolved in C_6D_6. The solvent and unreacted 1-chloroethyl chloroformate were distilled off. The residue was redissolved in diethyl ether and the solution filtered through a short pad of Celite on a sintered glass filter to eliminate the insoluble by-product [$(CH_3)_2NC(O)CHClCH_3$]. The crude product was purified by column chromatography after removal of the solvent.

E. Replacement of Cl with PR_2: The appropriate [(η^6-arene)Cr-$(CO)_3$] complex (1 equiv.) was dissolved in dry acetone and HPR_2 (1.1 equiv.) was added. A suspension of $TlPF_6$ (1.1 equiv.) in dry acetone (final concentration of Cr in acetone = 0.05 M) was added dropwise to this solution very slowly. A fine white precipitate consisting of TlCl formed immediately. The solution was stirred at room temperature overnight. NEt_3 (1.5 mL per millimol of Cr) was added, the solution stirred for a further 15 min and then filtered through a short pad of Celite on a sintered glass filter to remove TlCl. The solvent and excess NEt_3 were distilled off and the crude product purified by column chromatography.

(*S*)-*N*,*N*-Dimethyl-1-(*p*-tolyl)ethylamine [(*S*)-1]: This compound was prepared according to general procedure A from formaldehyde

(66.1 mL, 0.89 mol), formic acid (55.8 mL, 1.45 mol) and (*S*)-**1**-(*p*-tolyl)ethylamine (40.0 g, 0.30 mol). The reaction mixture was heated at 80 °C for 18 h. Distillation of the crude product under reduced pressure gave the protected amine as a colourless oil. Yield 37.1 g (77%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.27 (d, J = 6.7 Hz, 3 H, α-Me), 2.12 (s, 6 H, N*Me*$_2$), 2.15 (s, 3 H, *p*-Me), 3.10 (q, J = 6.7 Hz, 1 H, α-C*H*), 7.04 (d, J = 7.6 Hz, 2 H, H_{Ar}), 7.25 (d, J = 7.9 Hz, 2 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 20.77 (α-Me), 21.06 (*p*-Me), 43.34 (N*Me*$_2$), 65.92 (α-*C*H), 127.64 (C_{Ar}), 129.15 (C_{Ar}), 136.17 ($C_{Ar,ipso}$), 142.50 ($C_{Ar,ipso}$) ppm. MS (EI): *m*/*z* (%) 163 (13) [M$^+$], 148 (100) [M – Me], 132 (54) [M – NMe$_2$]. B.p. (30 Torr): 115 °C. $[\alpha]_D^{r.t.}$ = –61.4 (neat). $C_{11}H_{17}N$ (163.26): calcd. C 80.93, H 10.49, N 8.58; found C 80.40, H 10.27, N 9.03.

(*S*)-*N*,*N*-Dimethyl-1-(*p*-*tert*-butylphenyl)ethylamine [(*S*)-2]: This compound was prepared according to general procedure A by methylation of (*S*)-1-(4-*tert*-butylphenyl)ethylamine (10.00 g, 56.5 mmol) with formaldehyde (12.8 mL, 169.5 mmol) and formic acid (10.6 mL, 282.5 mmol). The crude product was purified by column chromatography (aluminium oxide; diethyl ether/hexane = 1:2) and the protected amine was isolated as a colourless oil. Yield 9.70 g (84%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30 (s, 9 H, *p*-*t*Bu), 1.35 (d, J = 6.8 Hz, 3 H, α-Me), 2.17 (s, 6 H, N*Me*$_2$), 3.22 (q, J = 6.8 Hz, 1 H, α-C*H*), 7.19 (d, J = 8.3 Hz, 2 H, H_{Ar}), 7.31 (d, J = 8.3 Hz, 2 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.05 (α-Me), 31.38 (*p*-C*Me*$_3$), 34.46 (*p*-*C*Me$_3$), 43.40 (N*Me*$_2$), 50.98 (α-*C*H), 125.43 (C_{Ar}), 125.48 (C_{Ar}), 143.78 ($C_{Ar,ipso}$), 149.90 ($C_{Ar,ipso}$) ppm.

(*R*)-*N*,*N*-Dimethyl-1-(*p*-chlorophenyl)ethylamine [(*R*)-3]: This compound was prepared according to general procedure A from formaldehyde (44.0 mL, 0.59 mol), formic acid (37.0 mL, 0.96 mol) and (*R*)-1-(*p*-chlorophenyl)ethylamine (30.5 g, 0.20 mol). The reaction mixture was heated at 80 °C for 38 h. Distillation of the crude product under reduced pressure gave the protected amine as a colourless oil. Yield 28.8 g (80%) ^{1}H NMR (500 MHz, C_6D_6): δ = 1.09 (d, J = 6.7 Hz, 3 H, α-Me), 2.00 (s, 6 H, N*Me*$_2$), 2.92 (q, J = 6.7 Hz, 1 H, α-C*H*), 7.02 (m, J = 8.5 Hz, 2 H, H_{Ar}), 7.13 (m, J = 7.9 Hz, 2 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 20.34 (α-Me), 43.09 (N*Me*$_2$), 65.28 (α-*C*H), 128.58 (C_{Ar}), 128.97 (C_{Ar}), 132.56 ($C_{Ar,ipso}$), 143.98 ($C_{Ar,ipso}$) ppm. MS (EI): *m*/*z* (%) 183 (12) [M$^+$], 168 (100) [M – Me], 132 (54) [M – NMe$_2$]. B.p. (0.1 Torr): 54 °C. $[\alpha]_D^{r.t.}$ = +60.1 (neat).

(*S*)-*N*,*N*-Dimethyl-1-(*o*-anisyl)ethylamine [(*S*)-4]: This compound was prepared according to general procedure A by methylation of (*S*)-1-(2-methoxyphenyl)ethylamine (50.00 g, 0.33 mol) with formaldehyde (75 mL, 0.99 mol) and formic acid (62.5 mL, 1.66 mol). The crude product was purified by column chromatography (aluminium oxide; diethyl ether/hexane = 1:2) and the protected amine was isolated as a light yellow oil. Yield 51.60 g (87%) ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.31 (d, J = 6.7 Hz, 3 H, α-Me), 2.21 (s, 6 H, N*Me*$_2$), 3.80 (s, 3 H, O*Me*), 3.84 (q, J = 6.7 Hz, 1 H, α-C*H*), 6.86 (d, J = 7.6 Hz, 1 H, H_{Ar}), 6.94 (t, J = 7.6 Hz, 1 H, H_{Ar}), 7.19 (t, J = 7.6 Hz, 1 H, H_{Ar}), 7.39 (d, J = 7.6 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (50 MHz, C_6D_6): δ = 21.16 (α-Me), 43.81 (N*Me*$_2$), 54.94 (O*Me*), 57.89 (α-*C*H), 110.63 (C_{Ar}), 121.01 (C_{Ar}) 127.49 (C_{Ar}), 128.00 (C_{Ar}), 133.84 ($C_{Ar,ipso}$), 157.09 ($C_{Ar,ipso}$) ppm.

(*S*)-*N*,*N*-Dimethyl-1-(*m*-anisyl)ethylamine [(*S*)-5]: This compound was prepared according to general procedure A by methylation of (*S*)-1-(3-methoxyphenyl)ethylamine (10.00 g, 66.20 mmol) with formaldehyde (15 mL, 0.20 mol) and formic acid (12.5 mL, 0.33 mol). The crude product was purified by column chromatography (Al_2O_3; diethyl ether/hexane = 1:2) and the protected amine was isolated as a light yellow oil. Yield 9.36 g (79%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.30 (d, J = 6.6 Hz, 3 H, α-Me), 2.16 (s, 6 H, N*Me*$_2$), 3.11 (q, J = 6.6 Hz, 1 H, α-C*H*), 3.78 (s, 3 H, O*Me*), 6.75–6.88 (m, 3 H, H_{Ar}), 7.20 (t, J = 8.1 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.35 (α-Me), 43.17 (N*Me*$_2$), 54.84 (O*Me*), 65.91 (α-*C*H), 111.97 (C_{Ar}), 112.63 (C_{Ar}) 119.60 (C_{Ar}), 128.84 (C_{Ar}), 145.76 ($C_{Ar,ipso}$), 159.30 ($C_{Ar,ipso}$) ppm.

(*R*)-*N*,*N*-Dimethyl-1-(*p*-anisyl)ethylamine [(*R*)-6]: This compound was prepared according to general procedure A from formaldehyde (54.0 mL, 0.72 mol), formic acid (45.0 mL, 1.17 mol) and (*R*)-1-(*p*-methoxyphenyl)ethylamine (36.0 g, 0.24 mol). The reaction mixture was heated at 80 °C for 13 h. Distillation of the crude product under reduced pressure gave the protected amine as a colourless oil. Yield 20.7 g (48%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.27 (d, J = 6.7 Hz, 3 H, α-Me), 2.12 (s, 6 H, N*Me*$_2$), 3.10 (q, J = 6.7 Hz, 1 H, α-C*H*), 3.34 (s, 3 H, O*Me*), 6.82 (d, J = 8.9 Hz, 2 H, H_{Ar}), 7.25 (d, J = 8.2 Hz, 2 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 20.65 (α-Me), 43.26 (N*Me*$_2$), 54.73 (α-*C*H), 65.45 (O*Me*), 113.90 (C_{Ar}), 128.63 (C_{Ar}), 137.34 ($C_{Ar,ipso}$), 159.05 ($C_{Ar,ipso}$) ppm. MS (EI): *m*/*z* (%) 179 (13) [M$^+$], 164 (100) [M – Me], 135 (35) [M – NMe$_2$], 105 (21) [M – NMe$_2$ – OMe]. B.p. (0.5 Torr): 68 °C. $[\alpha]_D^{r.t.}$ = +55.8 (neat). $C_{11}H_{17}NO$ (179.26): calcd. C 73.70, H 9.56, N 7.81; found C 73.65, H 9.00, N 8.40.

[{η^6-(*S*)-*N*,*N*-Dimethyl-1-(*p*-tolyl)ethylamine}Cr(CO)$_3$] [(*S*)-7]: This complex was prepared from $Cr(CO)_6$ (24.3 g, 110.0 mmol) and (*S*)-**1** (15.0 g, 92.0 mmol) in an 8:1 di-*n*-butyl ether/thf mixture (327 mL) according to general procedure B. The reaction mixture was refluxed for 60 h. The crude product was purified by column chromatography over aluminium oxide using diethyl ether as the sole eluent (R_f = 0.74). The yellow solid was crystallised from dichloromethane/hexane at –30 °C. Yield 19.1 g (69%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.08 (d, J = 6.7 Hz, 3 H, α-Me), 1.59 (s, 3 H, *p*-Me), 1.88 (s, 6 H, N*Me*$_2$), 3.07 (q, J = 6.7 Hz, 1 H, α-C*H*), 4.33 (d, J = 6.6 Hz, 1 H, H_{Ar}), 4.39 (d, J = 6.4 Hz, 1 H, H_{Ar}), 4.87 (d, J = 6.4 Hz, 1 H, H_{Ar}), 5.02 (d, J = 6.6 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 13.26 (α-Me), 19.91 (*p*-Me), 40.72 (N*Me*$_2$), 61.33 (α-*C*H), 91.28 (C_{Ar}), 92.09 (C_{Ar}), 93.08 (C_{Ar}), 97.27 (C_{Ar}), 109.29 ($C_{Ar,ipso}$), 109.63 ($C_{Ar,ipso}$), 233.92 (*C*O) ppm. MS (EI): *m*/*z* (%) 299 (16) [M$^+$], 255 (100) [M – NMe$_2$], 243 (31) [M – 2 CO], 215 (5) [M – 3 CO]. $[\alpha]_D^{r.t.}$ = –18.7 (*c* = 2.01, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1959, 1876 cm^{-1}. $C_{14}H_{17}CrNO_3$ (299.29): calcd. C 56.18, H 5.72, N 4.68; found C 56.02, H 5.68, N 4.73.

[{η^6-(*S*)-*N*,*N*-Dimethyl-1-(*p*-*tert*-butylphenyl)ethylamine}Cr(CO)$_3$] [(*S*)-8]: This complex was prepared from $Cr(CO)_6$ (12.50 g, 56.78 mmol) and (*S*)-**2** (9.70 g, 47.32 mmol) in an 8:1 mixture of di-*n*-butyl ether and thf (169 mL) according to general procedure B. The reaction mixture was refluxed for 55 h. The crude product was purified by column chromatography over aluminium oxide using diethyl ether as eluent. A yellow microcrystalline product was obtained after recrystallisation from diethyl ether/hexane at –30 °C. Yield 14.31 g (89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 (br. s, 12 H, *p*-*t*Bu, α-Me), 2.21 (s, 6 H, N*Me*$_2$), 3.49 (q, J = 6.7 Hz, 1 H, α-C*H*), 5.14–5.70 (br. m, 4 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.68 (α-Me), 31.42 (*p*-C*Me*$_3$), 34.22 (*p*-*C*Me$_3$), 41.12 (N*Me*$_2$), 61.39 (α-*C*H), 90.21 (C_{Ar}), 91.65 (C_{Ar}), 92.31 (C_{Ar}), 94.33 (C_{Ar}), 112.84 ($C_{Ar,ipso}$), 123.12 ($C_{Ar,ipso}$), 233.74 (*C*O) ppm. IR (hexane): ν_{CO} = 1969, 1899 cm^{-1}.

[{η^6-(*R*)-*N*,*N*-Dimethyl-1-(*p*-chlorophenyl)ethylamine}Cr(CO)$_3$] [(*R*)-9]: This complex was prepared from $Cr(CO)_6$ (21.6 g, 98.0 mmol) and (*R*)-**3** (15.0 g, 82.0 mmol) in an 8:1 di-*n*-butyl ether/thf mixture (281 mL) according to general procedure B. The reaction mixture was refluxed for 62 h. The product was purified by flash chromatography (aluminium oxide; diethyl ether, R_f = 0.73)

and recrystallisation from a layered mixture of di-*n*-butyl ether and hexane at –30 °C. Yield yellow crystals (43%). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.85 (d, J = 6.8 Hz, 3 H, α-Me), 1.78 (s, 6 H, NMe_2), 2.88 (q, J = 6.8 Hz, 1 H, α-CH), 4.61 (br. d, J = 6.7 Hz, 1 H, H_{Ar}), 4.64 (br. d, J = 6.4 Hz, 1 H, H_{Ar}), 4.68 (br. d, J = 6.4 Hz, 1 H, H_{Ar}), 4.81 (br. d, J = 6.1 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 13.32 (α-Me), 40.62 (NMe_2), 60.92 (α-CH), 89.80 (C_{Ar}), 90.34 (C_{Ar}), 91.93 (C_{Ar}), 95.92 (C_{Ar}), 108.34 ($C_{Ar,ipso}$), 112.89 ($C_{Ar,ipso}$), 232.28 (CO) ppm. MS (CI, isobutane): m/z (%) 320 (1) [M + H], 275 (100) [M – NMe_2], 263 (18) [M – 2 CO]. $[a]_D^{r.t.}$ = +9.7 (c = 1.18, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1981, 1888 cm^{-1}. $C_{13}H_{14}ClCrNO_3$ (319.71): calcd. C 48.84, H 4.41, N 4.38; found C 50.06, H 4.58, N 4.30.

[{η^6-(*R*)-*N*,*N*-Dimethyl-1-(*p*-anisyl)ethylamine}Cr(CO)$_3$] [(*R*)-10]: This complex was prepared from $Cr(CO)_6$ (22.1 g, 0.10 mol) and (*R*)-**6** (15.0 g, 0.84 mol) in an 8:1 di-*n*-butyl ether/thf mixture (281 mL) according to general procedure B. The crude product was purified by column chromatography (aluminium oxide; diethyl ether). R_f = 0.73 Crystallisation from dichloromethane/hexane at –30 °C afforded the product as yellow crystals. Yield 22.3 g (85%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.04 (d, J = 6.7 Hz, 3 H, α-Me), 1.90 (s, 6 H, NMe_2), 2.96 (q, J = 6.7 Hz, 1 H, α-CH), 2.99 (s, 3 H, OMe), 4.42 (d, J = 6.4 Hz, 1 H, H_{Ar}), 4.45 (d, J = 6.4 Hz, 1H H_{Ar}), 5.03 (d, J = 6.4 Hz, 1 H, H_{Ar}), 5.12 (d, J = 6.4 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 14.43 (α-Me), 40.87 (NMe_2), 55.09 (OMe), 61.22 (α-CH), 76.25 (C_{Ar}), 77.71 (C_{Ar}), 93.60 (C_{Ar}), 97.70 (C_{Ar}), 105. 70 ($C_{Ar,ipso}$), 143.34 ($C_{Ar,ipso}$), 233.86 (CO) ppm. MS: m/z (%) 315 (12) [M$^+$], 271 (100) [M – NMe_2], 259 (22) [M – 3 CO]. $[a]_D^{r.t.}$ = –9.5 (c = 1.00, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1970, 1873 cm^{-1}. $C_{14}H_{17}CrNO_4$ (315.29): calcd. C 53.33, H 5.43, N 4.44; found C 53.21, H 5.41, N 4.47.

