CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200501031

A New Approach to Enantiopure C_3-Symmetric Molecules

M. Paola Castaldi,[a] Susan E. Gibson,*[a] Matthew Rudd,[a] and Andrew J. P. White[b]

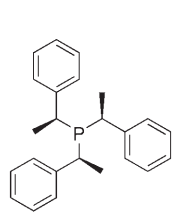
Abstract: Chiral base chemistry has been used to create three chiral centres in one pot on a C_3-symmetric substrate. The potential of this new approach to C_3-symmetric molecules is exemplified by the creation of an enantiopure C_{3v}-symmetric triol, triphosphane and tripyridine. A ruthenium complex of the last compound has been studied by X-ray crystallography.

Keywords: asymmetric synthesis · chiral bases · chromium · ruthenium · structure elucidation

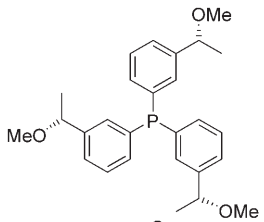
Introduction

Recent widespread interest in molecules with twofold rotational symmetry, and their successful application in several areas of chemical research, has led, quite naturally, to a significant interest in molecules with threefold rotational symmetry. Threefold symmetrical molecules are believed to have significant potential in fields as diverse as nonlinear optics, host–guest chemistry and catalysis.[1] For many of these applications, nonracemic chiral molecules are required, and the synthesis of such molecules is often nontrivial.

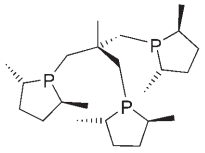
The success of the C_2-symmetric diphosphane binap [2,2′-bis(diphenylphosphino)-1,1′-binaphthalene], and the C_2-symmetric diol binol [1,1′-bi(2-naphthol)] in asymmetric catalysis has led, not surprisingly, to interest in the synthesis of C_3-symmetric phosphanes and alcohols. Monophosphanes, such as **1**[2] and **2**,[3] the tripodal triphosphanes **3**[4] and **4**,[5] and the tetradentate ligand **5**,[6] are representative of the type of phosphanes that have been synthesised and, in some cases, assayed in catalytic reactions. The catalytic activity of complexes of triol **6** has been studied in some detail,[7] whereas catalysis based on triol **7** has yet to be explored.[8] The triol **8**, built from axially chiral units, has recently been shown to form a titanium complex that gives promising yields (81–97%) and enantioselectivities (44–98%) in the alkylation of aromatic aldehydes with diethylzinc.[9] Similarly a titanium complex of the triol **9**, constructed from benzene-



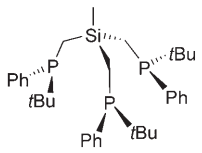
1



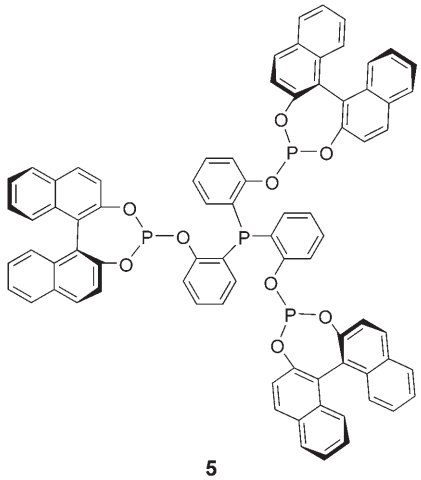
2



3



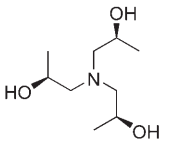
4



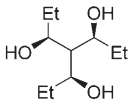
5

[a] M. P. Castaldi, Prof. S. E. Gibson, M. Rudd
Department of Chemistry, Imperial College London
South Kensington Campus, London SW7 2 AY (UK)
Fax: (+44) 207-594-5804
E-mail: s.gibson@imperial.ac.uk

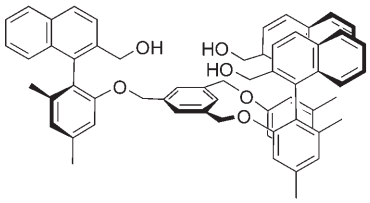
[b] Dr. A. J. P. White
Department of Chemical Crystallography
Imperial College London, South Kensington Campus
London SW7 2 AY (UK)



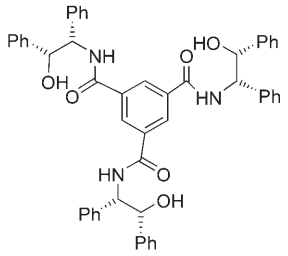
6



7



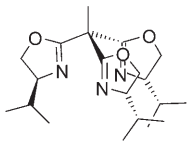
8



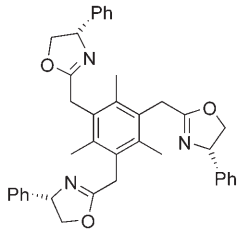
9

1,3,5-tricarboxylic acid and (−)-(1*R*,2*S*)-2-amino-1,2-diphenylethanol effects an enantioselective alkynylation of various aldehydes in the presence of diethylzinc.[10]

C_3-Symmetric tris(oxazolines) have been at the heart of several particularly interesting recent studies. For example, the tris(oxazoline) **10** binds to zinc to generate a complex that is reminiscent of the tris(histidine)zinc binding site found in many zinc-based peptidases. Indeed combining tris(oxazoline) **10** with zinc trifluoroacetate gave a catalyst that



10



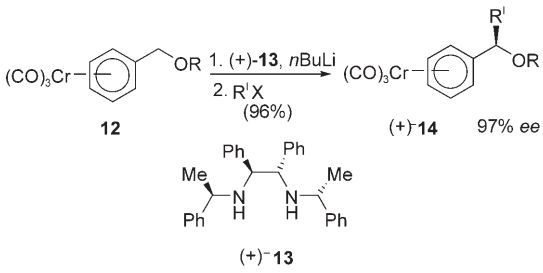
11

generated modest but significant enantioselectivities in the kinetic resolution of various phenyl ester derivatives of N-protected amino acids by transesterification with methanol.[11] Studies using the tris(oxazoline) **11** have demonstrated that it binds primary ammonium ions through tripod hydrogen-bonding and cation–π interactions. The phenyl substituents of **11** generate a C_3-symmetric "screw-sense" chiral environment that discriminates between α-chiral primary and β-chiral ammonium ions that carry a β-substituent which is a hydrogen-bond acceptor and can interact with one of the tripod hydrogen bonds to form a bifurcated hydrogen bond.[12]

Having discovered a chiral-base-mediated reaction that efficiently generates a single chiral centre,[13] we decided to determine whether or not the reaction could be used to generate three stereocentres in one pot and thus provide a new synthetic route to nonracemic, chiral C_3-symmetric molecules. Some of the results described herein have been presented in communication form.[14]

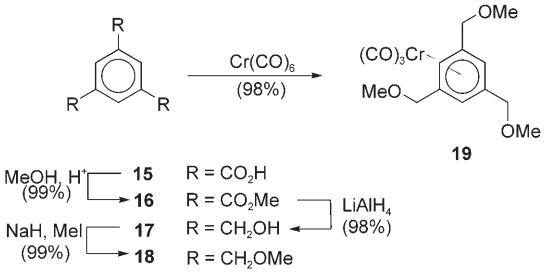
Results and Discussion

Tricarbonylchromium(0) complexes of alkyl benzyl ethers, such as **12**, react with *n*-butyllithium/chiral diamine **13** and an electrophile to give the chiral ether complexes **14** in high yield and enantiomeric excess (Scheme 1).[13] Working with the (+)-*R*,*S*,*S*,*R* enantiomer of the diamine,[15] derived from (*R*)-α-methylbenzylamine, gives the *R* configuration at the new stereocentre, presumably because of the preference of the base to abstract the pro-*R* benzylic proton.



Scheme 1.