[{η^6-(*S*,*R*p)-*N*,*N*-Dimethyl-1-[2-(diphenylphosphanyl)-4-tolyl]ethylamine}Cr(CO)$_3$] [(*S*,*R*p)-11]: This complex was prepared according to general procedure C by lithiation of (*S*)-**7** (6.0 g, 20.0 mmol) with *tert*-butyllithium (1.7 M in pentane; 13 mL, 22.8 mmol) and treatment of the lithiated species with chlorodiphenylphosphane (5.0 g, 22.8 mmol) in dry diethyl ether (400 mL). The crude product was purified by column chromatography (silica gel; diethyl ether/hexane, 1:4, R_f = 0.44). Yield yellow crystals 8.7 g (90%). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.79 (d, J = 6.7 Hz, 3 H, α-Me), 1.46 (s, 3 H, *p*-Me), 1.55 (s, 6 H, NMe_2), 4.52 (m, J = 6.4 Hz, 1 H, α-CH), 4.66 (dd, J = 6.1, J = 3.2 Hz, 1 H, H_{Ar}), 4.74 (d, J = 6.1 Hz, 1 H, H_{Ar}), 4.91 (s, 1 H, H_{Ar}), 7.03–7.13 (m, 6 H, *m*/*p*-H_{PAr}), 7.27 (m, J = 7.94 Hz, 2 H, *o*-H_{PAr}), 7.61 (m, J = 7.02 Hz, 2 H, *o*-H_{PAr}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 6.02 (α-Me), 19.75 (*p*-Me), 37.81 (NMe_2), 58.56 (d, $^3J_{C,P}$ = 14.3 Hz, α-CH), 88.75 (d, $J_{C,P}$ = 3.8 Hz, α-CH), 94.13 (C_{Ar}), 101.72 (d, $J_{C,P}$ = 3.9 Hz, C_{Ar}), 105 80 (d, $J_{C,P}$ = 1.7 Hz, $C_{Ar,ipso}$), 107.00 (d, $J_{C,P}$ = 25.7 Hz, $C_{Ar,ipso}$), 118.23 (d, $J_{C,P}$ = 19.2 Hz, $C_{Ar,ipso}$), 128.07 (d, $J_{C,P}$ = 1.6 Hz, C_{PAr}), 128.67 (d, $J_{C,P}$ = 6.0 Hz, C_{PAr}), 129.26 (C_{PAr}), 132.43 (d, $J_{C,P}$ = 20.3 Hz, C_{PAr}), 135.05 (d, $J_{C,P}$ = 19.7 Hz, C_{PAr}), 137.29 (d, $J_{C,P}$ = 15.9 Hz, C_{PAr}), 138.58 (d, $J_{C,P}$ = 6.0 Hz, C_{PAr}), 233.28 (CO) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –14.32 ppm. MS (CI, isobutane): m/z (%) 484 (15) [M + 1], 439 (100) [M – NMe_2], 399 (34) [M – 3 CO], 348 (18) [M – 3 CO – Cr]. $[a]_D^{r.t.}$ = +452.3 (c = 1.09, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1965, 1894 cm^{-1}. $C_{26}H_{26}CrNO_3P$ (483.47): calcd. C 64.59, H 5.42, N 2.90; found C 64.58, H 5.31, N 2.77.

[{η^6-(*S*,*R*p)-*N*,*N*-Dimethyl-1-[4-*tert*-butyl-2-(diphenylphosphanyl)-phenyl]ethylamine}Cr(CO)$_3$] [(*S*,*R*p)-12]: This complex was prepared according to general procedure C by lithiation of (*S*)-**8** (10.00 g, 29.33 mmol) with *tert*-butyllithium (1.7 M in pentane; 19.70 mL, 33.43 mmol) and treatment of the lithiated species with chlorodiphenylphosphane (7.38 g, 33.43 mmol) in dry diethyl ether (400 mL). The crude product was purified by column chromatography (aluminium oxide; diethyl ether). Yield yellow crystals 4.59 g (78%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.26 (br. s, 12 H, *p*-*t*Bu, α-Me), 1.89 (s, 6 H, NMe_2), 4.61 (m, J = 6.1 Hz, 1 H, α-CH), 5.21 (dd, J = 6.6, J = 3.4 Hz, 1 H, H_{Ar}), 5.34 (s, 1 H, H_{Ar}), 5.78 (dd, J = 6.6, J = 1.2 Hz, 1 H, H_{Ar}), 7.39–7.52 (m, 10 H, H_{PAr}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 5.78 (α-Me), 31.06 (*p*-CMe_3), 33.81 (*p*-CMe$_3$), 37.96 (NMe_2), 58.29 (d, J = 13.7 Hz, α-CH),88.60 (C_{Ar}), 92.76 (C_{Ar}), 99.45 (C_{Ar}), 104.11 (d, J = 24.5 Hz, $C_{Ar,ipso}$), 119.89 ($C_{Ar,ipso}$), 120.14 ($C_{Ar,ipso}$), 127.79–138.20 (C_{PAr}), 233.07 (CO) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.79 ppm. IR (CH_2Cl_2): ν_{CO} = 1970, 1904 cm^{-1}.

Lithiation of [{η^6-(*R*)-*N*,*N*-Dimethyl-1-(*p*-anisyl)ethylamine}Cr(CO)$_3$]: Following general procedure C, lithiation of (*R*)-**10** (4.26 g, 13.5 mmol) with *tert*-butyllithium (1.7 M in pentane; 9.5 mL, 16.2 mmol), followed by addition of chlorodiphenylphosphane (3.58 g, 16.2 mmol), produced a mixture of products. Column chromatography (aluminium oxide; hexane/diethyl ether 4:1→1:4) gave (*R*,*S*p)-**15**, (*R*,*R*p)-**13** and (*R*)-**14M**/(*S*)-**14m** in that order.

[{η^6-(*R*,*S*p)-*N*,*N*-Dimethyl-1-[2,5-bis(diphenylphosphanyl)-4-methoxyphenyl]ethylamine}Cr(CO)$_3$] [(*R*,*S*p)-15]: Yield orange crystals (1.92 g, 21%). R_f = 0.73 (aluminium oxide; diethyl ether/hexane, 1:1). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.66 (d, J = 6.7 Hz, 3 H, α-Me), 1.55 (s, 6 H, NMe_2), 2.80 (s, 3 H, OMe), 4.22 (m, J = 6.7 Hz, 1 H, α-CH), 4.91 (d, J = 2.44 Hz, 1 H, H_{Ar}), 5.16 (t, J = 2.44 Hz, 1 H, H_{Ar}), 7.01–7.16 (m, 12 H, *m*/*p*-H_{P1Ar}, *m*/*p*-H_{P2Ar}), 7.36 (m, J = 7.33 Hz, 2 H, *o*-H_{PAr}), 7.49 (m, J = 7.33 Hz, 2 H, *o*-H_{PAr}), 7.69 (m, J = 7.33 Hz, 2 H, *o*-H_{PAr}), 7.74 (m, J = 7.33 Hz, 2 H, *o*-H_{PAr}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 6.93 (α-Me), 37.98 (NMe_2), 55.44 (OMe), 58.61 (d, $J_{C,P}$ = 13.7 Hz, α-CH), 80.27 (d, $J_{C,P}$ = 3.3 Hz, C_{Ar}), 93.87 (d, $J_{C,P}$ = 25.7 Hz, $C_{Ar,ipso}$), 95.19 (d, $J_{C,P}$ = 3.3 Hz, C_{Ar}), 108.73 (d, $J_{C,P}$ = 27.9 Hz, $C_{Ar,ipso}$), 112.43 (d, $J_{C,P}$ = 18.1 Hz, $C_{Ar,ipso}$), 128.28 (C_{PAr}), 128.72 (d, $J_{C,P}$ = 6.0 Hz, C_{PAr}), 128.84 (d, $J_{C,P}$ = 6.6 Hz, C_{PAr}), 128.98 (d, $J_{C,P}$ = 7.1 Hz, C_{PAr}), 129.65 (C_{PAr}), 129.90 (C_{PAr}), 132.45 (d, $J_{C,P}$ = 20.2 Hz, C_{PAr}), 133.26 (d, $J_{C,P}$ = 20.8 Hz, C_{PAr}), 134.81 (d, $J_{C,P}$ = 15.4 Hz, C_{PAr}), 135.55 (d, $J_{C,P}$ = 21.9 Hz, C_{PAr}), 135.72 (d, $J_{C,P}$ = 20.9 Hz, C_{PAr}), 136.42 (d, $J_{C,P}$ = 16.5 Hz, C_{PAr}), 137.52 (d, $J_{C,P}$ = 14.3 Hz, C_{PAr}), 139.00 (d, $J_{C,P}$ = 6 Hz, $C_{Ar,ipso}$), 143.39 (d, $J_{C,P}$ = 9.9 Hz, C_{PAr}), 233.18 (CO) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –14.23 ($P_{o\text{-}CHMeNMe_2}$), –17.69 ($P_{o\text{-}OMe}$) ppm. MS (CI, isobutane): m/z (%) 684 (4) [M + 1], 599 (6) [M – 3 CO], 548 (38) [M – 3 CO – Cr], 455 (29) [M + H – NMe_2 – PPh_2], 364 (100) [M + H – 3 CO – Cr – PPh_2], 319 (41) [M + H – 3 CO – Cr – PPh_2 – H NMe_2]. $[a]_D^{r.t.}$ = –358.3 (c = 0.24, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1962, 1893 cm^{-1}. $C_{38}H_{35}CrNO_4P_2$ (683.64): calcd. C 66.76, H 5.16, N 2.05; found C 66.63, H 5.24, N 2.53.

[{η^6-(*R*,*R*p)-*N*,*N*-Dimethyl-1-[2-(diphenylphosphanyl)-4-methoxyphenyl]ethylamine}Cr(CO)$_3$] [(*R*,*R*p)-13]: Yield yellow crystals (2.02 g, 30%). R_f = 0.64 (aluminium oxide; diethyl ether/hexane, 1:1). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.82 (d, J = 6.7 Hz, 3 H, α-Me), 1.54 (s, 6 H, NMe_2), 2.87 (s, 3 H, OMe), 4.41 (m, J = 6.4 Hz, 1 H, α-CH), 4.58 (dd, J = 6.7, J = 2.4 Hz, 1 H, H_{Ar}) 4.80 (dd, J = 7.0, J = 3.0 Hz, 1H H_{Ar}), 5.10 (d, J = 2.1 Hz, 1 H, H_{Ar}), 6.68–7.11 (m, 6 H, *m*/*p*-H_{PAr}), 7.29 (m, J = 7.9 Hz, 2 H, *o*-H_{PAr}), 7.66 (m, J = 7.0 Hz, 2 H, *o*-H_{PAr}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 6.93 (α-Me), 37.89 (NMe_2), 55.27 (OMe), 58.40 (d, $J_{C,P}$ = 14.3 Hz, α-CH), 76.78 (C_{Ar}), 88.97 (d, $J_{C,P}$ = 3.3 Hz, C_{Ar}), 89.51 (d, $J_{C,P}$ = 3.8 Hz, C_{Ar}), 108.3 (d, $J_{C,P}$ = 27.4 Hz, $C_{Ar,ipso}$), 114.39 (d, $J_{C,P}$ = 18.6 Hz, C $C_{Ar,ipso}$), 127.91 (C_{PAr}), 128.07 (d, $J_{C,P}$ = 7.7 Hz, C_{PAr}), 128.71 (d, $J_{C,P}$ = 6.0 Hz, C_{PAr}), 129.47 (C_{PAr}), 132.53

(d, $J_{C,P}$ = 20.9 Hz, C_{PAr}), 135.17 (d, $J_{C,P}$ = 19.7 Hz, C_{PAr}), 136.67 (d, $J_{C,P}$ = 15.9 Hz, C_{PAr}), 138.45 (d, $J_{C,P}$ = 6.0 Hz, C_{PAr}), 140.25 (d, $J_{C,P}$ = 2.7 Hz, $C_{Ar,ipso}$), 233.45 (d, $J_{C,P}$ = 1.7 Hz, *C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –14.22 ppm. MS (CI, isobutane): *m*/*z* (%) 500 (4) [M + 1], 455 (100) [M – NMe_2], 415 (43) [M – 3 CO], 364 (45) [M – 3 CO – Cr], 319 (45) [M – 3 CO – Cr – $HNMe_2$]. $[\alpha]_D^{r.t.}$ = –480.9 (*c* = 0.22, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1965, 1882 cm^{-1}. $C_{26}H_{26}CrNO_4P$ (499.46): calcd. C 62.52, H 5.25, N 2.80; found C 62.08, H 5.01, N 2.97.

[{η^6-(*R*,*R*p)-*N*,*N*-Dimethyl-1-(3-(diphenylphosphanyl)-4-methoxyphenyl)ethylamine}Cr(CO)$_3$] [(*R*)-14M] and [{η^6-(*R*,*S*p)-*N*,*N*-Dimethyl-1-(3-(diphenylphosphanyl)-4-methoxyphenyl)ethylamine}Cr(CO)$_3$] [(*S*)-14m]: Yield yellow crystals (1.98 g, 30%). R_f = 0.15 (aluminium oxide; diethyl ether/hexane, 1:1) The two compounds eluted as a single fraction. Further attempts to separate the two diastereoisomers by column chromatography failed.
(*R*)-14M: ^{1}H NMR (500 MHz, C_6D_6): δ = 0.97 (d, *J* = 6.71 Hz, 3 H, α-Me), 1.88 (s, 6 H, N*Me*$_2$), 2.69 (q, *J* = 6.71 Hz, 1 H, α-C*H*), 2.91 (s, 3 H, O*Me*), 4.15 (dd, *J* = 6.71, *J* = 3.35 Hz, 1 H, H_{Ar}), 5.02 (t, *J* = 1.67 Hz, 1 H, H_{Ar}), 5.13 (dd, *J* = 6.71, *J* = 1.67 Hz, 1 H, H_{Ar}), 7.01–7.10 (m, 6 H, *m*/*p*-H_{PAr}), 7.43 (m, *J* = 7.33 Hz, 2 H, *o*-H_{PAr}), 7.59 (m, *J* = 7.33 Hz, 2 H, *o*- H_{PAr}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 15.60 (α-Me), 41.04 (N*Me*$_2$), 55.63 (O*Me*), 61.33 (α-*C*H), 71.61 (C_{Ar}), 92.66 (d, $J_{C,P}$ = 24.6 Hz, $C_{Ar,ipso}$), 92.84 (C_{Ar}), 101.73 (C_{Ar}), 104.753 ($C_{Ar,ipso}$), 128.29 (C_{PAr}), 128.79 (C_{PAr}), 128.98 (C_{PAr}), 133.22 (d, $J_{C,P}$ = 20.3 Hz, C_{PAr}), 134.92 (d, $J_{C,P}$ = 14.8 Hz,, C_{PAr}), 135.26 (d, $J_{C,P}$ = 20.9 Hz, C_{PAr}), 137.44 (d, $J_{C,P}$ = 14.8 Hz, C_{PAr}), 146.14 (d, $J_{C,P}$ = 13.7 Hz, $C_{Ar,ipso}$), 233.11 (*C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –18.57 ppm.

(*R*)-14m: ^{1}H NMR (500 MHz, C_6D_6): δ = 0.87 (d, *J* = 6.8 Hz, 3 H, α-Me), 1.92 (s, 6 H, N*Me*$_2$), 2.86 (q, *J* = 6.7 Hz, 1 H, α-C*H*), 2.91 (s, 3 H, O*Me*), 4.12 (dd, *J* = 6.7, *J* = 3.4 Hz, 1 H, H_{Ar}), 5.10 (t, *J* = 1.7 Hz, 1 H, H_{Ar}), 5.25 (dd, *J* = 6.7, *J* = 1.7 Hz, 1 H, H_{Ar}), 7.01–7.10 (m, 6 H, *m*/*p*-H_{PAr}), 7.43 (m, 2 H, *o*-H_{PAr}), 7.59 (m, *J* = 7.3 Hz, 2 H, *o*-H_{PAr}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 14.50 (α-Me), 40.87 (N*Me*$_2$), 55.58 (O*Me*), 61.23 (α-*C*H), 71.84 (C_{Ar}), 91.83 (d, $J_{C,P}$ = 24.1 Hz, $C_{Ar,ipso}$), 96.72 (C_{Ar}), 97. 34 (C_{Ar}), 128.77 (d, $J_{C,P}$ = 6.6 Hz, C_{PAr}), 128.98 (d, $J_{C,P}$ = 9.9 Hz, C_{PAr}), 129.81 (C_{PAr}), 133.09 (d, $J_{C,P}$ = 20.3 Hz, C_{PAr}), 135.06 (d, $J_{C,P}$ = 14.8 Hz, C_{PAr}), 135.33 (d, $J_{C,P}$ = 21.4 Hz, C_{PAr}), 137.54 (d, $J_{C,P}$ = 14.8 Hz, C_{PAr}), 146.26 (d, $J_{C,P}$ = 15.3 Hz, C_{Ar}), 233.26 (*C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –17.92 ppm. The absolute configuration of the two diastereomers has not been assigned.

Lithiation of [{η^6-(*R*)-*N*,*N*-Dimethyl-1-(*p*-chlorophenyl)ethylamine}-Cr(CO)$_3$] [(*R*)-9]: Following general procedure C, lithiation of (*R*)-**9** (4.77 g, 14.9 mmol) with *tert*-butyllithium (1.7 M in pentane; 8.8 mL, 14.9 mmol), followed by addition of chlorodiphenylphosphane (3.29 g, 14.9 mmol), produced a mixture of three products. Column chromatography (aluminium oxide; hexane→hexane/diethyl ether, 3:2) gave (*R*,*S*p)-**16**, (*R*,*R*p)-**16** and (*R*)-**17** in that order.

[{η^6-(*R*,*S*p)-*N*,*N*-Dimethyl-1-[4-chloro-2-(diphenylphosphanyl)phenyl]ethylamine}Cr(CO)$_3$] [(*R*,*S*p)-16]: Yield yellow crystals 5.0 g (67%). R_f = 0.54 (aluminium oxide; hexane/diethyl ether, 2:1). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.66 (d, *J* = 6.7 Hz, 3 H, α-Me), 1.47 (s, 3 H, N*Me*$_2$), 4.39 (m, *J* = 6.7 Hz, 1 H, α-C*H*), 4.45 (dd, *J* = 6.4, *J* = 2.8 Hz, 1 H, H_{Ar}), 5.04 (d, *J* = 5.8 Hz, 1 H, H_{Ar}), 5.26 (br. s, 1 H, H_{Ar}), 6.69 (m, 4 H, *m*/*p*-H_{PAr}), 7.09 (m, *J* = 7.3 Hz, 2 H, *m*/*p*-H_{PAr}), 7.20 (m, 2 H, *o*-H_{PAr}), 7.56 (m, *J* = 7.0 Hz, 2 H, *o*-H_{PAr}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 6.02 (α-Me), 37.78 (N*Me*$_2$), 58.40 (d, $J_{C,P}$ = 14.2 Hz, α-*C*H), 87.76 (d, $J_{C,P}$ = 3.3 Hz, C_{Ar}), 93.01 (C_{Ar}), 99.69 (d, $J_{C,P}$ = 3.8 Hz, C_{Ar}), 106.58 (d, $J_{C,P}$ = 29.7 Hz, $C_{Ar,ipso}$), 108.3 (d, $J_{C,P}$ = 4.4 Hz, $C_{Ar,ipso}$), 117.40 (d, $J_{C,P}$ = 19.2 Hz, $C_{Ar,ipso}$), 127.91 (C_{PAr}), 128.19 (C_{PAr}), 128.30 (C_{PAr}), 128.90 (d, $J_{C,P}$ = 6.1 Hz, C_{PAr}), 129.73 (C_{PAr}), 132.30 (d, $J_{C,P}$ = 20.8 Hz, C_{PAr}), 135.01 (d, $J_{C,P}$ = 20.3 Hz, C_{PAr}), 136.50 (d, $J_{C,P}$ = 14.8 Hz, C_{PAr}), 137.95 (d, $J_{C,P}$ = 6.0 Hz, C_{PAr}), 231.61 (*C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –14.41 ppm. MS (CI, isobutane): *m*/*z* (%) 504 (21) [M + H], 459 (100) [M – NMe_2], 419 (46) [M – 3 CO], 368 (15) [M – 3 CO – Cr]. $[\alpha]_D^{r.t.}$ = –401.9 (*c* = 0.21, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1976, 1912 cm^{-1}. $C_{25}H_{23}ClCrNO_3P$ (503.87): calcd. C 59.59, H 4.60, N 2.78; found C 60.56, H 4.81, N 2.74.

[{η^6-(*R*,*R*p)-*N*,*N*-Dimethyl-1-[4-chloro-2-(diphenylphosphanyl)phenyl]ethylamine}Cr(CO)$_3$] [(*R*,*R*p)-16]: Yield yellow crystals (0.53 g). The yield is only indicative as this fraction also contained the other diastereoisomer and traces of the product derived from metal–halogen exchange. Attempts to further purify the product by means of crystallisation failed. Only the ^{1}H and ^{31}P NMR spectra are reported. R_f = 0.42 (aluminium oxide; hexane/diethyl ether, 2:1). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.87 (d, *J* = 6.8 Hz, 3 H, α-Me), 2.00 (s, 3 H, N*Me*$_2$), 3.57 (m, 1 H, α-C*H*), 4.86 (dd, *J* = 4.9, *J* = 1.2 Hz, 1 H, H_{Ar}), 5.06 (dd, *J* = 1.7, *J* = 1.0 Hz, 1 H, H_{Ar}), 5.21 (dd, *J* = 6.8, *J* = 2.4 Hz, 1 H, H_{Ar}), 6.69 (m, 4 H, H_{PAr}), 7.02–7.05 (m, 6 H, H_{PAr}), 7.20–7.35 (m, 2 H, H_{PAr}), 7.51–7.65 (m, 2 H, H_{PAr}) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –17.53 ppm.

[{η^6-(*R*)-*N*,*N*-Dimethyl-1-[4-(diphenylphosphanyl)phenyl]ethylamine}Cr(CO)$_3$] [(*R*)-17]: Yield yellow crystals (1.30 g, 18%). R_f = 0.30 (aluminium oxide; hexane/diethyl ether, 3:2). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.92 (d, *J* = 7.0 Hz, 3 H, α-Me), 1.89 (s, 6 H, N*Me*$_2$), 3.25 (q, *J* = 7.0 Hz, 1 H, α-C*H*), 4.40 (dd, *J* = 6.4, *J* = 1.5 Hz, 1 H, H_{Ar}), 4.75 (m, *J* = 6.8 Hz, 1 H, H_{Ar}), 4.84 (ddd, *J* = 6.4, *J* = 4.2, *J* = 1.2 Hz, 1 H, H_{Ar}), 5.00 (ddd, *J* = 6.6, *J* = 5.4, *J* = 1.5 Hz, 1 H, H_{Ar}), 7.04–7.13 (m, 6 H, *m*/*p*-H_{PAr}), 7.39 (m, *J* = 7.3, *J* = 1.5 Hz, 2 H, *o*-H_{PAr}), 7.45 (m, *J* = 7.3 Hz, 2 H, *o*-H_{PAr}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 10.89 (α-Me), 40.55 (N*Me*$_2$), 61.04 (α-*C*H), 89.55 (d, $J_{C,P}$ = 3.3 Hz, C_{Ar}), 93.91 (d, $J_{C,P}$ = 6.0 Hz, C_{Ar}), 97.24 (d, $J_{C,P}$ = 11.5 Hz, C_{Ar}), 98.42 (d, $J_{C,P}$ = 19.2 Hz, C_{Ar}), 102.36 (d, $J_{C,P}$ = 19.2 Hz, $C_{Ar,ipso}$), 113.71 ($C_{Ar,ipso}$), 128.94 (d, $J_{C,P}$ = 1.1 Hz, C_{PAr}), 129.00 (d, $J_{C,P}$ = 1.1 Hz, C_{PAr}), 129.58 (d, $J_{C,P}$ = 12.1 Hz, C_{PAr}), 134.13 (d, $J_{C,P}$ = 10.9 Hz, C_{PAr}), 134.29 (d, $J_{C,P}$ = 11.0 Hz, C_{PAr}), 135.76 (d, $J_{C,P}$ = 12.6 Hz, C_{PAr}), 136.11 (d, $J_{C,P}$ = 12.6 Hz, C_{PAr}), 232.93 (*C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –7.83 ppm. MS (EI): *m*/*z* (%) 469 (8) [M$^+$], 385 (100) [M – 3 CO]. $[\alpha]_D^{r.t.}$ = –27.4 (*c* = 1.08, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1970, 1893 cm^{-1}. $C_{25}H_{24}CrNO_3P$ (469.44): calcd. C 63.96, H 5.15, N 3.00; found C 63.56, H 4.82, N 3.10.

[{η^6-(*R*,*S*p)-1-[4-Chloro-3-(diphenylphosphanyl)phenyl]ethylamine}Cr(CO)$_3$] [(*R*)-18M] and [{η^6-(*R*,*R*p)-1-[4-chloro-3-(diphenylphosphanyl)phenyl]ethylamine}Cr(CO)$_3$] [(*S*)-18m]: Following general procedure C, lithiation of (*R*)-**9** (056 g, 1.75 mmol) with LDA (2 M in pentane, 1.0 mL, 2.0 mmol), followed by addition of chlorodiphenylphosphane (0.44 g, 2.0 mmol), produced a nearly 1:1 ratio of two compounds. The two were collected as a single fraction after column chromatography (R_f = 0.47; aluminium oxide, diethyl ether). Further attempts to separate them failed. Analytical data refer to the clean fraction collected after flash chromatography. Yield yellow crystals 0.81 g (92%). M = major diastereoisomer; m = minor diastereoisomer. ^{1}H NMR (500 MHz, C_6D_6): δ = 0.74 (d, *J* = 6.8 Hz, 3 H, α-Me_m), 0.80 (d, *J* = 6.8 Hz, 3 H, α-Me_M), 1.78 (s, 6 H, N*Me*$_{2M}$), 1.83 (s, 6 H, N*Me*$_{2m}$), 2.64 (q, *J* = 6.8 Hz, 1 H, α-C*H*$_M$), 2.75 (q, *J* = 7.1 Hz, 1 H, α-C*H*$_m$), 4.66–4.94 (overlapping peaks, 3 H_{ArM} + 3 H_{Arm}), 7.04–7.10 (m, overlapping peaks, 6 H, H_{PArM} + 6 H, H_{PArm}), 7.27–7.40 (m, overlapping peaks, 2 H, H_{PArM} + 2 H, H_{PArm}), 7.50–7.60 (m, overlapping peaks, 2 H, H_{PArM} + 2 H, H_{PArm}) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –12.06 (P_M), –11.83 (P_m) ppm.

[{η⁶-(*S*,*R*p)-1-[2-(Diphenylphosphanyl)-4-tolyl]chloroethyl}Cr(CO)₃] [(*S*,*R*p)-19]: This complex was prepared from (*S*,*R*p)-**11** (6.45 g, 13.0 mmol) and 1-chloroethyl chloroformate (5.8 mL, 53.4 mmol) in thf (260 mL) according to general procedure D. The crude product was purified by column chromatography (R_f = 0.54; silica gel, ethyl acetate/hexane, 1:1). Yield yellow crystals (5.5 g, 86%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.39 (s, 3 H, *p*-Me), 1.47 (d, J = 6.7 Hz, 3 H, α-Me), 4.52 (d, J = 6.1 Hz, 1 H, H_{Ar}), 4.65 (s, 1 H, H_{Ar}), 4.87 (dd, J = 6.1, J = 2.5 Hz, 1 H, H_{Ar}), 5.89 (m, J = 8.8, J = 6.7 Hz, 1 H, α-C*H*), 7.01–7.12 (m, 6 H, *m*/*p*-H_{PAr}), 7.39 (m, J = 7.3 Hz, 2 H, *o*-H_{PAr}), 7.56 (t, J = 7.3 Hz, 2 H, *o*-H_{PAr}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 19.71 (*p*-Me), 23.84 (α-Me), 54.18 (d, $J_{C,P}$ = 29.6 Hz, α-*C*H), 89.63 (d, $J_{C,P}$ = 2.8 Hz, C_{Ar}), 93.50 (C_{Ar}), 98.30 (d, $J_{C,P}$ = 2.8 Hz, C_{Ar}), 104.88 (d, $J_{C,P}$ = 24.7 Hz, $C_{Ar,ipso}$), 107.60 ($C_{Ar,ipso}$), 115.28 (d, $J_{C,P}$ = 20.8 Hz, $C_{Ar,ipso}$), 128.71 (d, $J_{C,P}$ = 7.2 Hz, C_{PAr}), 129.98 (d, $J_{C,P}$ = 6.6 Hz, C_{PAr}), 129.42 (C_{PAr}), 130.02 (C_{PAr}), 134.12 (d, $J_{C,P}$ = 20.3 Hz, C_{PAr}), 134.54 (d, $J_{C,P}$ = 13.1 Hz, C_{PAr}), 134.94 (d, $J_{C,P}$ = 19.8 Hz, C_{PAr}), 135.76 (d, $J_{C,P}$ = 8.8 Hz, C_{PAr}), 232.49 (d, $J_{C,P}$ = 2.2 Hz, *C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –17.74 ppm. MS (CI, isobutane): *m*/*z* (%) 475 (66) [M + 1], 439 (33) [M – Cl], 390 (61) [M – 3 CO], 354 (22) [M – 3 CO – HCl], 305 (100). $[\alpha]_D^{r.t.}$ = +291.0 (*c* = 1.10, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1971, 1888 cm^{-1}. $C_{24}H_{20}ClCrO_3P$ (474.84): calcd. C 60.71, H 4.24; found C 60.87, H 4.38.

[{η⁶-(*S*,*R*p)-1-[4-*tert*-Butyl-2-(diphenylphosphanyl)phenyl]chloroethyl}Cr(CO)₃] [(*S*,*R*p)-20]: This complex was prepared according to general procedure D from (*S*,*R*p)-**12** (6.00 g, 11.43 mmol) and 1-chloroethyl chloroformate (6.54 g, 45.70 mmol) in dry thf (250 mL). The crude product was purified by column chromatography (aluminium oxide; ethyl acetate/hexane, 4:1). Yield yellow crystals 4.59 g (78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (s, 9 H, *p*-*t*Bu), 1.56 (d, J = 6.7 Hz, 3 H, α-Me), 5.12 (s, 1 H, H_{Ar}), 5.32 (br. s, 1 H, H_{Ar}), 5.65 (d, J = 5.5 Hz, 1 H, H_{Ar}), 5.93 (m, 1 H, α-C*H*), 7.35–7.39 (m, 10 H, H_{PAr}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.85 (α-Me), 30.93 (*pC*Me_3), 33.96 (*pC*Me_3), 54.15 (d, J = 28.2 Hz, α-*C*H), 86.12 (C_{Ar}), 92.87 (C_{Ar}), 97.10 (C_{Ar}), 101.55 (d, J = 24.5 Hz, $C_{Ar,ipso}$), 116.82 (d, J = 22.1 Hz, $C_{Ar,ipso}$), 121.48 ($C_{Ar,ipso}$), 128.34–135.95 (C_{PAr}), 232.19 (*C*O) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = –16.79 ppm. IR ($CHCl_3$): ν_{CO} = 1974, 1912 cm^{-1}.

[{η⁶-(*R*,*R*p)-1-[2-(Diphenylphosphanyl)-4-methoxyphenyl]chloroethyl}Cr(CO)₃] [(*R*,*R*p)-21]: This complex was prepared from (*R*,*R*p)-**13** and 1-chloroethyl chloroformate (2.07 mL, 19.0 mmol) according to general procedure D. The crude product was purified by column chromatography (R_f = 0.40 (silica gel; ethyl acetate/hexane, 3:7). Yield yellow crystals 2.02 g (85%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.52 (d, J = 6.7 Hz, 3 H, α-Me), 2.78 (s, 3 H, O*Me*), 4.29 (dd, J = 6.7, J = 2.1 Hz, 1 H, H_{Ar}), 4.77 (dd, J = 2.1, J = 1.2 Hz, 1 H, H_{Ar}), 5.08 (dd, J = 6.7, J = 2.7 Hz, 1 H, H_{Ar}), 5.72 (dq, J = 9.2, J = 6.7 Hz, 1 H, α-C*H*), 6.95–7.10 (m, 6 H, *m*/*p*-H_{PAr}), 7.41 (m, J = 7.6 Hz, 2 H, *o*-H_{PAr}), 7.58 (tm, J = 7.6 Hz, 2 H, *o*-H_{PAr}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 25.12 (α-Me), 53.89 (d, $J_{C,P}$ = 27.4 Hz, α-*C*H), 55.09 (O*Me*), 75.95 (C_{Ar}), 84.85 (d, $J_{C,P}$ = 1.7 Hz, C_{Ar}), 91.22 (d, $J_{C,P}$ = 3.3 Hz, C_{Ar}), 102.00 (C_{PAr}), 106.62 (d, $J_{C,P}$ = 24.6 Hz, $C_{Ar,ipso}$), 110.10 (C_{PAr}), 111.16 (d, $J_{C,P}$ = 19.7 Hz, $C_{Ar,ipso}$), 133.79 (d, $J_{C,P}$ = 13.7 Hz, C_{PAr}), 134.32 (d, $J_{C,P}$ = 20.8 Hz, C_{PAr}), 135.03 (d, $J_{C,P}$ = 29.8 Hz, C_{PAr}), 135.37 (d, $J_{C,P}$ = 8.8 Hz, C_{PAr}), 141.67 (d, $J_{C,P}$ = 1.6 Hz, $C_{Ar,ipso}$), 232.52 (d, $J_{C,P}$ = 2.7 Hz, *C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –16.69 ppm. MS (CI, isobutane): *m*/*z* (%) 491 (35) [M + 1], 455 (100) [M – Cl], 427 (33) [M – Cl – CO], 319 (91) [M – Cl – 3 CO – Cr]. $[\alpha]_D^{r.t.}$ = –311.9 (*c* = 0.21, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1970, 1894 cm^{-1}. $C_{24}H_{20}ClCrO_4P$ (490.84): calcd. C 58.73, H 4.11; found C 58.99, H 4.01.