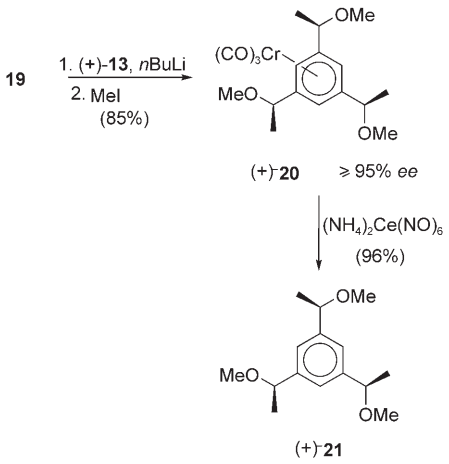
In order to determine whether or not this reaction could be used to create three chiral centres in a C_3-symmetric arrangement, the novel complex, tricarbonyl(1,3,5-trimethoxymethylbenzene)chromium(0) **19**, was required. Esterification of commercially available benzene-1,3,5-tricarboxylic acid (**15**) with methanol gave the known triester **16**[16a] in excellent yield (Scheme 2). Modification of the workup of a literature procedure[16b] for the reduction of **16** with lithium



Scheme 2.

aluminiumhydride gave triol **17**, which on treatment with four equivalents of sodium hydride followed by a slight excess of iodomethane smoothly gave the triether **18**.[17] Heating **18** with a slight excess of hexacarbonylchromium(0) in a 10:1 nBu_2O/THF for 24 h gave the required tricarbonylchromium(0) complex **19** as an air-stable yellow crystalline solid in 99% yield.

To deprotonate complex **19**, diamine (+)-**13** was treated with *n*-butyllithium, and complex **19** was added to the resulting deep red solution of the diamide. After stirring the now orange solution at −78°C, iodomethane was added which led to a colour change of the solution to yellow. After considerable experimentation, which included varying the relative amounts of complex **19**, diamine (+)-**13** and *n*-butyllithium, and a study of the effect of dilution on the product distribution, it proved possible to identify conditions (**19**/(+)-**13**/*n*-butyl lithium = 1:3:6) that minimised the production of mono- and dimethylated products and gave the trimethylated derivative **20** in an isolated yield of 85% (Scheme 3).



Scheme 3.

An X-ray crystallographic analysis of the yellow crystals (Figure 1a) confirmed that (+)-**20** was the *R*,*R*,*R* stereoisomer. The orientation of the tricarbonylchromium(0) "tripod" with respect to the trisubstituted aryl ring is such that the carbonyl groups are staggered with respect to the CH(Me)OMe substituents. Interestingly each of the CH(Me)OMe substituents has adopted an orientation that places the methoxy moiety "below" the aryl ring plane and it is also noticeable that the methoxy carbon atom is in each case oriented in a similar fashion, even though there is free rotation about its bond to oxygen. Each of the CH(Me)OMe substituents is oriented similarly with respect to the central aryl ring, the Ar-C-H dihedral angles being approximately 25, 19 and 18° for the three substituents. Overall these conformations mean that the structure has approximate C_3 symmetry, giving the molecule a propeller-like conformation (Figure 1b).

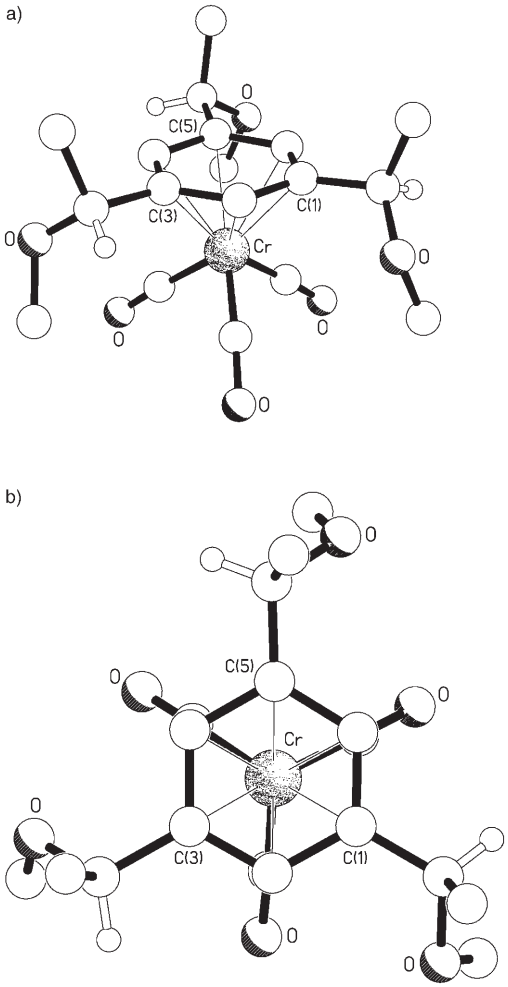


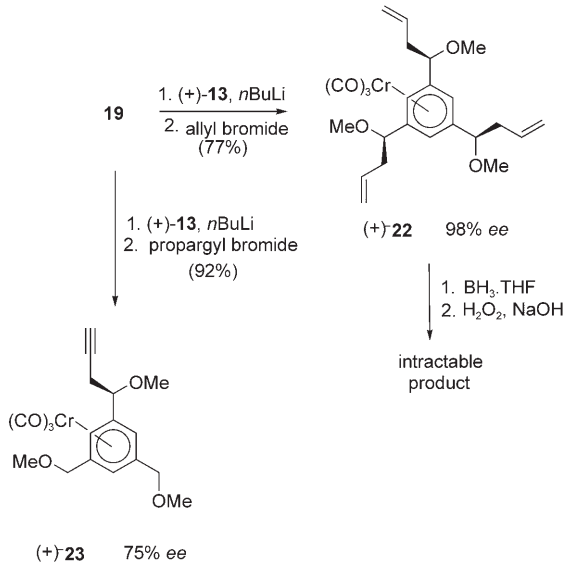
Figure 1. View of the X-ray crystallographic structure of (+)-**20** depicting a) the molecular structure of the trimethylated complex, b) the C_3-symmetric nature of the complex.

To assess the enantiomeric purity of (+)-**20**, its enantiomer (−)-**20** was synthesised using the enantiomer of the diamine derived from (*S*)-α-methylbenzylamine, that is, (−)-**13**. HPLC analysis of the two enantiomers revealed that the *ee* of (+)- and (−)-**20** was 95%.

The tricarbonylchromium(0) unit was subsequently removed from (+)-**20**. Stirring (+)-**20** in methanol in the presence of two equivalents of ceric ammonium nitrate at room temperature for 15 min resulted in a 96% yield of analytically pure C_3-symmetric triether (+)-**21** (Scheme 3). As there was no evidence for epimerisation and diastereoisomer generation during this step, as judged by high-field NMR spectroscopy, it was reasonably assumed that inversion of stereochemistry at all three centres had not occurred and that the enantiopurity of (+)-**20** was uncompromised by the decomplexation step.

Having established that three chiral centres may be installed in one pot using the model electrophile iodomethane, we started to consider the introduction of functional groups that could be used directly or indirectly to bind to metals.