[{η⁶-(*R*,*S*p)-1-[4-chloro-2-(diphenylphosphanyl)phenyl]chloroethyl}-Cr(CO)₃] [(*R*,*S*p)-22]: This complex was prepared as follows. (*R*,*S*p)-**16** (1.80 g, 3.6 mmol) was dissolved in dry diethyl ether (70 mL), the solution was cooled to –40 °C and 1-chloroethyl chloroformate (1.56 mL, 14.3 mmol) added dropwise. This solution was warmed slowly overnight. As a ^{31}P NMR check revealed only 50% conversion, the solution was again cooled to –40 °C and two more equivalents of 1-chloroethyl chloroformate (0.78 mL, 7.1 mmol) were added. The mixture was stirred at room temperature until complete conversion. Solvent and volatiles were distilled off, dry diethyl ether was added and the mixture filtered through a short pad of Celite on a sintered glass filter. The solvent was evaporated and the crude product was used for the next step. Yield (of crude product): yellow crystals (1.42 g, 90%). ^{1}H NMR (200 MHz, C_6D_6): δ = 1.32 (d, J = 6.8 Hz, 3 H, α-Me), 4.66 (dd, J = 6.6, J = 2.9 Hz, 1 H, H_{Ar}), 4.82 (dd, J = 6.6, J = 1.7 Hz, 1 H, H_{Ar}), 4.99 (dd, J = 1.7, J = 0.7 Hz, 1 H, H_{Ar}), 5.72 (dq, J = 9.3, J = 6.8 Hz, 1 H, α-C*H*), 7.10–6.99 (m, 6 H, *m*/*p*-H_{PAr}), 7.33 (m, 2 H, *o*-H_{PAr}), 7.49 (m, 2 H, *o*-H_{PAr}) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –17.53 ppm.

[{η⁶-(*S*,*R*p)-1-[2-(Diphenylphosphanyl)-4-tolyl]ethyldiphenylphosphane}Cr(CO)₃] [(*S*,*R*p)-23a]: This complex was prepared from (*S*,*R*p)-**19** (1.07 g, 2.5 mmol), diphenylphosphane (0.51 g, 2.7 mmol) and $TlPF_6$ (0.95 g, 2.7 mmol) in dry acetone (50 mL) according to general procedure E. The crude product was purified by column chromatography (R_f = 0.42; aluminium oxide; dichloromethane/hexane, 1:4). Yield yellow crystals (1.0 g, 64%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.34 (dd, J = 7.0, J = 5.0 Hz, 3 H, α-Me), 1.44 (s, 3 H, *p*Me), 4.39 (ddd, J = 6.7, J = 3.4, J = 1.5 Hz, 1 H, H_{Ar}), 4.47 (dd, J = 6.7, J = 1.0 Hz, 1 H, H_{Ar}), 4.91 (dq, J = 9.5, J = 7.0 Hz, 1 H, α-C*H*), 5.00 (t, J = 1.5 Hz, H_{Ar}), 6.95–7.16 (m, 12 H, H_{PAr}), 7.21 (m, 2 H, H_{PAr}), 7.25 (m, J = 7.0 Hz, 2 H, H_{PAr}), 7.52 (m, J = 7.0 Hz, 2 H, H_{PAr}), 7.74 (m, J = 7.6 Hz, 2 H, H_{PAr}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 16.25 (α-Me), 19.71 (*p*Me), 33.14 (dd, J = 24.4 Hz, α-*C*H), 90.10 (dd, $J_{C,P}$ = 4.8 Hz, C_{Ar}), 94.00 (C_{Ar}), 100.04 (d, $J_{C,P}$ = 2.2 Hz, C_{Ar}), 104.86 (d, $J_{C,P}$ = 18.7 Hz, $C_{Ar,ipso}$), 106.23 ($C_{Ar,ipso}$), 121.44 (dd, $J_{C,P}$ = 22.5 Hz, $C_{Ar,ipso}$), 128.57 (d, $J_{C,P}$ = 7.6 Hz, C_{PAr}), 128.62 (d, $J_{C,P}$ = 4.4 Hz, C_{PAr}), 128.93 (d, $J_{C,P}$ = 6.6 Hz, C_{PAr}), 129.24 (C_{PAr}), 129.83 (d, $J_{C,P}$ = 3.9 Hz, C_{PAr}), 131.60 (d, $J_{C,P}$ = 15.3 Hz, C_{PAr}), 134.15 (d, $J_{C,P}$ = 23.6 Hz, C_{PAr}), 134.54 (dd, $J_{C,P}$ = 20.3, $J_{C,P}$ = 2.2 Hz, C_{PAr}), 135.05 (d, $J_{C,P}$ = 19.7 Hz, C_{PAr}), 135.77 (d, $J_{C,P}$ = 13.7 Hz, C_{PAr}), 136.28 (d, $J_{C,P}$ = 9.8 Hz, C_{PAr}) 136.44 (d, $J_{C,P}$ = 22.5 Hz, C_{PAr}), 137.04 (d, $J_{C,P}$ = 19.2 Hz, C_{PAr}), 233.34 (*C*O) ppm. ^{31}P NMR (202 MHz, C_6D_6): δ = –17.56 (d, $J_{P,P}$ = 18.3 Hz, *o*PPh_2), 8.47 (d, $J_{P,P}$ = 18.3 Hz, α-PPh_2) ppm. MS (CI, isobutane): *m*/*z* (%) 625 (20) [M + 1], 540 (22) [M – 3 CO], 489 (54) [M – 3 CO – Cr], 439 (100) [M – PPh_2]. $[\alpha]_D^{r.t.}$ = +293.6 (*c* = 1.00, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1965, 1894 cm^{-1}. $C_{36}H_{30}CrO_3P_2$ (624.57): calcd. C 69.23, H 4.84; found C 69.14, H 5.26.

[{η⁶-(*S*,*R*p)-1-[2-(Diphenylphosphanyl)-4-tolyl]ethyldicyclohexylphosphane}Cr(CO)₃] [(*S*,*R*p)-23b]: This complex was prepared from (*S*,*R*p)-**19** (1.45 g, 3.0 mmol), dicyclohexylphosphane (0.59 g, 3.0 mmol) and $TlPF_6$ (1.04 g, 3.0 mmol) in dry acetone (60 mL) according to general procedure E. The crude product was purified by column chromatography (R_f = 0.54; aluminium oxide; diethyl ether/hexane, 1:4). Yield yellow crystals (1.2 g, 63%). Crystals suitable for X-ray structure determination were grown from a layered mixture of dichloromethane and hexane at –30 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.00–1.23 (m, 10 H, H_{PCy_2}), 1.34 (m, 1 H,

H_{PCy_2}), 1.39 (dd, J = 7.0, J = 3.4 Hz, 3 H, α-Me), 1.45 (s, 3 H, *p*Me), 1.48–1.80 (m, 11 H, H_{PCy_2}), 4.24 (dq, J = 7.0 Hz, 1 H, α-C*H*), 4.78 (br. d, J = 6.4 Hz, 1 H, H_{Ar}), 4.84 (m, J = 6.4, J = 3.35, J = 0.6 Hz, 1 H, H_{Ar}), 5.10 (t, J = 1.2 Hz, 1 H, H_{Ar}), 7.14 (m, J = 7.3 Hz, 4 H, H_{PPh_2}), 7.47 (m, J = 7.6 Hz, 2 H, H_{PPh_2}), 7.65 (m, J = 7.6 Hz, 2 H, H_{PPh_2}), 7.70 (m, J = 7.6 Hz, 2 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 15.32 αMe), 19.63 (*p*Me), 26.64 (d, $J_{C,P}$ = 3.9 Hz, C_{PCy_2}), 27.03 (d, $J_{C,P}$ = 12.1 Hz, C_{PCy_2}), 27.45 (d, $J_{C,P}$ = 8.2 Hz, C_{PCy_2}), 27.82 (d, $J_{C,P}$ = 5.4 Hz, C_{PCy_2}), 28.05 (d, $J_{C,P}$ = 13.7 Hz, C_{PCy_2}), 30.02 (d, $J_{C,P}$ = 9.3 Hz, C_{PCy_2}), 30.38 (d, $J_{C,P}$ = 5.5 Hz, C_{PCy_2}), 31.58 (dd, $J_{C,P}$ = 21.4 Hz, α-*C*H), 31.70 (d, $J_{C,P}$ = 12.6 Hz, C_{PCy_2}), 33.48 (d, $J_{C,P}$ = 21.4 Hz, C_{PCy_2}), 33.89 (d, $J_{C,P}$ = 23.5 Hz, C_{PCy_2}), 88.93 (dd, $J_{C,P}$ = 4.1, $J_{C,P}$ = 3.8 Hz, C_{Ar}), 94.92 (C_{Ar}), 101.98 (d, $J_{C,P}$ = 2.8 Hz, C_{Ar}), 104.70 (dd, $J_{C,P}$ = 24.1, $J_{C,P}$ = 3.3 Hz, $C_{Ar,ipso}$), 105 41 ($C_{Ar,ipso}$), 124.78 (dd, $J_{C,P}$ = 22.5, $J_{C,P}$ = 19.2 Hz, $C_{Ar,ipso}$), 128.47 (C_{PPh_2}), 128.78 (d, $J_{C,P}$ = 7.1 Hz, C_{PPh_2}), 133.90 (dd, $J_{C,P}$ = 18.6, $J_{C,P}$ = 2.7 Hz, C_{PPh_2}), 135.39 (d, $J_{C,P}$ = 20.9 Hz, C_{PPh_2}), 137.35 (dd, $J_{C,P}$ = 14.3, $J_{C,P}$ = 3.9 Hz, C_{PPh_2}),138.42 (dd, $J_{C,P}$ = 7.1, $J_{C,P}$ = 2.7 Hz, C_{PPh_2}), 233.41 (*C*O) ppm. ^{31}P NMR (202 MHz, C_6D_6): δ = –18.71 (d, $J_{P,P}$ = 38.3 Hz, PPh_2), 15.85 (d, $J_{P,P}$ = 38.3 Hz, PCy_2) ppm. MS (CI, isobutane): *m*/*z* (%) 637 (82) [M + 1], 580 (16) [M – 2 CO], 552 (100) [M – 3 CO], 501 (16) [M – 3 CO – Cr]. $[\alpha]_D^{r.t.}$ = +549.7 (*c* = 0.62, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1963, 1887 cm^{-1}. $C_{36}H_{42}CrO_3P_2$ (636.67): calcd. C 67.91, H 6.65; found C 69.12, H 7.75.

[{η^6-(*S*,*R*p)-1-[2-(Diphenylphosphanyl)-4-tolyl]ethyldi-*tert*-butylphosphane}Cr(CO)$_3$] [(*S*,*R*p)-23c]: This complex was prepared from (*S*,*R*p)-**19** (1.02 g, 2.4 mmol), di-*tert*-butylphosphane (0.34 g, 2.6 mmol) and $TlPF_6$ (0.91 g, 2.6 mmol) in dry acetone (48 mL) according to general procedure E. The crude product was purified by column chromatography (aluminium oxide; dichloromethane/hexane, 1:4). R_f = 0.71. Yield yellow crystals (0.88 g, 62%). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.92 [d, J = 9.0 Hz, 9 H, P(C*Me*$_3$)$_2$], 1.21, [d, J = 10.7 Hz, 9 H, P(C*Me*$_3$)$_2$], 1.48 (s, 3 H, *p*Me), 1.55 (dd, J = 7.0, J = 2.7 Hz, 3 H, α-Me), 4.44 (m, J = 7.0 Hz, 1 H, α-C*H*), 4.75 (dd, J = 6.7, J = 3.4 Hz, 1 H, H_{Ar}), 4.80 (br. d, J = 6.7 Hz, 1 H, H_{Ar}), 5.23 (br. s, 1 H, H_{Ar}), 7.06 (m, J = 7.3 Hz, 2 H, H_{PPh_2}), 7.10–7.16 (m, 4 H, H_{PPh_2}), 7.45 (m, J = 7.0 Hz, 2 H, H_{PPh_2}), 7.71 (m, J = 7.0 Hz, 2 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 15.54 (α-Me), 19.58 (*p*Me), 31.59 [dd, $J_{C,P}$ = 13.2, $J_{C,P}$ = 3.3 Hz, P(C*Me*$_3$)$_2$], 32.20 [dd, $J_{C,P}$ = 13.2, $J_{C,P}$ = 3.3 Hz, P(C*Me*$_3$)$_2$], 34.67 (d, $J_{C,P}$ = 31.8 Hz, α-*C*H), 34.85 [d, $J_{C,P}$ = 22 Hz, P(*C*Me$_3$)$_2$], 35.15 [d, $J_{C,P}$ = 23 Hz, P(*C*Me$_3$)$_2$], 89.44 (d, $J_{C,P}$ = 3.8 Hz, C_{Ar}), 95.05 (C_{Ar}), 103.26 (d, $J_{C,P}$ = 2.8 Hz, C_{Ar}), 104.15 (d, $J_{C,P}$ = 28.5 Hz, $C_{Ar,ipso}$), 105.09 ($C_{Ar,ipso}$), 125.28 (dd, $J_{C,P}$ = 20.9 Hz, $C_{Ar,ipso}$), 128.08 (d, $J_{C,P}$ = 4.9 Hz, C_{PPh_2}), 128.9 (C_{PPh_2}), 128.72 (d, $J_{C,P}$ = 6.6 Hz, C_{PPh_2}), 129.55 (C_{PPh_2}), 133.66 (dd, $J_{C,P}$ = 18.7, $J_{C,P}$ = 2.8 Hz, C_{PPh_2}), 135.56 (d, $J_{C,P}$ = 20.9 Hz, C_{PPh_2}), 138.11 (dd, $J_{C,P}$ = 15.4, $J_{C,P}$ = 7.7 Hz, C_{PPh_2}), 139 67 (dd, $J_{C,P}$ = 5 Hz, C_{PPh_2}), 233.42 (*C*O) ppm. ^{31}P NMR (202 MHz, C_6D_6): δ = –19.79 (d, $J_{P,P}$ = 61.7 Hz, PPh_2), 49.33 [d, $J_{P,P}$ = 61.7 Hz, P(CMe$_3$)$_2$] ppm. MS (CI, isobutane): *m*/*z* (%) 585 (87) [M + 1], 527 (100) [M – CMe$_3$], 500 (22) [M – 3 CO], 439 (74) [M – P(CMe$_3$]$_2$. $[\alpha]_D^{r.t.}$ = +435.2 (*c* = 1.01, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1962, 1891 cm^{-1}. $C_{32}H_{38}CrO_3P_2$ (584.59): calcd. C 65.75, H 6.55; found C 65.56, H 6.39.