We looked first at allyl bromide and propargyl bromide with a view to using a hydroboration/oxidation sequence to generate a triol with the former, and to using click chemistry[18] with the latter to generate heterocyclic donors in the form of 1,2,3-triazoles. Reaction of the triether complex **19** with the chiral diamine (+)-**13**/*n*BuLi followed by quenching with allyl bromide indeed created three chiral centres to produce (+)-**22** in 77% yield and 98% ee (Scheme 4). In

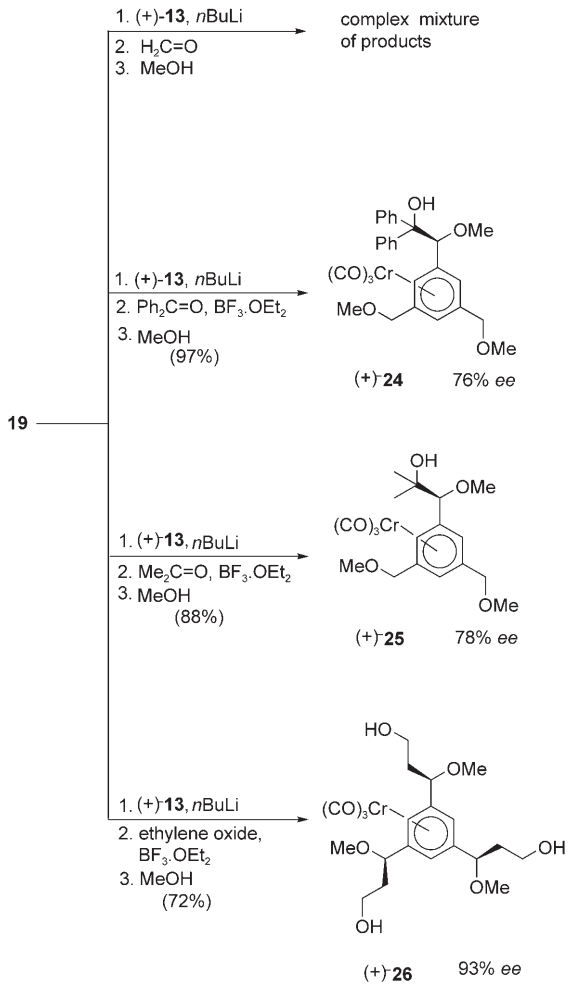


Scheme 4.

contrast, addition of propargyl bromide resulted in the creation of just one chiral centre and the production of the monoalkyne (+)-**23** in modest enantiopurity (75% ee). Disappointingly, all efforts to date to generate a triol from the trialkene (+)-**22** through hydroboration/oxidation generated intractable mixtures.

In view of the range of potential uses of C_3-symmetric triols, a second approach to these compounds was investigated. This initially involved quenching the reaction mixture with the aldehyde methanal, and the ketones benzophenone and propanone (Scheme 5). Whilst methanal delivered a complex mixture of products, the ketone quenches led to the isolation of monoalcohols (+)-**24** and (+)-**25** in high yields but modest enantiopurity (76 and 78% respectively). In contrast to the results obtained with benzophenone and propanone, quenching with ethylene oxide led to the generation and isolation of triol (+)-**26** in good yield (72%) and acceptable enantiomeric excess (93%). It is anticipated that this triol will not only be interesting to study as a C_3-symmetric ligand for transition metals, but will also act as a gateway to many other C_3-symmetric molecules (e.g. esters, aldehydes, imines).

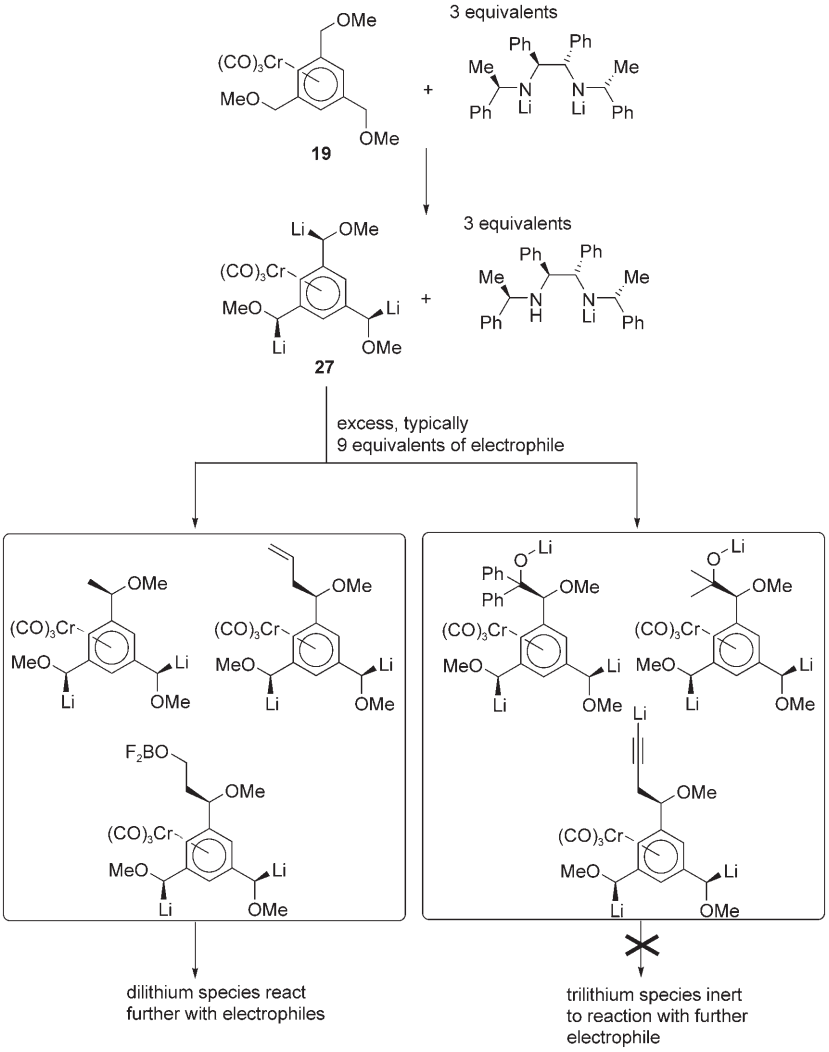
The production of mono- and triadducts in the reactions described above may be explained as follows. In a typical reaction six equivalents of *n*-butyllithium are reacted with three equivalents of diamine (+)-**13** to generate three equiv-



Scheme 5.

alents of dilithium amide and six equivalents of butane. Addition of triether complex **19** could then lead either to the formation of a monoanion followed by a sequential quench, deprotonation, quench, deprotonation, quench sequence or to the formation of a trianion followed by sequential quenching of the three anions. In view of the successful use of iodomethane and allyl bromide (added in excess, typically nine equivalents), that is, electrophiles that should readily react with and quench any dilithium amide present in the reaction mixture, it is tentatively proposed that deprotonation at the benzylic positions of the complex takes place before the addition of the electrophile; that is, reaction of complex **19** with three equivalents of dilithium amide produces a trianion represented here by structure **27** (Scheme 6), an almost certainly over-simplified version of the true structure.

Why does this proceed to react three times with iodomethane, allyl bromide and ethylene oxide but just once with benzophenone, acetone and propargyl bromide? Inspection of the putative species that react further and those that do not reveal that in the former group a dilithium species can be invoked (it has been assumed that the primary



Scheme 6.

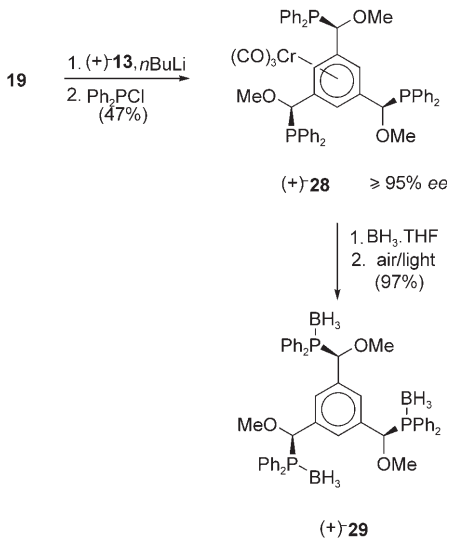
alkoxide generated from ethylene oxide reacts with the trifluoroborane present in the reaction mixture, a process that is less facile for the tertiary alkoxides formed from benzophenone and propanone), whilst in the second group a new trilithium species can be envisaged. Why the dilithium compounds proceed to react with more electrophile to generate ultimately triadducts of high enantiomeric purity, whilst the new trilithium compounds are resistant to further electrophilic attack and generate monoadducts of modest enantiopurity on work-up, is as yet unclear, but is probably a function of the properties of higher order species.

In view of the huge success enjoyed by phosphanes in transition-metal chemistry in general and asymmetric catalysis in particular, we next investigated the possibility of generating a nonracemic chiral triphosphane using the chiral-base methodology. Treatment of **19** with (+)-**13**/*n*-butyllithium followed by a chlorodiphenylphosphane quench indeed gave the yellow crystalline triphosphane (+)-**28** in acceptable yield and high enantiopurity (Scheme 7).

An X-ray crystal structure of (+)-**28** confirmed both its structure and its absolute configuration (Figure 2). The structure of (+)-**28** is similar to that of (+)-**20**, with the carbonyl groups staggered with respect to the aryl substituents, the methoxy groups oriented "below" the aryl ring plane and the methoxy groups all adopting similar conformations, with the carbon atom in each case being oriented "downwards". Each of the $CH(PPh_2)OMe$ substituents is oriented similarly with respect to the central aryl ring, the Ar-C-H dihedral angles being about 35, 39 and 40°. Overall the structure has approximate C_3-symmetry and a propeller-like conformation.

Attempts to oxidatively remove the tricarbonylchromium(0) unit and concomitantly oxidize the phosphanes to phosphane oxides led to complex mixtures of products. Treatment with $H_3B{\cdot}THF$ followed by aerial oxidation, however, gave an excellent yield of the chromium-free triphosphane protected as its triborane derivative (+)-**29**. It is anticipated that this novel phosphane will find interesting applications in asymmetric catalysis.

In a second attempt to introduce heterocyclic donor atoms onto the C_3 scaffold, we investi-



Scheme 7.

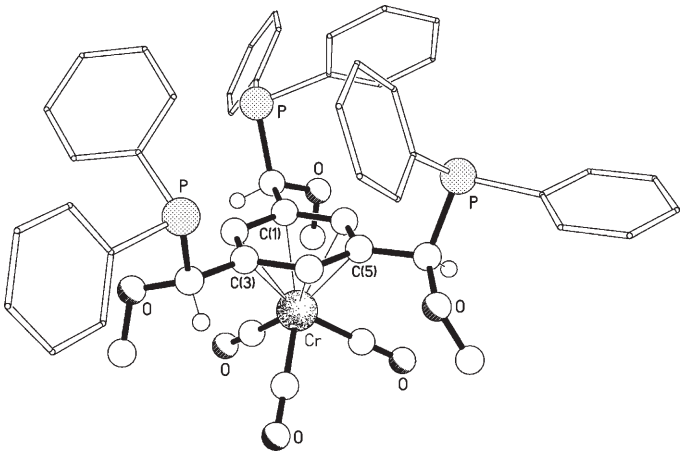
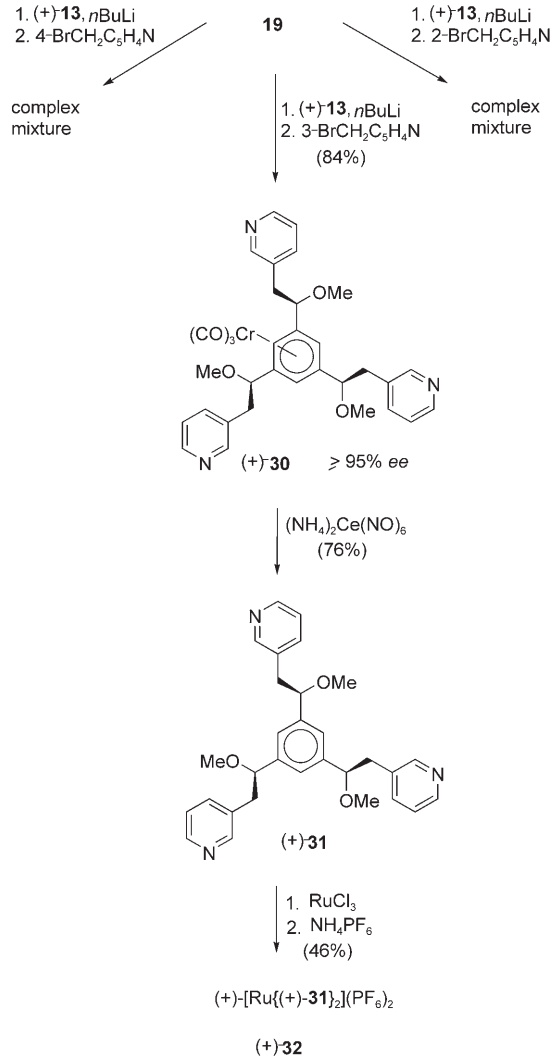


Figure 2. The molecular structure of the triphosphane (+)-**28**.

gated the effectiveness of bromomethylpyridines as electrophiles in the chiral base reaction. Although 4- and 2-bromomethylpyridine gave complex mixtures, 3-bromomethylpyridine (which is less susceptible to deprotonation) reacted smoothly to provide the tripyridine complex (+)-**30** as a yellow fluffy solid in good yield and excellent enantiomeric excess (Scheme 8). Oxidative removal of the tricarbonylchromium(0) unit by using ceric ammonium nitrate proceeded smoothly to give the chromium-free tripyridine (+)-**31** in good yield.

In a first attempt to explore the transition-metal chemistry of a C_3-symmetric compound synthesized by means of our new approach, (+)-**31** was treated with ruthenium(III) trichloride. Anion exchange with ammonium hexafluorophosphate led to yellow crystals of a complex that was identified as (+)-[Ru{(+)-**31**}$_2$](PF$_6$)$_2$, that is, complex (+)-**32**, by X-ray crystallography.

The X-ray structure of (+)-**32** (Figure 3a) shows the geometry at the ruthenium centre to be close to ideal octahedral, the *cis* N-Ru-N angles ranging between 89.15(18) and 90.59(19)° with the *trans* angles being no more that 1° away from linear; the Ru–N coordination distances are in the range 2.129(5)–2.142(5) Å. The two chiral tripyridine ligands both coordinate to the metal centre in a facial manner and it is noticeable that the *trans*-pyridyl units are nearly coplanar with each other. The coordination of each ligand is approximately threefold symmetric (Figure 3b) and these molecular C_3 axes are almost colinear, the vectors between the metal and the A and B aryl-ring centroids subtending an angle of approximately 179° at the ruthenium atom. It is evident from Figure 3a and b, however, that the two ligands do not adopt similar conformations, there being marked differences in the torsion angles about the bonds linking the chiral carbon centres to their parent C$_6$ aromatic rings. For the ligand based around ring A, the Ar-C-O torsion angles are about 11, 11 and 10°, whilst for the ring B ligands the equivalent angles are approximately 59, 57 and 56°; that is, for the ring A ligand, the oxygen atoms are approximately coplanar with the C$_6$ ring, whilst for the ring B ligand it is



Scheme 8.

the hydrogen atoms on the chiral centres that lie in the same plane as the C$_6$ ring, the oxygen atoms being oriented away from the ruthenium centre. Despite these different conformations, the Ru···A and Ru···B separations are only slightly different, being approximately 5.62 and 5.59 Å, respectively. In contrast the difference in conformations of the two ligands does affect intermolecular cation···anion interactions, each ligand being involved in a different pattern of C–H···F contacts. For the ring A ligand, each of the hydrogen atoms on the chiral carbon centres links to a PF$_6$ fluorine atom, whilst for the ring B ligand the shortest C–H···F distances are for protons on the methyl groups of the methoxy substituents on the chiral carbon centres (Figure 3c).