[{η^6-(*S*,*R*p)-1-[4-*tert*-Butyl-2-(diphenylphosphanyl)phenyl]dicyclohexylphosphanylethane}Cr(CO)$_3$] [(*S*,*R*p)-24]: This complex was prepared according to general procedure E from (*S*,*R*p)-**20** (4.59 g, 8.88 mmol), dicyclohexylphosphane (2.00 g, 10.13 mmol) and $TlPF_6$ (3.10 g, 8.88 mmol) in dry acetone (170 mL). The crude product was purified by column chromatography (aluminium oxide; diethyl ether). Yield yellow microcrystalline powder (3.70 g, 61%). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.95 (s, 9 H, C*Me*$_3$), 1.00–1.23 (m, 11 H, H_{PCy_2}), 1.44 (dd, J = 7.0, J = 3.7 Hz, 3 H, α-Me), 1.47–1.91 (m, 11 H, H_{PCy_2}), 4.35 (dq, J = 7.0 Hz, 1 H, α-C*H*), 4.69 (dd, J = 6.7, J = 4 Hz, 1 H, H_{Ar}), 5.40 (dd, J = 6.7, J = 1.5 Hz, 1 H, H_{Ar}), 5.62 (t, J = 1.5 Hz, 1 H, H_{Ar}), 7.02–7.48 (m, 10 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 14.48 (α-Me), 26.64–30.35 (10 C, C_{PCy_2}), 30.93 (C*Me*$_3$), 31.14 (*C*Me$_3$), 31.82 (dd, $J_{C,P}$ = 21.3 Hz, α-*C*H), 33.63 (d, $J_{C,P}$ = 22.1 Hz, C_{PCy_2}), 33.83 (d, $J_{C,P}$ = 16.3 Hz, C_{PCy_2}), 86.54 (t, $J_{C,P}$ = 3.8 Hz, C_{Ar}), 88.17 (C_{Ar}), 99.77 (d, $J_{C,P}$ = 3.8 Hz, C_{Ar}), 101.48 (d, $J_{C,P}$ = 24.0 Hz, $C_{Ar,ipso}$), 119.58 ($C_{Ar,ipso}$), 126.47 ($C_{Ar,ipso}$), 126.66–139.11 (m, 12 C, C_{PPh_2}), 233.50 (*C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –20.83 (d, $J_{P,P}$ = 46.7 Hz, PPh_2), 15.73 (d, $J_{P,P}$ = 46.7 Hz, PCy_2) ppm. $[\alpha]_D^{r.t.}$ = +306.27 (*c* = 0.07, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1968, 1903 cm^{-1}. $C_{39}H_{48}CrO_3P_2$ (678.75): calcd. C 69.01, H 7.13; found C 69.01, H 7.13.

[{η^6-(*R*,*R*p)-1-[2-(Diphenylphosphanyl)-4-methoxyphenyl]ethyldiphenylphosphane}Cr(CO)$_3$] [(*R*,*R*p)-25a]: This complex was prepared from (*R*,*R*p)-**21** (0.78 g, 1.59 mmol), diphenylphosphane (0.32 g, 1.70 mmol) and $TlPF_6$ (0.60 g, 1.70 mmol) in acetone (32 mL) according to general procedure E. The crude product was purified by column chromatography (R_f = 0.42; aluminium oxide; hexane/dichloromethane, 4:1). Yield yellow crystals (0.90 g, 88% yield). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.41 (dd, J = 6.9, J = 5.6 Hz, 3 H, α-Me), 2.81 (s, 3 H, O*Me*), 4.20 (dd, J = 7.0, J = 2.4 Hz, 1 H, H_{Ar}), 4.65 (dq, J = 9.1, J = 7.0 Hz, 1 H, α-C*H*), 4.68 (ddd, J = 7.0, J = 3.0, J = 1.8 Hz, 1 H, H_{Ar}), 5.09 (dd, J = 2.4, J = 1.2 Hz, 1 H, H_{Ar}), 6.94–7.15 (m, 14 H, H_{PPh_2}), 7.29 (m, J = 7.0 Hz, 2 H, H_{PPh_2}), 7.51 (m, J = 7.9 Hz, 2 H, H_{PPh_2}), 7.74 (m, J = 7.0 Hz, 2 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 18.12 (α-Me), 32.48 (t, $J_{C,P}$ = 23.1 Hz, α-*C*H), 56.18 (O*Me*), 76.05 (C_{Ar}), 86.82 (C_{Ar}), 91.24 (dd, $J_{C,P}$ = 7.0, $J_{C,P}$ = 3.0 Hz, C_{Ar}), 106.48 (d, $J_{C,P}$ = 22.5 Hz, $C_{Ar,ipso}$), 117.20 (t, $J_{C,P}$ = 21.2 Hz, $C_{Ar,ipso}$), 128.71 (d, $J_{C,P}$ = 7.7 Hz, C_{PPh_2}), 128.97 (d, $J_{C,P}$ = 6.5 Hz, C_{PPh_2}), 129.53 (C_{PPh_2}), 131.73 (d, $J_{C,P}$ = 15.9 Hz, C_{PPh_2}), 134.57 (d, $J_{C,P}$ = 22.5 Hz, C_{PPh_2}), 134.85 (d, $J_{C,P}$ = 20.9 Hz, C_{PPh_2}), 135.06 (d, $J_{C,P}$ = 20.3 Hz, C_{PPh_2}), 135.59 (d, $J_{C,P}$ = 7.7 Hz, C_{PPh_2}), 136.28 (d, $J_{C,P}$ = 22.5 Hz, C_{PPh_2}), 137.25 (d, $J_{C,P}$ = 18.6 Hz, C_{PPh_2}), 140.80 ($C_{Ar,ipso}$), 233.51 (*C*O) ppm. ^{31}P NMR (202 MHz, C_6D_6): δ = 5.02 (d, $J_{P,P}$ = 11.0 Hz, α-PPh_2), –17.99 (d, $J_{P,P}$ = 11.0 Hz, *o*PPh_2) ppm. MS (CI, isobutane): *m*/*z* (%) 505 (22) [M + H – 3 CO – Cr], 319 (100) [M – 3 CO – Cr –HPPh_2]. $[\alpha]_D^{r.t.}$ = –286.4 (*c* = 0.22, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1964, 1892 cm^{-1}. $C_{36}H_{30}CrO_4P_2$ (640.57): calcd. C 67.50, H 4.72; found C 67.57, H 5.27.

[{η^6-(*R*,*R*p)-1-[2-(Diphenylphosphanyl)-4-methoxyphenyl]ethyldicyclohexylphosphane}Cr(CO)$_3$] [(*R*,*R*p)-25b]: This complex was prepared from (*R*,*R*p)-**21**, dicyclohexylphosphane (0.47 g, 2.36 mmol) and $TlPF_6$ (0.82 g, 2.36 mmol) in acetone (47 mL) according to general procedure E. The crude product was purified by column chromatography (R_f = 0.51; aluminium oxide; hexane/diethyl ether, 2:1). Yield yellow crystals (1.18 g, 77% yield). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.08–1.36 (m, 8 H, H_{PCy_2}), 1.45–1.70 (m, 14 H, H_{PCy_2}), 1.47 (dd, J = 7.0, J = 4.5 Hz, 3 H, α-Me), 2.84 (s, 3 H, O*Me*), 4.00 (m, J = 7.0 Hz, 1 H, α-C*H*), 4.47 (dd, J = 7.0, J = 2.4 Hz, 1 H, H_{Ar}), 5.13 (ddd, J = 7.0, J = 3.0, J = 1.5 Hz, 1 H, H_{Ar}), 5.19 (dd, J = 2.4, J = 0.9 Hz, 1 H, H_{Ar}), 7.00–7.11 (m, 6 H, H_{PPh_2}), 7.47 (m, J = 7.0 Hz, 2 H, H_{PPh_2}), 7.70 (m, J = 7.3 Hz, 2 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 17.60 (α-Me), 26.65 (d, $J_{C,P}$ = 10.4 Hz, C_{PCy_2}), 27.12 (d, $J_{C,P}$ = 11.5 Hz, C_{PCy_2}), 27.41 (d, $J_{C,P}$ = 8.2 Hz, C_{PCy_2}), 27.89 (d, $J_{C,P}$ = 6.0 Hz, C_{PCy_2}), 28.01 (d, $J_{C,P}$ = 13.2 Hz, C_{PCy_2}), 30.13 (d, $J_{C,P}$ = 10.4 Hz, C_{PCy_2}), 30.44 (d, $J_{C,P}$ = 6.6 Hz, C_{PCy_2}), 30.68 (dd, $J_{C,P}$ = 26.3, $J_{C,P}$ = 19.7 Hz, α-*C*H), 31.43 (d, $J_{C,P}$ = 17.0 Hz, C_{PCy_2}), 31.79 (C_{PCy_2}), 31.95 (d, $J_{C,P}$

= 7.7 Hz, C_{PCy_2}), 33.43 (d, $J_{C,P}$ = 20.9 Hz, C_{PCy_2}), 33.65 (d, $J_{C,P}$ = 21.9 Hz, C_{PCy_2}), 55.25 (O*Me*), 77.13 (C_{Ar}), 88.36 (d, $J_{C,P}$ = 2.2 Hz, C_{Ar}), 90.58 (dd, $J_{C,P}$ = 7.1, $J_{C,P}$ = 3.3 Hz, C_{Ar}), 105.37 (dd, $J_{C,P}$ = 24.7, $J_{C,P}$ = 3.3 Hz, $C_{Ar,ipso}$), 120.89 (dd, $J_{C,P}$ = 21.4, $J_{C,P}$ = 19.8 Hz, $C_{Ar,ipso}$), 128.41 (d, $J_{C,P}$ = 7.1 Hz, C_{PPh_2}), 128.84 (d, $J_{C,P}$ = 7.1 Hz, C_{PPh_2}), 129.89 (C_{PPh_2}), 134.22 (dd, $J_{C,P}$ = 19.2, $J_{C,P}$ = 2.2 Hz, C_{PPh_2}), 135.46 (d, $J_{C,P}$ = 20.3 Hz, C_{PPh_2}), 136.09 (dd, $J_{C,P}$ = 14.8, $J_{C,P}$ = 2.7 Hz, C_{PPh_2}), 137.74 (d, $J_{C,P}$ = 7.7 Hz, C_{PPh_2}), 140.00 (d, $J_{C,P}$ = 1.7 Hz, $C_{Ar,ipso}$), 233.68 (d, $J_{C,P}$ = 1.7 Hz, *C*O) ppm. ^{31}P NMR (202 MHz, C_6D_6): δ = 15.49 (d, $J_{P,P}$ = 26.0 Hz, PCy_2), –17.48 (d, $J_{P,P}$ = 26.0 Hz, PPh_2) ppm. MS (CI, isobutane): *m*/*z* (%) 653 (72) [M + H], 568 (100) [M – 3 CO], 517 (85) [M – 3 CO – Cr], 433 (44) [M – 3 CO – Cr – C_6H_{12}]. $[\alpha]_D^{r.t.}$ = –309.5 (*c* = 0.21, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1963, 1886 cm^{-1}. $C_{36}H_{42}CrO_4P_2$ (652.67): calcd. C 66.25, H 6.49; found C 66.00, H 6.74.

[{η^6-(*R*,*R*p)-1-[2-(Diphenylphosphanyl)-4-methoxyphenyl]ethyldi-*tert*-butylphosphane}Cr(CO)$_3$] [(*R*,*R*p)-25c]: This complex was prepared from (*R*,*R*p)-**21** (0.91 g, 1.82 mmol), di-*tert*-butylphosphane (0.29 g, 2.00 mmol) and $TlPF_6$ (0.70 g, 2.00 mmol) in acetone (36 mL) according to general procedure E. The crude product was purified by column chromatography (R_f = 0.34; aluminium oxide; hexane/dichloromethane, 4:1→neat dichloromethane). Yield yellow crystals (0.84 g, 78%). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.94 [d, *J* = 11.0 Hz, 9 H, P(C*Me*$_3$)$_2$], 1.18 [d, *J* = 10.7 Hz, 9 H, P(C*Me*$_3$)$_2$], 1.58 (dd, *J* = 7.4, *J* = 2.5 Hz, 3 H, α-Me), 2.86 (s, 3 H, O*Me*), 4.32 (m, *J* = 7.0 Hz, 1 H, α-C*H*), 4.86 (dd, *J* = 6.7, *J* = 3.0 Hz, 1 H, H_{Ar}), 4.55 (dd, *J* = 6.7, *J* = 1.6 Hz, 1 H, H_{Ar}), 5.40 (d, *J* = 1.5 Hz, 1 H, H_{Ar}), 7.00–7.10 (m, 6 H, H_{PPh_2}), 7.44 (dd, *J* = 7.4 Hz, 2 H, H_{PPh_2}), 7.70 (dd, *J* = 7.0 Hz, 2 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 16.32 (α-Me), 31.51 [dd, $J_{C,P}$ = 13.2, $J_{C,P}$ = 3.3 Hz, P(C*Me*$_3$)$_2$], 32.22 [d, $J_{C,P}$ = 14.3 Hz, P(C*Me*$_3$)$_2$], 34.29 [d, $J_{C,P}$ = 15.4 Hz, P(*C*Me$_3$)$_2$], 34.51 (dd, $J_{C,P}$ = 22.5, $J_{C,P}$ = 15.3 Hz, α-*C*H), 34.98 [d, $J_{C,P}$ = 35.6 Hz, P(*C*Me$_3$)$_2$], 55.38 (O*Me*), 77.96 (C_{Ar}), 89.69 (d, $J_{C,P}$ = 3.9 Hz, C_{Ar}), 90.76 (C_{Ar}), 104.83 (d, $J_{C,P}$ = 30.2 Hz, $C_{Ar,ipso}$), 121.53 (m, $J_{C,P}$ = 20.8 Hz, C_{Ar}), 128.72 (d, $J_{C,P}$ = 6.5 Hz, C_{PPh_2}), 129.68 (C_{PPh_2}), 133.81 (dd, $J_{C,P}$ = 19.2, $J_{C,P}$ = 2.9 Hz, C_{PPh_2}), 135.63 (d, $J_{C,P}$ = 20.3 Hz, C_{PPh_2}), 137.20 (C_{PPh_2}), 139.10 ($C_{Ar,ipso}$), 139.34 (d, $J_{C,P}$ = 5.0 Hz, C_{PPh_2}), 233.63 (*C*O) ppm. ^{31}P NMR (202 MHz, C_6D_6): δ = –18.58 (d, $J_{P,P}$ = 54.3 Hz, PPh_2), 48.07 [d, $J_{P,P}$ = 54.3 Hz, P(CMe$_3$)$_2$] ppm. MS (CI, isobutane): *m*/*z* (%) 601 (39) [M + H], 543 (32) [M – CMe$_3$], 516 (54) [M – 3 CO], 465 (100) [M – 3 CO – Cr], 407 (83) [M – 3 CO – Cr – HCMe$_3$]. $[\alpha]_D^{r.t.}$ = –436.4 (*c* = 0.22, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1963, 1889 cm^{-1}. $C_{32}H_{38}CrO_4P_2$ (600.599): calcd. C 63.99, H 6.38; found C 63.83, H 6.32.

[{η^6-(*R*,*S*p)-1-[4-Chloro-2-(diphenylphosphanyl)phenyl]ethyldiphenylphosphane}Cr(CO)$_3$] [(*R*,*S*p)-26a]: This complex was prepared from (*R*,*S*p)-**22** (0.54 g, 1.1 mmol), diphenylphosphane (0.23 g, 1.2 mmol) and $TlPF_6$ (0.44 g, 1.2 mmol) in dry acetone (22 mL) according to general procedure E. The crude product was purified by column chromatography (R_f = 0.53; aluminium oxide; diethyl ether/hexane, 1:4). Yield yellow crystals (0.20 g, 28%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.22 (dd, *J* = 6.9, *J* = 4.9 Hz, 3 H, α-Me), 4.24 (d, *J* = 6.6 Hz, 1 H, H_{Ar}), 4.76 (d, *J* = 6.8 Hz, 1 H, H_{Ar}), 4.80 (dd, *J* = 9.1, *J* = 6.9 Hz, 1 H, α-C*H*), 5.36 (d, *J* = 1.4 Hz, 1 H, H_{Ar}), 6.93–7.12 (m, 16 H, H_{PPh_2}), 7.45 (m, *J* = 7.7 Hz, 2 H, H_{PPh_2}), 7.66 (m, *J* = 7.7 Hz, 2 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 16.07 (α-Me), 33.01 (m, $J_{C,P}$ = 24.2 Hz, α-*C*H), 89.06 (C_{Ar}), 92.97 (C_{Ar}), 98.10 (C_{Ar}), 104.43 (d, $J_{C,P}$ = 25.7 Hz, $C_{Ar,ipso}$), 108.84 ($C_{Ar,ipso}$), 120.68 (m, $J_{C,P}$ = 21.4 Hz, $C_{Ar,ipso}$), 128.54 (C_{PPh_2}), 128.66 (C_{PPh_2}), 128.72 (C_{PPh_2}), 129.14 (d, $J_{C,P}$ = 7.1 Hz, C_{PPh_2}), 129.40 (C_{PPh_2}), 129.95 (C_{PPh_2}), 130.25 (C_{PPh_2}), 131.55 (d, $J_{C,P}$ = 15.9 Hz, C_{PPh_2}), 133.76 (d, $J_{C,P}$ = 23.1 Hz, C_{PPh_2}), 134.43 (d, $J_{C,P}$ = 20.8 Hz, C_{PPh_2}), 134.98 (d, $J_{C,P}$ = 20.9 Hz, C_{PPh_2}), 135.53 (d, $J_{C,P}$ = 7.1 Hz, C_{PPh_2}), 126.20 (d, $J_{C,P}$ = 22.5 Hz, C_{PPh_2}), 136.68 (d, $J_{C,P}$ = 19.2 Hz, C_{PPh_2}), 231.71 (*C*O) ppm. ^{31}P NMR (202 MHz, C_6D_6): δ = 7.33 (d, $J_{P,P}$ = 18.3 Hz, *a*PPh_2), –18.93 (d, $J_{P,P}$ = 18.3 Hz, *o*PPh_2) ppm. MS (CI, isobutane): *m*/*z* (%) 645 (22) [M + H], 560 (14) [M – 3 CO], 509 (48) [M + H – 3 CO – Cr], 459 (100) [M – PPh_2], 432 (28) [M – 3 CO – Cr – Ph], 323 (42) [M – 3 CO – Cr – PPh_2]. $[\alpha]_D^{r.t.}$ = –248.1 (*c* = 0.10, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1976, 1912 cm^{-1}. $C_{35}H_{27}ClCrO_3P_2$ (644.99): calcd. C 65.18, H 4.22; found C 65.84, H 4.74.

[{η^6-(*R*,*S*p)-1-[4-Chloro-2-(diphenylphosphanyl)phenyl]ethyldicyclohexylphosphane}Cr(CO)$_3$] [(*R*,*S*p)-26b]: This complex was prepared from (*R*,*S*p)-**22** (0.62 g, 1.25 mmol), dicyclohexylphosphane (0.25 g, 1.25 mmol) and $TlPF_6$ (0.44 g, 1.25 mmol) in dry acetone (25 mL) according to general procedure E. The crude product was purified by column chromatography (R_f = 0.69, aluminium oxide; diethyl ether/hexane, 1:4). Yield yellow crystals (0.30 g, 36%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.00–1.19 (m, 7 H, H_{PCy_2}), 1.27 (dd, *J* = 7.3, *J* = 3.7 Hz, 3 H, α-Me), 1.30–1.46 (m, 4 H, H_{PCy_2}), 1.48–1.76 (m, 11 H, H_{PCy_2}), 4.13 (m, *J* = 7.3 Hz, 1 H, α-C*H*), 4.66 (ddd, *J* = 6.7, *J* = 3.4, *J* = 0.9 Hz, 1 H, H_{Ar}), 5.08 (dd, *J* = 6.7, *J* = 1.8 Hz, 1 H, H_{Ar}), 5.49 (m, *J* = 1.8 Hz, 1 H, H_{Ar}), 7.01–7.10 (m, 6 H, H_{PPh_2}), 7.40 (m, *J* = 7.6 Hz, 2 H, H_{PPh_2}), 7.74 (m, *J* = 7.6 Hz, 2 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 15.17 (α-Me), 26.59 (d, $J_{C,P}$ = 4.9 Hz, C_{PCy_2}), 27.01 (d, $J_{C,P}$ = 11.5 Hz, C_{PCy_2}), 27.44 (d, $J_{C,P}$ = 7.7 Hz, C_{PCy_2}), 27.80 (d, $J_{C,P}$ = 15.9 Hz, C_{PCy_2}), 27.88 (d, $J_{C,P}$ = 23.5 Hz, C_{PCy_2}), 30.40 (d, $J_{C,P}$ = 9.3 Hz, C_{PCy_2}), 30.18 (C_{PCy_2}), 30.33 (d, $J_{C,P}$ = 6.6 Hz, C_{PCy_2}), 31.57 (dd, $J_{C,P}$ = 26.8, $J_{C,P}$ = 20.3 Hz, α-*C*H), 31.59 (d, $J_{C,P}$ = 12.0 Hz, C_{PCy_2}), 31.74 (d, $J_{C,P}$ = 20.8 Hz, C_{PCy_2}), 33.55 (d, $J_{C,P}$ = 14.8 Hz, C_{PCy_2}), 33.72 (d, $J_{C,P}$ = 15.9 Hz, C_{PCy_2}), 87.89 (dd, $J_{C,P}$ = 3.8 Hz, C_{Ar}), 93.89 (C_{Ar}), 100.10 (d, $J_{C,P}$ = 2.8 Hz, C_{Ar}), 103.57 (dd, $J_{C,P}$ = 27.9, $J_{C,P}$ = 2.7 Hz, $C_{Ar,ipso}$), 107.52 (d, $J_{C,P}$ = 3.8 Hz, $C_{Ar,ipso}$), 124.13 (dd, $J_{C,P}$ = 21.9, $J_{C,P}$ = 19.2 Hz, $C_{Ar,ipso}$), 128.29 (C_{PPh_2}), 128.35 (C_{PPh_2}), 128.59 (C_{PPh_2}), 129. 01 (d, $J_{C,P}$ = 7.7 Hz, C_{PPh_2}), 130.42 (C_{PPh_2}), 133.76 (dd, $J_{C,P}$ = 18.6, $J_{C,P}$ = 2.7 Hz, C_{PPh_2}), 135.33 (d, $J_{C,P}$ = 21.4 Hz, C_{PPh_2}), 136.80 (dd, $J_{C,P}$ = 14.3, $J_{C,P}$ = 4.4 Hz, C_{PPh_2}), 137.83 (dd, $J_{C,P}$ = 7.1, $J_{C,P}$ = 2.7 Hz, C_{PPh_2}), 231.75 (*C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = 15.20 (d, $J_{P,P}$ = 39.3 Hz, PCy_2), –20.17 (d, $J_{P,P}$ = 39.3 Hz, PPh_2) ppm. MS (CI, isobutane): *m*/*z* (%) 657 (68) [M + H], 572 (44) [M – 3 CO], 521 (100) [M – 3 CO – Cr], 433 (32) [M – 3 CO – Cr – C_6H_{12}]. $[\alpha]_D^{r.t.}$ = –346.0 (*c* = 0.20, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1973, 1906 cm^{-1}.

[{η^6-(*R*,*S*p)-1-[4-Chloro-2-(diphenylphosphanyl)phenyl]ethyldi-*tert*-butylphosphane}Cr(CO)$_3$] [(*R*,*S*p)-26c]: This complex was prepared from (*R*,*S*p)-**22** (0.48 g, 0.97 mmol), di-*tert*-butylphosphane (0.16 g, 1.07 mmol) and $TlPF_6$ (0.37 g, 1.07 mmol) in dry acetone (20 mL) according to general procedure E. The crude product was purified by column chromatography (R_f = 0.54; aluminium oxide; dichloromethane/hexane, 4:1). Yield yellow crystals (0.18 g, 31%). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.86 [d, *J* = 10.7 Hz, 9 H, P(C*Me*$_3$)$_2$], 1.17 [d, *J* = 10.5 Hz, 9 H, P(C*Me*$_3$)$_2$], 1.41 (dd, *J* = 7.3, *J* = 2.7 Hz, 3 H, α-Me), 4.32 (m, *J* = 4.6 Hz, 1 H, α-C*H*), 4.56 (dd, *J* = 6.8, *J* = 3.7 Hz, 1 H, H_{Ar}), 5.12 (dd, *J* = 6.8, *J* = 1.7 Hz, 1 H, H_{Ar}), 5.61 (d, *J* = 1.7 Hz, 1 H, H_{Ar}), 7.02–7.11 (m, 6 H, H_{PPh_2}), 7.36 (m, *J* = 7.6 Hz, 2 H, H_{PPh_2}), 7.62 (m, *J* = 7.6, *J* = 1.9 Hz, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 15.35 (α-Me), 31.55 [dd, $J_{C,P}$ = 13.2, $J_{C,P}$ = 3.8 Hz, P(C*Me*$_3$)$_2$], 32.15 [d, $J_{C,P}$ = 13.7 Hz, P(C*Me*$_3$)$_2$], 34.54 [d, $J_{C,P}$ = 32.0 Hz, P(*C*Me$_3$)$_2$], 34.74 (d, $J_{C,P}$ = 37.0 Hz, α-*C*H), 35.08 [d, $J_{C,P}$ = 32.0 Hz, P(C*Me*$_3$)$_2$], 88.37 (C_{Ar}), 94.09 (C_{Ar}), 101.36 (C_{Ar}), 103.62 (d, $J_{C,P}$ = 29.6 Hz, $C_{Ar,ipso}$), 107.02 (d, $J_{C,P}$ = 3.9 Hz, $C_{Ar,ipso}$), 124.65 (dd, $J_{C,P}$ = 21.1 Hz, $C_{Ar,ipso}$), 127.91

(C_{PPh_2}), 128.13 (C_{PPh_2}), 128.29 (C_{PPh_2}), 128.94 (d, $J_{C,P}$ = 6.6 Hz, C_{PPh_2}), 129.94 (C_{PPh_2}), 133.45 (dd, $J_{C,P}$ = 18.6, $J_{C,P}$ = 3.3 Hz, C_{PPh_2}), 135.49 (d, $J_{C,P}$ = 21.4 Hz, C_{PPh_2}), 137.56 (dd, $J_{C,P}$ = 15.3, $J_{C,P}$ = 7.7 Hz, C_{PPh_2}), 139.03 (m, $J_{C,P}$ = 4.4 Hz, C_{PPh_2}), 231.75 (*C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –21.06 (d, $J_{P,P}$ = 63.2 Hz, PPh_2), 48.78 [d, $J_{P,P}$ = 63.2 Hz, $P(CMe_3)_2$] ppm. MS (CI, isobutane): *m*/*z* (%) 605 (88) [M + H], 547 (45) [M – CMe_3], 520 (15) [M – 3 CO], 459 (14) [M – $P(CMe_3)_2$, 391 (100) [M – 3 CO – Cr – Ph], 407 (83) [M – 3 CO – Cr – $HCMe_3$]. $[\alpha]_D^{r.t.}$ = –445.4 (*c* = 0.22, $CHCl_3$). IR ($CHCl_3$): ν_{CO} = 1974, 1910 cm^{-1}.

Preparation of [{η^6-(*S*)-*N*,*N*-Dimethyl-1-(2-methoxyphenyl)ethylamine}Cr(CO)$_3$] [(*S*,*S*p)-28] and [(*S*,*R*p)-28]. Thermolysis with Cr(CO)$_6$: Reaction of (*S*)-**4** (4.00 g, 22.00 mmol) and $Cr(CO)_6$ (6.00 g, 27.00 mmol) in a 8:1 mixture of di-*n*-butyl ether and thf (81 mL) for 50 h according to general procedure B afforded (*S*,*S*p)-**28** and (*S*,*R*p)-**28** in a 25:75 ratio (Scheme 8). The two diastereomers were collected as a single fraction after flash chromatography (aluminium oxide; diethyl ether). Yield 4.65 g (66%).

Arene Exchange with [(η^6-Naphthalene)Cr(CO)$_3$]: (*S*,*S*p)-**28** was prepared in a high-pressure Schlenk tube from (*S*)-**4** (0.86 g, 4.78 mmol) and [(η^6-naphthalene)$Cr(CO)_3$] (1.50 g, 5.68 mmol) in di-*n*-butyl ether (25 mL). After all reagents and the solvent had been mixed, a catalytic amount of thf (0.53 g, 7.35 mmol) was added, the reaction mixture was degassed by means of ultrasound and three freeze-pump-thaw cycles and then heated in the dark at 75 °C for 95 h. The reaction mixture was then filtered through a short pad of Celite, the solvent was distilled off on a rotary evaporator and the residue was taken up in diethyl ether and purified by flash chromatography (aluminium oxide; diethyl ether/hexane = 1:10→1:2). A yellow crystalline product was isolated after evaporation of the solvents. Crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a solution of the compound in diethyl ether at –30 °C. Yield 0.91 g (60%).

[{η^6-(*S*,*S*p)-*N*,*N*-Dimethyl-1-(2-methoxyphenyl)ethylamine}Cr(CO)$_3$] [(*S*,*S*p)-28]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.38 (d, *J* = 6.8 Hz, 3 H, α-Me), 2.37 (s, 6 H, N*Me*$_2$), 3.35 (q, *J* = 6.8 Hz, 1 H, α-C*H*), 3.74 (s, 3 H, O*Me*), 4.89 (t, *J* = 6.3 Hz, 1 H, H_{Ar}), 5.00 (d, *J* = 6.6 Hz, 1 H, H_{Ar}), 5.50 (t, *J* = 6.6 Hz, 1 H, H_{Ar}), 5.84 (d, *J* = 6.6 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.84 (α-Me), 43.46 (N*Me*$_2$), 55.61 (O*Me*), 60.60 (α-*C*H), 73.88 (C_{Ar}), 84.83 (C_{Ar}), 94.17 (C_{Ar}), 96.56 (C_{Ar}), 105.39 ($C_{Ar,ipso}$), 141.39 ($C_{Ar,ipso}$), 233.41 (*C*O) ppm. IR (hexane): ν_{CO} = 1972, 1903. ^{1}H NMR (200 MHz, C_6D_6): δ = 1.12 (d, *J* = 6.6 Hz, 3 H, α-Me), 2.23 (s, 6 H, N*Me*$_2$), 2.93 (s, 3 H, O*Me*), 3.37 (q, *J* = 6.8 Hz, 1 H, α-C*H*), 4.01 (d, *J* = 6.3 Hz, 1 H, H_{Ar}), 4.15 (t, *J* = 6.1 Hz, 1 H, H_{Ar}), 4.64 (t, *J* = 6.3 Hz, 1 H, H_{Ar}), 5.62 (d, *J* = 6.3 Hz, 1 H, H_{Ar}) ppm.

[{η^6-(*S*,*R*p)-*N*,*N*-Dimethyl-1-(2-methoxyphenyl)ethylamine}Cr(CO)$_3$] [(*S*,*R*p)-28]: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (d, *J* = 7.1 Hz, 3 H, α-Me), 2.24 (s, 6 H, N*Me*$_2$), 3.74 (s, 3 H, O*Me*), 4.00 (q, *J* = 7.1 Hz, 1 H, α-C*H*), 4.90 (t, *J* = 6.1 Hz, H_{Ar}), 5.66 (d, *J* = 6.1 Hz, 1 H, H_{Ar}), 5.52 (t, *J* = 6.3 Hz, 1 H, H_{Ar}), 4.98 (d, *J* = 6.6 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.10 (α-Me), 41.16 (N*Me*$_2$), 54.35 (O*Me*), 55.93 (α-*C*H), 73.12 (C_{Ar}), 84.36 (C_{Ar}), 94.46 (C_{Ar}), 94.61 (C_{Ar}), 102.65 ($C_{Ar,ipso}$), 142.29 ($C_{Ar,ipso}$), 233.12 (*C*O) ppm. IR (hexane): ν_{CO} = 1973, 1903 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ = 1.22 (d, *J* = 6.8 Hz, 3 H, α-Me), 1.95 (s, 6 H, N*Me*$_2$), 2.93 (s, 3 H, O*Me*), 3.86 (q, *J* = 7.1 Hz, 1 H, α-C*H*), 3.99 (d, *J* = 6.6 Hz, 1 H, H_{Ar}), 4.08 (t, *J* = 6.3 Hz, H_{Ar}), 4.68 (t, *J* = 6.1 Hz, 1 H, H_{Ar}), 5.19 (d, *J* = 6.1 Hz, 1 H, H_{Ar}) ppm.

(*S*)-*N*,*N*-Dimethyl-1-[2-methoxy-3-(trimethylsilyl)phenyl]ethylamine [(*S*)-29]: (*S*)-**4** (5 g, 27.93 mmol, 1 equiv.) was dissolved in diethyl ether (200 mL) and the solution cooled to –50 °C. *t*BuLi (1.7 M in pentane; 19.00 mL, 32.30 mmol, 1.15 equiv.) was added dropwise and the reaction mixture stirred at –50 °C for 24 h. After addition of chlorotrimethylsilane (15.17 g, 139.65 mmol, 5 equiv.), the resulting mixture was warmed to room temperature, stirred at that temperature for 80 h and then filtered through a short pad of Celite in order to remove LiCl. The solvent and excess $ClSiMe_3$ were distilled off on a rotary evaporator and the crude product was purified by column chromatography (aluminium oxide; diethyl ether/hexane, 1:1) to afford (*S*)-**29** as a light yellow oil. Yield 6.89 g (98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.41 (s, 9 H, Si*Me*$_3$), 1.47 (d, *J* = 6.7 Hz, 3 H, α-Me), 2.30 (s, 6 H, N*Me*$_2$), 3.75 (q, *J* = 6.7 Hz, 1 H, α-C*H*), 3.85 (s, 3 H, O*Me*), 6.23 (t, *J* = 7.3 Hz, 1 H, H_{Ar}), 7.42 (d, *J* = 7.3 Hz, 1 H, H_{Ar}), 7.59 (d, *J* = 7.6 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.03 (Si*Me*$_3$), 20.91 (α-Me), 43.43 (N*Me*$_2$), 57.95 (O*Me*), 62.79 (α-*C*H), 124.16 (C_{Ar}), 129.58 (C_{Ar}), 132.52 ($C_{Ar,ipso}$), 133.84 (C_{Ar}), 136.90 ($C_{Ar,ipso}$), 163.14 ($C_{Ar,ipso}$) ppm.