Conclusion

A short and versatile route to enantiopure C_3-symmetric molecules, utilizing chiral-base methodology to install three stereocentres in one pot has been devised and tested. Of the

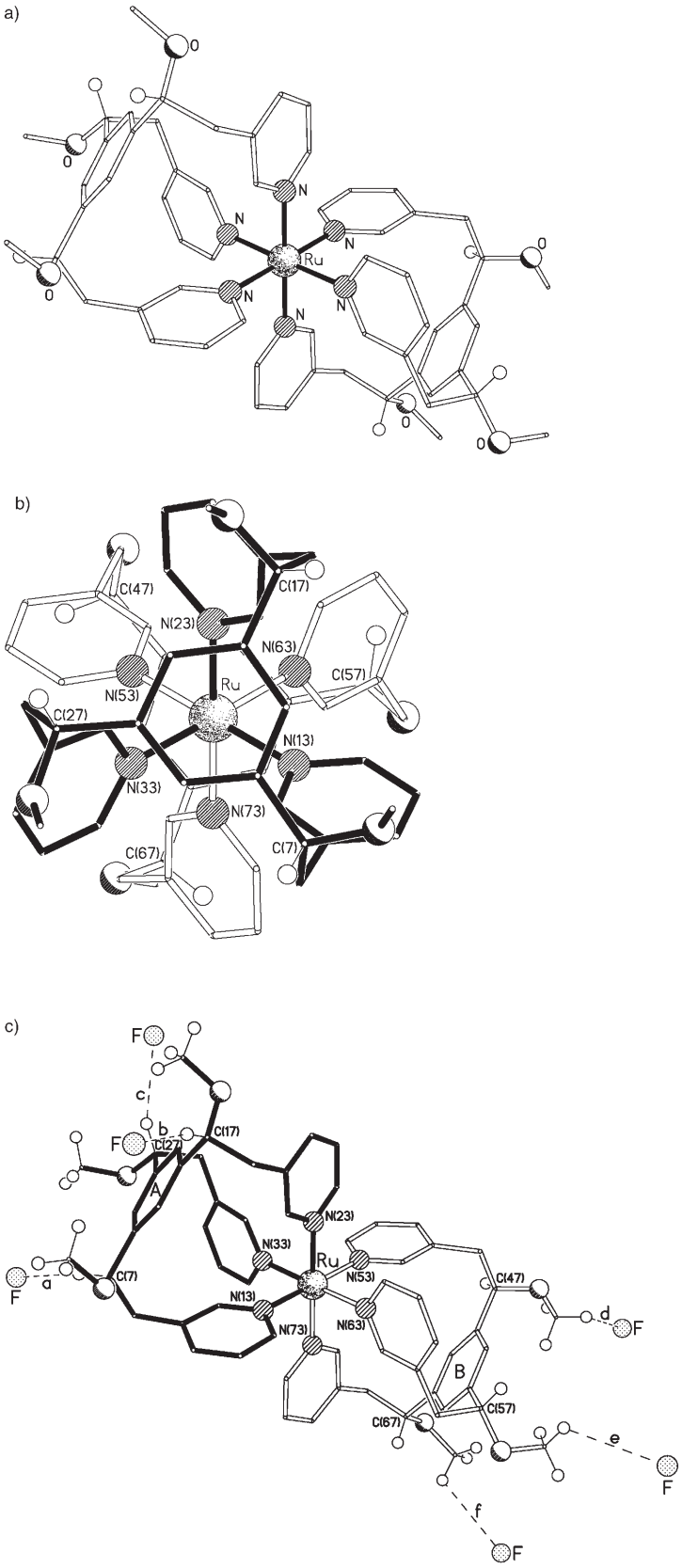


Figure 3. Views of the X-ray crystallographic structure of (+)-**32** depicting a) the molecular structure of the ruthenium dication in (+)-**32**, b) the C_3-symmetric nature of the two tripyridine ligands, and c) the C–H···F contacts.

electrophiles examined, benzophenone, propanone, methanal and propargyl bromide proved to be unsuitable, giving either monoderivatives or an intractable product mixture, but iodomethane, allyl bromide, ethylene oxide, chlorodiphenylphosphane and 3-bromomethylpyridine all gave good to excellent yields of enantiopure triderivates. The straightforward synthesis of a ruthenium complex of a C_3-symmetric tripyridine generated in this study serves to demonstrate the potential of our approach for generating new ligands for transition-metal complexes.

Experimental Section

All reactions involving the use of organometallic compounds were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques.[19] Reactions involving the use of arene tricarbonylchromium(0) complexes were protected from sunlight. Chiral diamine (+)-**13** was prepared by a literature procedure.[15] Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and used immediately. Dichloromethane (DCM) was distilled from calcium hydride and also used immediately. Methanol (MeOH) was distilled from calcium hydride and stored under an inert atmosphere over 3 Å molecular sieves. Chlorodiphenylphosphine was distilled prior to use and then stored under nitrogen. Acetone was purchased from the Aldrich Chemical Company (ACS grade) and stored under nitrogen over 3 Å molecular sieves. All other reagents were used as purchased from commercial sources. The concentrations of the alkyllithium compounds were determined by titration against diphenylacetic acid in THF.[20] Flash column chromatography was performed with BDH silica gel (330–70 μm particle size). Thin-layer chromatography (TLC) was performed on Merck TLC plates coated with Merck silica gel 60. Melting points were recorded on a Buchi 510 melting point apparatus in open capillaries and are uncorrected. Optical rotations were recorded on a Perkin–Elmer 241 Polarimeter using a 1 dm path length and with concentrations given as g mL^{-1}. IR spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrometer. NMR spectra were recorded at room temperature on Bruker AC300F A360 and AM500 instruments; J values are reported in Hz and chemical shifts in ppm. Mass spectra were recorded on Micromass Platform II and Micromass AutoSpec-Q spectrometers at Imperial College London or JEOL AX 505W spectrometer at Kings College London. Elemental analyses were performed by the London Metropolitan University microanalytical service. Analytical HPLC was performed using a Unicam Crystal 200 pump, a Unicam 100 UV-Vis detector and Daicel Chiralcel OD-H and Chiralpak AD columns (25×0.46 cm).

Trimethyl benzene-1,3,5-tricarboxylate (16):[16a] A 500 mL flask was charged with benzene-1,3,5-tricarboxylic acid (**15**; 10.00 g, 47.6 mmol), MeOH (200 mL) and a magnetic stirrer. Sulfuric acid (2.5 mL) was added carefully to the mixture and a reflux condenser was fitted. The reaction mixture was stirred vigorously and heated at reflux for 24 h before being allowed to cool to room temperature. A saturated solution of sodium hydrogencarbonate (100 mL) was slowly added to neutralise the mixture and the contents of the flask were transferred to a separating funnel. The layers were partitioned and the aqueous layer extracted with diethyl ether (3×100 mL). The organic layers were combined, dried ($MgSO_4$) and concentrated in vacuo to give **16** as a white solid (11.90 g, 99%). R_f=0.37 (silica gel; hexane/ethyl acetate 4:1); m.p. 144–145 °C (lit. m.p.[16] 145–147 °C); IR (CH_2Cl_2): $\tilde{\nu}_{max}$=1730 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ=4.00 (s, 9H; OCH_3×3), 8.88 ppm (s, 3H; C$_{Ar}H$×3); ^{13}C NMR (75 MHz, $CDCl_3$): δ=52.6 (OCH_3×3), 131.2 (C_{Ar}H×3), 134.6 (C_{Ar}×3), 165.5 ppm (C$OOCH_3$×3); MS (EI): m/z (%): 252 (33) [M^+], 221 (100) [M^+−OCH$_3$], 193 (18) [M^+−CO_2CH_3], 161 (11) [M^+−CO_2CH_3−CH_3OH].

1,3,5-Tris(hydroxymethyl)benzene (17):[16b] A 500 mL flask containing a magnetic stirrer was placed under an inert atmosphere and charged with lithium aluminiumhydride (2.40 g, 63.0 mmol). THF (150 mL) was added

through a syringe. The suspension was vigorously stirred and then cooled to 0 °C before a solution of triester **16** (6.00 g, 23.8 mmol) in THF (150 mL) was introduced through a cannula over a period of 10 min. After the addition was complete a condenser was fitted and the reaction mixture heated at reflux for 24 h before being allowed to cool to room temperature. Upon cooling, water (100 mL) was carefully added. The mixture was then filtered through Celite pad and the filter cake was washed thoroughly with $CHCl_3$ (100 mL). The volatiles were removed in vacuo to give **17** as a white solid (3.90 g, 99 %). $R_f = 0.36$ (silica gel; chloroform/methanol 9:1); m.p. 75–76 °C (lit. m.p.[17] 77 °C); IR ($CHCl_3$): $\tilde{\nu}_{max} = 3286\ cm^{-1}$ (OH); ^1H NMR (300 MHz, D_2O): $\delta = 4.53$ (s, 6H; $CH_2 \times 3$), 7.20 ppm (s, 3H; $C_{Ar}H \times 3$); ^{13}C NMR (75 MHz, D_2O): $\delta = 63.6$ ($CH_2 \times 3$), 125.6 ($C_{Ar}H \times 3$), 140.9 ppm ($C_{Ar} \times 3$); MS (EI): *m*/*z* (%): 168 (100) [M^+], 150 (17) [$M^+ - H_2O$], 137 (78) [$M^+ - CH_2OH$], 119 (40) [$M^+ - CH_2OH - H_2O$], 104 (51) [$M^+ - 2CH_3OH$].

1,3,5-Tris(methoxymethyl)benzene (18):[17] Sodium hydride (3.40 g, 60 % dispersion in mineral oil, 71.4 mmol) previously washed with pentane, was placed in a 250 mL flask. THF (60 mL) was added by means of a syringe and the suspension was cooled to 0 °C. Triol **17** (3.00 g, 17.9 mmol) was added portion-wise to the reaction mixture over 10 min. A condenser was fitted and the mixture heated at reflux for 2 h before being allowed to cool to room temperature. Iodomethane (4.90 mL, 80.3 mmol) was added through a syringe and the reaction mixture was stirred for 14 h before a saturated ammonium chloride solution (50 mL) was carefully added. The layers were separated, the aqueous layer was extracted with dichloromethane (3 × 100 mL) and the combined organic layers washed with brine (100 mL), dried ($MgSO_4$) and concentrated in vacuo to give **18** as a colourless oil (3.70 g, 99 %). $R_f = 0.33$ (silica gel; hexane/ethyl acetate 4:1); IR (CH_2Cl_2): $\tilde{\nu}_{max} = 1104\ cm^{-1}$ (C–O); ^1H NMR (360 MHz, $CDCl_3$): $\delta = 3.31$ (s, 9H; $OCH_3 \times 3$), 4.38 (s, 6H; $CH_2 \times 3$), 7.16 ppm (s, 3H; $C_{Ar}H \times 3$); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 58.6$ ($OCH_3 \times 3$), 74.8 ($CH_2 \times 3$), 126.6 ($C_{Ar}H \times 3$), 139.0 ppm ($C_{Ar} \times 3$); MS (EI): *m*/*z* (%): 210 (70) [M^+], 178 (79) [$M^+ - OCH_3$], 165 (100) [$M^+ - OCH_3 - CH_3 + H$]; elemental analysis calcd (%) for $C_{12}H_{18}O_3$ (210.13): C 68.54, H 8.63; found: C 68.46, H 8.69.

Tricarbonyl[1,3,5-tris(methoxymethyl)benzene]chromium(0) (19): A 250 mL round-bottomed flask containing a stirrer bar and fitted with a reflux condenser was placed under an inert atmosphere of nitrogen and charged with compound **18** (3.60 g, 17.2 mmol), hexacarbonylchromium(0) (4.20 g, 19.1 mmol), dry THF (18 mL) and dry di-*n*-butyl ether (180 mL). The suspension was thoroughly saturated with nitrogen, before it was heated to 140 °C and maintained under an inert atmosphere at the same temperature for 24 h. The yellow reaction mixture was then allowed to cool to room temperature. Filtration of the crude product through Celite followed by evaporation of the solvent afforded **19** as a yellow crystalline solid (5.70 g, 99 %). $R_f = 0.36$ (silica gel; hexane/ethyl acetate 3:1); m.p. 90–92 °C; IR (neat): $\tilde{\nu}_{max} = 1967$ (C≡O) 1891 cm^{-1} (C≡O); ^1H NMR (360 MHz, $CDCl_3$): $\delta = 3.39$ (s, 9H; $OCH_3 \times 3$), 4.16 (s, 6H; $CH_2 \times 3$), 5.25 ppm (s, 3H; $C_{Cr}H \times 3$); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 59.4$ ($OCH_3 \times 3$), 73.1 ($CH_2 \times 3$), 90.0 ($C_{Cr}H \times 3$), 108.4 ($C_{Cr} \times 3$), 232.3 ppm (C≡O × 3); MS (EI): *m*/*z* (%): 346 (30) [M^+], 262 (48) [$M^+ - 3CO$], 231 (20) [$M^+ - 3CO - OCH_3$], 172 (100) [$M^+ - 3CO - 3OCH_3$]; elemental analysis calcd (%) for $C_{15}H_{18}CrO_6$ (346.29): C 52.03, H 5.24; found: C 52.12, H 5.33.

(+)-(*R*,*R*,*R*)-Tricarbonyl[1,3,5-tris(1-methoxyethyl)benzene]chromium(0) ((+)-20): *n*-Butyllithium (5.60 mL, 2.50 M in hexanes, 13.9 mmol) was added dropwise to a stirred solution of diamine (+)-**13** (2.915 g, 6.93 mmol) in dry THF (204 mL) at −78 °C under an inert atmosphere. The solution was then allowed to warm to room temperature over a period of 30 min. The resulting deep red solution was recooled to −78 °C and a solution of heat-gun-dried lithium chloride (0.293 g, 6.93 mmol) in THF (35 mL) was added dropwise through a cannula. The reaction mixture was stirred for a further 5 min before a precooled (−78 °C) solution of complex **19** (0.800 g, 2.31 mmol) in THF (10 mL) was introduced dropwise through a short cannula. After stirring the orange solution at −78 °C for a period of 60 min, iodomethane (0.87 mL, 13.9 mmol) was added in one portion, which resulted in a colour change of the solution to yellow. The reaction mixture was then stirred for 60 min at −78 °C before MeOH (3 mL) was added and the solvent removed in vacuo. Purification of the residue by flash column chromatography (silica gel; hexane/ethyl acetate 10:0→4:1) afforded (+)-**20** as a fluffy yellow solid (0.770 g, 85 %). $R_f = 0.32$ (silica gel; hexane/ethyl acetate 4:1). Enantiomeric excess was determined by HPLC analysis (Chiralpak AD, *n*-hexane/propan-2-ol 99.5:0.5, 0.5 mL min^{-1}, 330 nm); *S*,*S*,*S* enantiomer $t_r = 18.4$ min (minor); *R*,*R*,*R* enantiomer $t_r = 21.2$ min (major): ≥95 % *ee*; $[\alpha]_D^{20} = +113$ ($c = 0.0058$ in $CHCl_3$); m.p. 85–88 °C; IR (neat): $\tilde{\nu}_{max} = 1960$ (C≡O) 1884 cm^{-1} (C≡O); ^1H NMR (360 MHz, $CDCl_3$): $\delta = 1.38$ (d, $J = 6.5$ Hz, 9H; $CHCH_3 \times 3$), 3.41 (s, 9H; $OCH_3 \times 3$), 4.04 (q, $J = 6.5$ Hz, 3H; $CHCH_3 \times 3$), 5.40 ppm (s, 3H; $C_{Cr}H \times 3$); ^{13}C NMR (90 MHz, $CDCl_3$): $\delta = 23.2$ ($CHCH_3 \times 3$), 57.9 ($OCH_3 \times 3$), 77.3 ($CHCH_3 \times 3$), 89.3 ($C_{Cr}H \times 3$), 112.5 ($C_{Cr} \times 3$), 233.1 ppm (C≡O × 3); MS (EI): *m*/*z* (%): 388 (37) [M^+], 304 (64) [$M^+ - 3CO$], 273 (32) [$M^+ - 3CO - OCH_3$], 237 (100) [$M^+ - Cr(CO)_3 - CH_3$]; elemental analysis calcd (%) for $C_{18}H_{24}CrO_6$ (388.37): C 55.66, H 6.23; found: C 55.80, H 6.22.