Preparation of [{η^6-(*S*)-*N*,*N*-Dimethyl-1-[2-methoxy-3-(trimethylsilyl)phenyl]ethylamine}Cr(CO)$_3$] [(*S*,*S*p)-30 and (*S*,*R*p)-30]. Thermolysis with Cr(CO)$_6$: Reaction of (*S*)-**29** (2.80 g, 11.00 mmol) and $Cr(CO)_6$ (3.00 g, 14.00 mmol) in an 8:1 mixture of di-*n*-butyl ether and thf (40.5 mL) for 48 h according to general procedure B afforded (*S*,*R*p)-**30** and (*S*,*S*p)-**30** in an 87.5:12.5 ratio (Scheme 9). The two diastereomers were collected as a single fraction after flash chromatography (aluminium oxide; diethyl ether). Yield 3.03 g (79%). Crystals of (*S*,*R*p)-**30** suitable for X-ray analysis were grown by slow diffusion of hexane into a solution of this fraction in diethyl ether.

Arene Exchange with [(η^6-Naphthalene)Cr(CO)$_3$]: (*S*,*S*p)-**30** was prepared in a high-pressure Schlenk tube from (*S*)-**29** (1.20 g, 4.78 mmol) and [(η^6-naphthalene)$Cr(CO)_3$] (1.50 g, 5.68 mmol) in di-*n*-butyl ether (25 mL). After all reagents and the solvent had been mixed, a catalytic amount of thf (0.53 g, 7.35 mmol) was added, the reaction mixture was degassed by means of ultrasound and three freeze-pump-thaw cycles and then heated in the dark at 75 °C for 78 h. The reaction mixture was filtered through a short pad of Celite, the solvent was distilled off on a rotary evaporator and the residue was taken up in diethyl ether and purified by flash chromatography (aluminium oxide; diethyl ether/hexane, 3:1). After evaporation of the solvents, the product was obtained as a yellow-orange powder in a mixture with unreacted [(η^6-naphthalene)-$Cr(CO)_3$]. The desired product was isolated in high purity after a second chromatographic purification (silica gel; diethyl ether/hexane, 1:7). Yield yellow crystals (1.30 g, 70%).

[{η^6-(*S*,*S*p)-*N*,*N*-Dimethyl-1-[2-methoxy-3-(trimethylsilyl)phenyl]-ethylamine}Cr(CO)$_3$] [(*S*,*S*p)-30]: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.35 (s, 9 H, Si*Me*$_3$), 1.43 (d, *J* = 6.3 Hz, 3 H, α-Me), 2.34 (s, 6 H, N*Me*$_2$), 3.06 (q, *J* = 6.3 Hz, 1 H, α-C*H*), 3.89 (s, 3 H, O*Me*), 4.83 (t, *J* = 7.1 Hz, 1 H, H_{Ar}), 5.44 (d, *J* = 5.9 Hz, 1 H, H_{Ar}), 5.79 (d, *J* = 6.6 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.31 (Si*Me*$_3$), 21.31 (α-Me), 44.06 (N*Me*$_2$), 62.07 (O*Me*), 64.11 (α-*C*H), 86.39 (C_{Ar}), 94.13 ($C_{Ar,ipso}$), 97.96 (C_{Ar}), 100.57 (C_{Ar}), 109.75 ($C_{Ar,ipso}$), 146.36 ($C_{Ar,ipso}$), 233.42 (*C*O) ppm. IR (hexane): ν_{CO} = 1975, 1906 cm^{-1}.

[{η^6-(*S*,*R*p)-*N*,*N*-Dimethyl-1-[2-methoxy-3-(trimethylsilyl)phenyl]-ethylamine}Cr(CO)$_3$] [(*S*,*R*p)-30]: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.48 (s, 9 H, Si*Me*$_3$), 1.40 (d, *J* = 6.0 Hz, 3 H, α-Me), 2.36 (s, 6 H, N*Me*$_2$), 3.93 (q, *J* = 6.8 Hz, 1 H, α-C*H*), 4.00 (s, 3 H, O*Me*), 4.97 (t, *J* = 6.0 Hz, 1 H, H_{Ar}), 5.58 (d, *J* = 5.8 Hz, 1 H, H_{Ar}), 5.88 (d, *J* = 6.0 Hz, 1 H, H_{Ar}) ppm. The X-ray structure is shown in Figure 6.

(*S*)-*N*,*N*-Dimethyl-1-[2-methoxy-3,6-bis(trimethylsilyl)phenyl]ethylamine [(*S*)-31]: This complex was prepared by deprotonation of (*S*)-**29** (4.00 g, 15.94 mmol, 1 equiv.) with *t*BuLi (1.7 M in pentane; 10.70 mL, 18.17 mmol, 1.14 equiv.) for 24 h at –50 °C in diethyl ether (150 mL) and then treatment of the lithiated species with chlorotrimethylsilane (8.65 g, 79.70 mmol, 5 equiv.). The reaction mixture was warmed up to room temperature overnight and then filtered through short pad of Celite in order to remove LiCl. The solvent and the excess of $ClSiMe_3$ were distilled off on a rotary evaporator and the crude product was purified by column chromatography (aluminium oxide; diethyl ether/hexane, 1:1). Yield light yellow oil (4.62 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.34 (s, 9 H, SiMe_3), 0.35 (s, 9 H, SiMe_3), 1.47 (d, J = 7.0 Hz, 3 H, α-Me), 2.20 (s, 6 H, NMe_2), 3.61 (q, J = 7.0 Hz, 1 H, α-CH), 3.80 (s, 3 H, OMe), 7.35 (d, J = 7.3 Hz, 1 H, H_{Ar}), 7.42 (d, J = 7.3 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.24 (SiMe_3), 2.72 (SiMe_3), 21.23 (α-Me), 45.03 (NMe_2), 62.81 (OMe), 62.97 (α-CH), 131.83 (C_{Ar}), 133.60 (C_{Ar}), 134.37 ($C_{Ar,ipso}$), 141.44 ($C_{Ar,ipso}$), 144.72 ($C_{Ar,ipso}$), 163.60 ($C_{Ar,ipso}$) ppm.

Preparation of [{η^6-(*S*,*R*p)-*N*,*N*-Dimethyl-1-[2-methoxy-3,6-bis(trimethylsilyl)phenyl]ethylamine}Cr(CO)$_3$] [(*S*,*R*p)-32]. Thermolysis with Cr(CO)$_6$: Treatment of (*S*)-**31** (2.50 g, 7.74 mmol) with $Cr(CO)_6$ (2.21 g, 10.00 mmol) in an 8:1 mixture of di-*n*-butyl ether and thf (40.5 mL) for 45 h according to general procedure B afforded (*S*,*R*p)-**32** in 94% diastereomeric purity (NMR; Scheme 10). The crude product was purified by column chromatography (aluminium oxide; diethyl ether/hexane, 1:1). Yield 2.90 g (82%).

Arene Exchange with [(η^6-Naphthalene)Cr(CO)$_3$]: (*S*,*R*p)-**32** was prepared in a high-pressure Schlenk tube from (*S*)-**31** (1.51 g, 4.68 mmol) and [(η^6-naphthalene)$Cr(CO)_3$] (1.50 g, 5.68 mmol) in di-*n*-butyl ether (25 mL). After all reagents and the solvent had been mixed, a catalytic amount of thf (0.53 g, 7.35 mmol) was added, the reaction mixture was degassed by means of ultrasound and three freeze-pump-thaw cycles and then heated in the dark at 75 °C for 140 h. The reaction mixture was filtered through a short pad of Celite and the solvent distilled off on a rotary evaporator to afford (*S*,*R*p)-**31** in >99% *de* (NMR). The crude product was purified by flash chromatography (aluminium oxide; diethyl ether/hexane, 1:7) to yield 1.14 g of yellow crystals (53%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.37 (s, 9 H, SiMe_3), 0.42 (s, 9 H, SiMe_3), 1.44 (d, J = 7.0 Hz, 3 H, α-Me), 2.16 (s, 6 H, NMe_2), 3.13 (q, J = 7.0 Hz, 1 H, α-CH), 3.74 (s, 3 H, OMe), 4.84 (d, J = 6.4 Hz, 1 H, H_{Ar}), 5.51 (d, J = 6.1 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.40 (SiMe_3), 2.38 (SiMe_3), 25.07 (α-Me), 45.35 (NMe_2), 59.66 (OMe), 62.67 (α-CH), 91.28 ($C_{Ar,ipso}$), 93.32 (C_{Ar}), 103.03 (C_{Ar}), 105.12 ($C_{Ar,ipso}$), 118.63 ($C_{Ar,ipso}$), 146.41 ($C_{Ar,ipso}$), 233.60 ($C_{Ar,ipso}$) ppm. IR (hexane): ν_{CO} = 1970, 1900 cm^{-1}.

Preparation of [{η^6-(*S*,*R*p)-*N*,*N*-Dimethyl-1-(2-methoxyphenyl)ethylamine}Cr(CO)$_3$] [(*S*,*R*p)-28]: (*S*,*R*p)-**31** (1.61 g, 3.51 mmol) was dissolved in thf (30 mL) and the solution cooled to 0 °C. Tetra-*n*-butylammonium fluoride (1 M in thf; 9.00 mL, 9.00 mmol) was added dropwise and the solution stirred at 0 °C for 4 h (Scheme 10). After addition of distilled water the reaction mixture was extracted several times with diethyl ether. The combined organic phases were concentrated on a rotary evaporator and the residue was purified by column chromatography (aluminium oxide; diethyl ether) to afford (*S*,*R*p)-**28** in diastereomerically pure form as yellow crystals. Yield 0.62 g (56%).

(*S*)-*N*,*N*-Dimethyl-1-[2-(diphenylphosphanyl)-3-methoxyphenyl]-ethylamine [(*S*)-33]: This complex was prepared by deprotonating (*S*)-**5** (1.00 g, 5.58 mmol, 1 equiv.) with *t*BuLi (1.7 M in pentane; 3.75 mL, 6.37 mmol, 1.14 equiv.) for 24 h at –50 °C in diethyl ether (100 mL) and then treating the lithiated species with chlorodiphenylphosphane (1.4 g, 6.37 mmol, 1.14 equiv.). The reaction mixture was warmed to room temperature overnight and then filtered through a short pad of Celite in order to remove LiCl. The solvent was distilled off on a rotary evaporator and the crude product purified by column chromatography (silica gel; diethyl ether/hexane, 1:1). Yield white crystals (1.25 g, 89%). Crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a solution of the compound in diethyl ether at –30 °C (diethyl ether/hexane, 1:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.25 (d, J = 6.4 Hz, 3 H, α-Me), 2.10 (s, 6 H, NMe_2), 3.11 (s, 3 H, OMe), 4.62 (m, J = 6.4, J = 2.4 Hz, 1 H, α-CH), 6.59 (dd, J = 8.2, J = 1.2 Hz, 1 H, H_{Ar}), 7.10–7.34 (m, 12 H, $10H_{PPh_2}$ + $2H_{Ar}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.72 (α-Me), 42.98 (NMe_2), 54.64 (OMe), 62.48 (d, $J_{C,P}$ = 31.8 Hz, α-CH), 110.25 (C_{Ar}), 119.35 (d, $J_{C,P}$ = 7.1 Hz, C_{Ar}), 122.54 (d, $J_{C,P}$ = 20.3 Hz, $C_{Ar,ipso}$), 127.01 (C_{PPh_2}), 127.15 (C_{PPh_2}), 127.54 (C_{PPh_2}), 127.60 (C_{PPh_2}), 127.62 (C_{PPh_2}), 127.65 (C_{PPh_2}), 131.62 (C_{Ar}), 131.64 (C_{PPh_2}), 131.90 (C_{PPh_2}), 132.06 (C_{PPh_2}), 132.22 (C_{PPh_2}), 137.44 (d, $J_{C,P}$ = 9.3 Hz, C_{PPh_2}), 138.35 (d, $J_{C,P}$ = 11.0 Hz, C_{PPh_2}), 154.45 (d, $J_{C,P}$ = 24.7 Hz, $C_{Ar,ipso}$), 161.80 (d, $J_{C,P}$ = 3.3 Hz, $C_{Ar,ipso}$) ppm. ^{31}P NMR (81 MHz, $CDCl_3$): δ = –23.98 ppm.

(*S*)-*N*,*N*-Dimethyl-1-[3-methoxy-2-(trimethylsilyl)phenyl]ethylamine [(*S*)-34]: This complex was prepared by deprotonation of (*S*)-**5** (5.00 g, 27.93 mmol, 1 equiv.) with *t*BuLi (1.7 M in pentane; 19.00 mL, 32.30 mmol, 1.14 equiv.) for 24 h at –50 °C in diethyl ether (200 mL) and then treatment of the lithiated species with chlorotrimethylsilane (15.17 g, 139.65 mmol, 5 equiv.). The reaction mixture was warmed to room temperature, stirred at that temperature for 10 d and then filtered through a short pad of Celite in order to remove LiCl. The solvent and excess $ClSiMe_3$ were distilled off on a rotary evaporator and the crude product was purified by column chromatography (aluminium oxide; diethyl ether/hexane, 1:1). Yield light yellow oil (6.16 g, 88%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.35 (s, 9 H, SiMe_3), 1.29 (d, J = 6.4 Hz, 3 H, α-Me), 2.19 (s, 6 H, NMe_2), 3.49 (q, J = 6.4 Hz, 1 H, α-CH), 3.75 (s, 3 H, OMe), 6.69 (d, J = 7.3 Hz, 1 H, H_{Ar}), 7.17–7.35 (m, 2 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.12 (SiMe_3), 22.91 (α-Me), 44.16 (NMe_2), 54.87 (OMe), 63.85 (α-CH), 107.95 (C_{Ar}), 119.24 (C_{Ar}), 125.56 ($C_{Ar,ipso}$), 130.50 (C_{Ar}), 153.91 ($C_{Ar,ipso}$), 164.46 ($C_{Ar,ipso}$) ppm. $[\alpha]_D^{r.t.}$ = –80.36 (c = 0.21, $CHCl_3$).

[{η^6-(*S*,*R*p)-*N*,*N*-Dimethyl-1-[3-methoxy-2-(trimethylsilyl)phenyl]-ethylamine}Cr(CO)$_3$] [(*S*,*R*p)-35]: This complex was prepared in a high-pressure Schlenk tube from (*S*)-**34** (2.03 g, 8.10 mmol) and [(η^6-naphthalene)$Cr(CO)_3$] (2.56 g, 9.70 mmol) in di-*n*-butyl ether (40 mL). After all reagents and the solvent had been mixed, a catalytic amount of thf (0.9 g, 10.88 mmol) was added, the reaction mixture was degassed by means of ultrasound and three freeze-pump-thaw cycles and then heated in the dark at 75 °C for 72 h. The reaction mixture was then filtered through a short pad of Celite and the solvent was distilled off on a rotary evaporator to give the desired product in 86% *de* (NMR). The crude product was taken up in diethyl ether and purified by flash chromatography (aluminium oxide; diethyl ether/hexane, 3:1). A yellow-orange powder contaminated with unreacted [(η^6-naphthalene)$Cr(CO)_3$] was obtained after evaporation of the solvents. The product was isolated in high purity (*de* > 98%) after a second chromatographic purification (silica gel; diethyl ether/hexane, 1:7). Yield 2.24 g (71%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.45 (s, 9 H, SiMe_3), 11.01 (d, J = 6.8 Hz, 3 H, α-Me), 2.22 (s, 6 H, NMe_2), 3.00 (s, 3 H, OMe), 3.53 (q, J = 7.2 Hz, 1 H, α-CH), 4.15 (d, J = 6.8 Hz, 1 H, H_{Ar}), 5.07 (t, J = 6.8 Hz, 1 H, H_{Ar}), 5.33 (d, J = 6.4 Hz, 1 H, H_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 2.98 (SiMe_3), 23.21

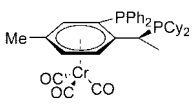
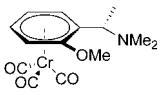
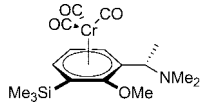
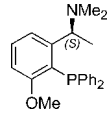
(α-Me), 44.02 (N*Me*$_2$), 54.93 (O*Me*), 60.54 (α-*C*H), 75.05 (C_{Ar}), 85.51 (C_{Ar}), 93.94 (C_{Ar}), 100.00 ($C_{Ar,ipso}$), 115.40 ($C_{Ar,ipso}$), 147.25 ($C_{Ar,ipso}$), 234.74 (*C*O) ppm. IR (hexane): ν_{CO} = 1965, 1895 cm^{-1}.