(+)-(*R*,*R*,*R*)-1,3,5-Tris(1-methoxyethyl)benzene ((+)-21): Ceric ammonium nitrate (0.317 g, 0.58 mmmol) was added to a solution of complex (+)-**20** (0.115 g, 0.29 mmol) in MeOH (6 mL). The resulting mixture was stirred at room temperature for 15 min before being filtered through Celite and evaporated. Purification of the crude product by flash column chromatography (silica gel; hexane/ethyl acetate 100:0→95:5) afforded (+)-**21** as a white solid (0.070 g, 96 %). $R_f = 0.32$ (silica gel; hexane/ethyl acetate 9:1); m.p. 238–240 °C; $[\alpha]_D^{20} = +157$ ($c = 0.019$ in $CHCl_3$); IR (CH_2Cl_2): $\tilde{\nu}_{max} = 3054$ (=CH), 1114 cm^{-1} (C-O-C); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.44$ (d, $J = 6.5$ Hz, 9H; $CHCH_3 \times 3$), 3.24 (s, 9H; $OCH_3 \times 3$), 4.31 (q, $J = 6.5$ Hz, 3H; $CHCH_3 \times 3$), 7.16 ppm (s, 3H; $C_{Ar}H \times 3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 23.7$ ($CHCH_3 \times 3$), 56.4 ($OCH_3 \times 3$), 79.6 ($CHCH_3 \times 3$), 123.1 ($C_{Ar}H \times 3$), 143.9 ppm ($C_{Ar} \times 3$); MS (EI): *m*/*z* (%): 252 (7) [M^+], 237 (100) [$M^+ - CH_3$]; elemental analysis calcd (%) for $C_{15}H_{24}O_3$ (252.34): C 71.39, H 9.58; found: C 71.31, H 9.57.

(+)-(*R*,*R*,*R*)-Tricarbonyl[1,3,5-tris(1-methoxybutyl-3-ene)benzene]chromium(0) ((+)-22): *n*-Butyllithium (2.40 mL, 2.50 M in hexanes, 6.0 mmol) was added dropwise to a stirred solution of diamine (+)-**13** (1.260 g, 3.00 mmol) in dry THF (24 mL) at −78 °C. The solution was allowed to warm to room temperature over a period of 30 min and was then recooled to −78 °C. A solution of heat-gun-dried lithium chloride (0.127 g, 3.00 mmol) in THF (8 mL) was added through a cannula and the reaction mixture was stirred for a further 5 min before a precooled solution (−78 °C) of complex **19** (0.346 g, 1.00 mmol) in THF (8 mL) was introduced dropwise through a short cannula. Stirring was continued for 60 min before allyl bromide (0.78 mL, 9.0 mmol) was added in one portion through a syringe. Stirring was then continued for a further 1.5 h at −78 °C before MeOH (2 mL) was added and the solvent removed in vacuo. Purification of the resulting residue by flash column chromatography (silica gel; hexane/diethyl ether 99:1 → 95:5) afforded (+)-**22** as a yellow solid (0.360 g, 77 %). $R_f = 0.70$ (silica gel; hexane/diethyl ether 2:1). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/propan-2-ol 99:1, 0.5 mL min^{-1}, 330 nm); *S*,*S*,*S* enantiomer $t_r = 8.4$ min (minor); *R*,*R*,*R* enantiomer $t_r = 10.2$ min (major): 98 % *ee*. $[\alpha]_D^{20} = +75$ ($c = 0.023$ in $CHCl_3$); m.p. 99–101 °C; IR (CH_2Cl_2): $\tilde{\nu}_{max} = 1962$ (C≡O), 1884 cm^{-1} (C≡O); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.42$ (ddd, $J = 6.3$, 7.0, 20.7 Hz, 3H; $CH(OCH_3)CHH \times 3$), 2.49 (ddd, $J = 4.0$, 5.2, 20.7 Hz, 3H; $CH(OCH_3)CHH \times 3$), 3.54 (s, 9H; $OCH_3 \times 3$), 4.04 (dd, $J = 5.2$, 6.3 Hz, 3H; $CH(OCH_3)CH_2 \times 3$), 4.99 (dd, $J = 1.4$, 17.1 Hz, 3H; $CH_2CH{=}CHH$ (*E*) × 3), 5.06 (dd, $J = 1.4$, 10.1 Hz, 3H; $CH_2CH{=}CHH$ (*Z*) × 3), 5.40 (s, 3H; $C_{Cr}H \times 3$), 5.76 ppm (dddd, $J = 4.0$, 7.0, 10.1, 17.1 Hz, 3H; $CH_2CH{=}CH_2 \times 3$); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 42.7$ ($CHCH_2CH \times 3$), 58.6 ($OCH_3 \times 3$), 80.5 ($CH(OCH_3) \times 3$), 88.6 ($C_{Cr}H \times 3$), 109.7 ($C_{Cr}CH \times 3$), 118.3 ($CH_2CH{=}CH_2 \times 3$), 133.1 ($CH_2CH{=}CH_2 \times 3$), 233.2 ppm (C≡O × 3); MS (EI): *m*/*z* (%): 466 (42) [M^+], 425 (20) [$M^+ - C_3H_5$], 382 (100) [$M^+ - 3CO$], 350 (13) [$M^+ - 3CO - CH_3OH$], 341 (19) [$M^+ - 3CO - C_3H_5$], 318 (18) [$M^+ - 3CO - 2CH_3OH$], 288 (77) [$M^+ - 3CO - 2OCH_3 - CH_3OH$], 248 (20) [$M^+ - Cr(CO)_3 - 2C_3H_5$]; elemental analysis calcd (%) for $C_{24}H_{30}CrO_6$ (466.49): C 61.79, H 6.48; found: C 61.94, H 6.41.

(+)-(*R*)-Tricarbonyl[1-(1-methoxybut-3-ynyl)-3,5-bis(methoxymethyl)-benzene]chromium(0) ((+)-23): *n*-Butyllithium (2.64 mL, 2.27 M in hex-

anes, 6.0 mmol) was added to diamine (+)-**13** (1.260 g, 3.00 mmol) in THF (40 mL) at −78 °C. The solution was allowed to warm to room temperature (30 min) and was recooled to −78 °C. Heat-gun-dried lithium chloride (0.127 g, 3.00 mmol) in THF (10 mL) was added through a cannula and the reaction mixture was stirred for 5 min before a solution of complex **19** (0.346 g, 1.00 mmol) in THF (6 mL) was introduced. The reaction mixture was stirred for 1 h, then propargyl bromide (1.01 mL, 80 % in toluene, 9.0 mmol) was added through a syringe. Stirring was continued for a further 1 h at −78 °C before MeOH (2 mL) was added and the solvent removed in vacuo. Purification of the resulting residue by flash column chromatography (silica gel; hexane/diethyl ether 9:1→5:5) afforded (+)-**23** as a yellow oil (0.345 g, 92 %). R_f = 0.18 (silica gel; hexane/diethyl ether 4:1). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/propan-2-ol 95:5, 0.5 mL min^{-1}, 330 nm); *R* enantiomer t_r = 20.2 min (major); *S* enantiomer t_r = 22.3 min (minor): 75 % *ee*. $[\alpha]_D^{20}$ = +26 (c = 0.034 in $CHCl_3$); IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 1967 (C≡O), 1890 cm^{-1} (C≡O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (virt t, J = 2.5 Hz, 1H; $CHCH_2C{\equiv}CH$), 2.65–2.70 (m, 2H; $CHCH_2C{\equiv}CH$), 3.470 (s, 3H; OCH_3) 3.474 (s, 3H; OCH_3) 3.60 (s, 3H; OCH_3), 4.11 (virt t, J = 5.7 Hz, 1H; $CHCH_2C{\equiv}CH$), 4.17–4.28 (m, 4H; $CH_2OCH_3\times2$), 5.35 (s, 1H; $C_{Cr}H$), 5.42 (s, 1H; $C_{Cr}H$), 5.58 ppm (s, 1H; $C_{Cr}H$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.3 ($CHCH_2C{\equiv}CH$), 58.6 ($CHOCH_3$), 59.0 ($CH_2OCH_3\times2$), 71.6 ($CHCH_2C{\equiv}CH$), 72.7, 72.9 (CH_2OCH_3), 79.0 ($CHCH_2C{\equiv}CH$), 79.5 ($CHCH_2C{\equiv}CH$), 89.2, 89.3, 91.3 ($C_{Cr}H$), 106.6, 106.8 ($C_{Cr}CH_2$), 111.1 ($C_{Cr}CH$), 232.5 ppm ($C{\equiv}O\times3$); MS (EI): *m*/*z* (%): 384 (24) [M^+], 353 (4) [M^+-OCH_3], 345 (18) [$M^+-CH_2C{\equiv}CH$], 300 (100) [M^+-3CO], 269 (12) [$M^+-3CO-OCH_3$], 261 (14) [$M^+-3CO-CH_2C{\equiv}CH$], 240 (30) [$M^+-3CO-2OCH_3+2H$], 209 (67) [$M^+-3CO-3OCH_3+2H$]; elemental analysis calcd (%) for $C_{18}H_{20}CrO_6$ (384.34): C 56.25, H 5.24; found: C 56.34, H 5.25.