[{η^6-(*S*,*S*p)-*N*,*N*-Dimethyl-1-(3-methoxyphenyl)ethylamine}Cr(CO)$_3$] [(*S*,*S*p)-36]: (*S*,*R*p)-**35** (2.03 g, 5.23 mmol) was dissolved in thf (18 mL) and the solution cooled to 0 °C. Tetra-*n*-butylammonium fluoride (1 M in thf, 6.38 mL, 6.38 mmol) was added dropwise and the solution was stirred at 0 °C for 4 h. After addition of distilled water the reaction mixture was extracted several times with diethyl ether. The combined organic phases were concentrated on a rotary evaporator and the residue was purified by column chromatography (silica gel; diethyl ether/acetone) to afford (*S*,*S*p)-**36** as yellow crystals. Yield 1.41 g (85%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.8 Hz, 3 H, α-Me), 1.89 (s, 6 H, N*Me*$_2$), 3.02 (s, 3 H, O*Me*), 3.39 (q, *J* = 6.8 Hz, 1 H, α-C*H*), 4.25 (d, *J* = 6.6 Hz, H_{Ar}), 4.52 (d, *J* = 6.3 Hz, 1 H, H_{Ar}), 4.80 (t, *J* = 6.6 Hz, 1 H, H_{Ar}), 4.95 (s, 1 H, H_{Ar}) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 10.49 (α-Me), 40.58 (N*Me*$_2$), 55.65 (O*Me*), 61.20 (α-*C*H), 75.78 (C_{Ar}), 79.26 (C_{Ar}), 88.48 (C_{Ar}), 93.98 (C_{Ar}), 114.42 ($C_{Ar,ipso}$), 142.53 ($C_{Ar,ipso}$), 233.06 (*C*O) ppm. IR (hexane): ν_{CO} = 1970, 1900 cm^{-1}.

[{η^6-(*S*,*S*p)-*N*,*N*-Dimethyl-1-[2-(diphenylphosphanyl)-6-methoxyphenyl]ethylamine}Cr(CO)$_3$] [(*S*,*S*p)-37]: This complex was prepared according to general procedure C by lithiation of (*S*,*S*p)-**28** (0.45 g, 1.43 mmol) with *tert*-butyllithium (1.7 M in pentane; 0.96 mL, 1.63 mmol) and treatment of the lithiated species with chlorodiphenylphosphane (0.36 g, 1.63 mmol) in dry diethyl ether (25 mL). The crude product was purified by column chromatography (aluminium oxide; diethyl ether/hexane, 2:1). Yield yellow crystals (0.38 g, 54%). Crystals suitable for X-ray analysis were grown by means of slow diffusion of hexane into a solution of the compound in diethyl ether at –30 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (d, *J* = 6.7 Hz, 3 H, α-Me), 1.76 (s, 6 H, N*Me*$_2$), 3.72 (s, 3 H, O*Me*), 4.47 (d, *J* = 5.2 Hz, 1 H, H_{Ar}), 4.55 (dq, *J* = 6.7, *J* = 2.4 Hz, 1 H, α-C*H*), 5.25–5.29 (m, 2 H, H_{Ar}), 7.20–7.33 (m, 10 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.74 (α-Me), 38.90 (N*Me*$_2$), 56.01 (O*Me*), 60.17 (d, $J_{C,P}$ = 19.2 Hz, α-*C*H), 77.54 (C_{Ar}), 90.74 (C_{Ar}), 94.18 (d, $J_{C,P}$ = 1.9 Hz, C_{Ar}), 107.83 (d, $J_{C,P}$ = 18.2 Hz, $C_{Ar,ipso}$), 110.54 (d, $J_{C,P}$ = 24.0 Hz, $C_{Ar,ipso}$), 127.74–134.83 (10 C, C_{PPh_2}), 136.56 (d, $J_{C,P}$ = 17.3 Hz, C_{PPh_2}), 137.58 (d, $J_{C,P}$ = 5.6 Hz, C_{PPh_2}), 140.52 (d, $J_{C,P}$ = 3.8 Hz $C_{Ar,ipso}$), 233.36 (*C*O) ppm. ^{31}P NMR (81 MHz, $CDCl_3$): δ = –11.22 ppm. IR (hexane): ν_{CO} = 1970, 1896 cm^{-1}. $C_{26}H_{26}CrNO_4P$: calcd. C 62.52, H 5.21, N 2.80; found 62.61, H 6.05, N 2.39.

[{η^6-(*S*,*S*p)-*N*,*N*-Dimethyl-1-[2-(diphenylphosphanyl)-5-methoxyphenyl]ethylamine}Cr(CO)$_3$] [(*S*,*S*p)-38]: This complex was prepared according to general procedure C by lithiation of (*S*,*S*p)-**36** (1.36 g, 4.30 mmol) with *tert*-butyllithium (1.7 M in pentane; 2.90 mL, 4.90 mmol) and treatment of the lithiated species with chlorodiphenylphosphane (1.80 g, 4.90 mmol) in dry diethyl ether (250 mL; see Scheme 15). The crude product was purified by column chromatography (silica gel; diethyl ether/hexane, 1:6). Yield 1.22 g (57%); yellow crystals. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82 (d, *J* = 6.7 Hz, 3 H, α-Me), 1.45 (s, 6 H, N*Me*$_2$), 3.01 (s, 3 H, O*Me*), 3.97 (d, *J* = 6.4 Hz, 1 H, H_{Ar}), 4.65 (m, 1 H, α-C*H*), 4.92 (d, *J* = 6.7 Hz, 1 H, H_{Ar}), 5.05 (s, 1 H, H_{Ar}), 7.06–7.56 (m, 10 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 5.48 (α-Me), 37.85

Table 5. Crystallographic data, data collection and structure refinement parameters for (*S*,*R*p)-**23b**, (*S*,*S*p)-**28**, (*S*,*R*p)-**30** and (*S*)-**33**.

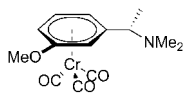
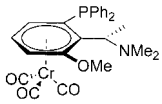
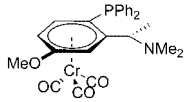
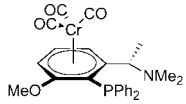
	 (*S*,*R*p)-**23b**	 (*S*,*S*p)-**28**	 (*S*,*R*p)-**30**	 (*S*)-**33**
Empirical formula	$C_{36}H_{42}Cr_1O_3P_2$	$C_{14}H_{17}CrNO_4$	$C_{17}H_{25}CrNO_4Si$	$C_{23}H_{26}NOP$
Formula mass	636.68	315.29	387.47	363.44
Crystal habit, colour	hexagonal prism, yellow	rod, yellow	rod, yellow	rod, colourless
Crystal dimensions [mm]	0.74 × 0.39 × 0.37	0.90 × 0.16 × 0.14	0.22 × 0.05 × 0.05	0.53 × 0.26 × 0.16
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	C_2	$P2_1$
a [Å]	12.7113(14)	6.612(6)	41.416(7)	9.099(12)
b [Å]	34.4771(17)	9.932(10)	6.7122(12)	12.294(16)
c [Å]	7.8497(4)	22.04(2)	22.578(4)	18.36(2)
β [°]			112.069(4)	92.79(3)
V [Å^3]	3440.1(5)	1447(2)	5816.6(18)	2051(4)
Z	4	4	12	4
D [g cm^{-3}]	1.229	1.447	1.327	1.177
F(000)	1344	656	2448	776
μ(Mo-K_α) [cm^{-1}]	0.458	0.802	0.671	0.145
Diffractometer	Enraf Nonius CAD4	Bruker Smart CCD	Bruker Smart CCD	Bruker Smart CCD
T [K]	293(2)	153(2)	110(2)	293(2)
θ range [°]	3.1–26.0	1.9–28.3	1.7–25.2	2.0–28.3
Reflections collected	9867	19784	24383	50905
Unique refl.	6725	3582	9823	8929
R_{int}	0.083	0.0283	0.0941	0.0365
Reflections observed	3278	3464	6761	7561
Parameters refined	381	185	655	477
R_1	0.0740	0.0412	0.0611	0.0407
wR_2	0.1507	0.1001	0.1337	0.1093
Flack parameter	–0.01(4)	0.03(3)	0.00(3)	–0.06(6)
GooF	0.999	1.313	1.002	1.026
Diff. peak/hole [e Å^{-3}]	0.34/–0.24	0.55/–0.29	0.40/–0.51	0.30/–0.141

(N*Me*$_2$), 55.08 (O*Me*), 58.98 (d, $J_{C,P}$ = 14.4 Hz, α-*C*H), 73.95 (C_{Ar}), 79.62 (C_{Ar}), 99.61 (C_{Ar}), 100.33 (d, $J_{C,P}$ = 24.0 Hz, $C_{Ar,ipso}$), 120.88 (d, $J_{C,P}$ = 21.1 Hz, $C_{Ar,ipso}$), 128.75 (d, $J_{C,P}$ = 5.8 Hz C_{PPh_2}), 129.18 (C_{PPh_2}), 132.31 (d, $J_{C,P}$ = 20.1 Hz, C_{PPh_2}), 135.24 (d, $J_{C,P}$ = 21.1 Hz, C_{PPh_2}), 137.62 (d, $J_{C,P}$ = 14.4 Hz, C_{PPh_2}), 139.00 (d, $J_{C,P}$ = 6.7 Hz, C_{PPh_2}), 142.94 ($C_{Ar,ipso}$), 233.01 (*C*O) ppm. ^{31}P NMR (81 MHz, $CDCl_3$): δ = –16.74 ppm. IR (hexane): ν_{CO} = 1972, 1908 cm^{-1}. $C_{26}H_{26}NO_4PCr$ (499.46): calcd. C 62.52, H 5.21, N 2.80; found C 62.78, H 5.54, N 2.89.

[{η^6-(*S*,*Sp*)-*N*,*N*-Dimethyl-1-[2-(diphenylphosphanyl)-3-methoxyphenyl]ethylamine}Cr(CO)$_3$] [(*S*,*Sp*)-40]: A 1:1 mixture of (*S*,*Sp*)-**36** and (*S*,*Rp*)-**36** (4.20 g, 13.33 mmol, 1 equiv.) was dissolved in diethyl ether (250 mL). The solution was cooled to –80 °C and *tert*-butyllithium (1.7 M in pentane; 8.94 mL, 15.20 mmol, 1.14 equiv.) was added dropwise (Scheme 16). After stirring for 4 h at –80 °C, chlorodiphenylphosphane (3.35 g, 15.20 mmol, 1.14 equiv.) was added dropwise. The reaction mixture was warmed to room temperature overnight, filtered through a short pad of celite to remove LiCl and the solvent removed in vacuo. Three compounds were detected in the NMR spectrum of the crude product: (*S*,*Sp*)-**38**, **39** and (*S*,*Sp*)-**40** in a 31:20:49 ratio. The crude product was purified by column chromatography (aluminium oxide; diethyl ether/hexane, 1:7). Only (*S*,*Sp*)-**40** was isolated and further purified by column chromatography on silica gel. Yield yellow crystals (0.64 g, 22%). Crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a solution of the complex in diethyl ether at –30 °C. ^{1}H NMR (200 MHz, C_6D_6): δ = 0.85 (d, J = 6.3 Hz, 3 H, α-Me), 1.69 (s, 6 H, N*Me*$_2$), 2.59 (s, 3 H, O*Me*), 3.87 (d, J = 7.3 Hz, 1 H, H_{Ar}), 4.20 (d, J = 7.3 Hz, 1 H, H_{Ar}), 4.83 (m, 1 H, α-C*H*), 4.97 (t, J = 7.3 Hz, 1 H, H_{Ar}), 7.07–7.31 (m, 8 H, H_{PPh_2}), 7.79 (t, J = 8.3 Hz, 2 H, H_{PPh_2}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 5.80 (α-Me), 38.03 (N*Me*$_2$), 54.51 (O*Me*), 58.88 (d, $J_{C,P}$ = 22.1 Hz, α-*C*H), 71.48 (C_{Ar}), 82.47 (C_{Ar}), 94.03 (C_{Ar}), 121.98 (d, $J_{C,P}$ = 8.6 Hz, $C_{Ar,ipso}$), 123.60 (d, $J_{C,P}$ = 25.9 Hz, $C_{Ar,ipso}$), 127.41–135.83 (10 C, C_{PPh_2}), 137.60 (d, $J_{C,P}$ = 14.2 Hz, 1 C, C_{PPh_2}), 139.90 (d, $J_{C,P}$ = 6.5 Hz, 1 C, C_{PPh_2}), 146.80 ($C_{Ar,ipso}$), 233.24 (*C*O) ppm. ^{31}P NMR (81 MHz, C_6D_6): δ = –10.70 ppm. IR (hexane): ν_{CO} = 1971, 1903 cm^{-1}.

X-ray Structure Determination: Crystal data and details of the structure determinations are listed in Tables 5 and 6. Data collection was performed with a Bruker Smart CCD (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator) fitted with an area detector for (*S*,*Sp*)-**28**, (*S*,*Rp*)-**30**, (*S*)-**33**, and (*S*,*Sp*)-**40** and an Enraf Nonius CAD4 diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator) for (*S*,*Rp*)-**23b**, (*S*,*Sp*)-**36**, (*S*,*Sp*)-**37** and (*S*,*Sp*)-**38**. The unit-cell parameters were obtained by least-squares refinement of up to 8096 reflections for the area detector and 25 reflections for the CAD4 point detector. The structures were solved by direct methods (SHELXS-97)[29] and refined by full-matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97).[29] The SADABS[30] program was used for absorption correction of the structures. All non-hydrogen atoms were refined anisotropically. All H-atoms were introduced at their idealised positions and were refined using a riding model. The absolute configuration was confirmed by evaluation of the Flack[31] parameter. Displacement ellipsoid plots were obtained with PLATON.[32]

Table 6. Crystallographic data, data collection and structure refinement parameters for (*S*,*Sp*)-**36**, (*S*,*Sp*)-**37**, (*S*,*Sp*)-**38** and (*S*,*Sp*)-**40**.

	 (*S*,*Sp*)-**36**	 (*S*,*Sp*)-**37**[a]	 (*S*,*Sp*)-**38**	 (*S*,*Sp*)-**40**
Empirical formula	$C_{14}H_{17}CrNO_4$	$C_{26}H_{26}CrNO_4P$	$C_{26}H_{26}CrNO_4P$	$C_{26}H_{26}CrNO_4P$
Formula mass	315.29	499.45	499.45	499.45
Crystal habit, colour	plate, pale yellow	rod, yellow	irregular, yellow	platelet, yellow
Crystal dimensions [mm]	0.52 × 0.35 × 0.12	0.83 × 0.20 × 0.15	0.70 × 0.60 × 0.20	0.85 × 0.28 × 0.06
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a [Å]	7.012(3)	12.0203(10)	7.8948(5)	8.2725(10)
b [Å]	8.509(4)	13.3439(10)	14.8611(17)	10.8788(13)
c [Å]	24.36(1)	15.6855(10)	42.615(5)	29.045(3)
V [Å^3]	1453.4(11)	2515.9(3)	4999.8(9)	2613.9(5)
Z	4	4	8	4
D [g cm^{-3}]	1.44	1.319	1.327	1.269
F(000)	656	1040	2080	1040
μ(Mo-K_α) [cm^{-1}]	0.798	0.549	0.053	0.0529
Diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4	Bruker Smart CCD
T [K]	223(2)	293(2)	223(2)	200(2)
θ range [°]	2.4–26.0	2.0–25.0	2.4–26.0	2.0–28.3
Reflections collected	12629	6688	14852	36050
Unique refl.	2851	3419	9801	6499
R_{int}	0.145	0.0426	0.0536	0.0614
Reflections observed	1940	2492	7770	5482
Parameters refined	185	302	655	477
R_1	0.0656	0.0416	0.0436	0.0547
wR_2	0.1459	0.0895	0.0915	0.1325
Flack parameter	0.02(5)	–0.02(3)	–0.008(17)	0.01(3)
GooF	0.954	1.034	1.065	1.066
Diff. peak/hole [e Å^{-3}]	0.73/–1.46	0.19/–0.24	0.35/–0.28	0.60/–0.36

[a] Due to a technical problem with the diffractometer the intensity data collection for the crystal of (*S*,*Sp*)-**37** had to be stopped at about 73% completion; the data are, however, sufficient to ensure a reliable assignment of the absolute configuration.

Due to a technical problem with the diffractometer the intensity data collection for the sample of (*S*,*S*p)-**37** had to be stopped at about 73% completion; the data are, however, sufficient to ensure a reliable assignment of the absolute configuration.

CCDC-648702 to -648709 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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