(+)-(*R*)-Tricarbonyl[1-(2-hydroxy-1-methoxy-2,2-diphenylethyl)-3,5-bis-(methoxymethyl)benzene]chromium(0) ((+)-24): *n*-Butyllithium (0.72 mL, 2.50 M in hexanes, 1.8 mmol) was added dropwise to a stirred solution of diamine (+)-**13** (0.378 g, 0.90 mmol) in THF (10 mL) at −78 °C. The solution was allowed to warm to room temperature over a period of 30 min and was recooled to −78 °C. A solution of heat-gun-dried lithium chloride (0.038 g, 0.90 mmol) in THF (5 mL) was added through a cannula and the reaction mixture was stirred for a further 5 min before a precooled solution (−78 °C) of complex **19** (0.104 g, 0.30 mmol) in THF (5 mL) was introduced dropwise through a short cannula. Stirring was continued for 60 min, then benzophenone (0.492 g, 2.70 mmol) in THF (2 mL) was added in one portion through a cannula followed immediately by $BF_3{\cdot}OEt_2$ complex (0.23 mL, 1.8 mmol). The reaction mixture was stirred for a further 1 h at −78 °C before MeOH (1 mL) was added and the solvent removed in vacuo. Purification of the resulting residue by flash column chromatography (silica gel; hexane/diethyl ether 9:1→7:3) afforded (+)-**24** as a yellow oil, which solidified upon standing (0.154 g, 97 %). R_f = 0.45 (silica gel; hexane/diethyl ether 1:1). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/propan-2-ol 90:10, 0.5 mL min^{-1}, 330 nm); *R* enantiomer t_r = 14.8 min (major); *S* enantiomer t_r = 31.4 min (minor): 76 % *ee*. $[\alpha]_D^{20}$ = +9 (c = 0.009 in $CHCl_3$); m.p. 99–101 °C; IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 1964 (C≡O), 1888 cm^{-1} (C≡O); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.04 (s, 1H; OH), 3.20 (s, 3H; OCH_3), 3.43 (s, 3H; OCH_3), 3.66 (s, 3H; OCH_3), 3.69 (d, J = 12.2 Hz, 1H; $CHH(OCH_3)$), 3.90 (d, J = 12.2 Hz, 1H; $CHH(OCH_3)$), 4.12 (d, J = 12.1 Hz, 1H; $CHH(OCH_3)$), 4.21 (d, J = 12.1 Hz, 1H; $CHH(OCH_3)$), 4.45 (s, 1H; $CHC(OH)Ph_2$), 4.80 (s, 1H; $C_{Cr}H$), 5.49 (s, 1H; $C_{Cr}H$), 5.70 (s, 1H; $C_{Cr}H$), 7.20–7.55 ppm (m, 10H; $C_{Ar}H$); ^{13}C NMR (90 MHz, $CDCl_3$): δ = 58.5, 58.6, 59.6 (OCH_3), 72.1, 72.7 (CH_2), 81.4 ($CPh_2(OH)$), 84.7 ($CHCPh_2(OH)$), 93.0, 93.2, 94.0 ($C_{Cr}H$), 104.8, 104.6, 104.7 ($C_{Cr}C$), 127.0, 127.2, 127.4, 128.0, 128.2 ($C_{Ar}H$), 142.6, 144.8 ($C_{Ar}C$), 232.8 ppm ($C{\equiv}O\times3$); MS (EI): *m*/*z* (%): 528 (47) [M^+], 497 (9) [M^+-OCH_3], 444 (49) [M^+-3CO], 344 (11) [$M^+-Cr(CO)_3-OCH_3-OH$], 281 (6) [$M^+-Cr(CO)_3-3OCH_3-H_2O$], 209 (100) [$M^+-Cr(CO)_3-Ph_2COH$], 178 (99) [$M^+-Cr(CO)_3-Ph_2COH-OCH_3$]; elemental analysis calcd (%) for $C_{24}H_{30}CrO_6$ (528.12): C 63.63, H 5.35; found: C 63.59, H 5.38.

(+)-(*R*)-Tricarbonyl[1-(2-hydroxy-1-methoxy-2-methylpropyl)-3,5-bis-(methoxymethyl)benzene]chromium(0) (+)-25: *n*-Butyllithium (1.32 mL, 2.27 M in hexanes, 3.0 mmol) was added to diamine (+)-**13** (0.630 g, 1.50 mmol) in THF (20 mL) at −78 °C. The solution was allowed to warm to room temperature (30 min) and was recooled to −78 °C. Heat-gun-dried lithium chloride (0.064 g, 1.50 mmol) in THF (5 mL) was added through a cannula and the reaction mixture was stirred for 5 min before a solution of complex **19** (0.176 g, 0.50 mmol) in THF (3 mL) was introduced. The reaction mixture was stirred for 1 h, then acetone (0.33 mL, 4.5 mmol) was added followed immediately by $BF_3{\cdot}OEt_2$ complex (0.38 mL, 3.0 mmol). Stirring was continued for a further 1 h at −78 °C before MeOH (2 mL) was added and the solvent removed in vacuo. Purification of the resulting residue by flash column chromatography (silica gel; hexane/diethyl ether 9:1→1:1) afforded (+)-**25** as a yellow oil (0.177 g, 88 %). R_f = 0.20 (silica gel; hexane/diethyl ether 1:2). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/propan-2-ol 90:10, 0.5 mL min^{-1}, 330 nm); *R* enantiomer t_r = 14.5 min (major); *S* enantiomer t_r = 16.3 min (minor): 78 % *ee*. $[\alpha]_D^{20}$ = +38 (c = 0.010 in $CHCl_3$); IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 1966 (C≡O), 1890 cm^{-1} (C≡O); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (s, 3H; $C(CH_3)(CH_3)OH$), 1.22 [s, 3H; $C(CH_3)(CH_3)OH$], 2.21 (s, 1H; OH), 3.46 (s, 6H; $CH_2OCH_3\times2$), 3.69 (s, 3H; $CHOCH_3$), 3.71 (s, 1H; $CHC(CH_3)_2OH$), 4.08–4.27 (m, 4H; $CH_2OCH_3\times2$), 5.42 (s, 1H; $C_{Cr}H$), 5.58 (s, 1H; $C_{Cr}H$), 5.70 ppm (s, 1H; $C_{Cr}H$); ^{13}C NMR (90 MHz, $CDCl_3$): δ = 25.4, 25.7 [$C(CH_3)_2OH$], 58.9 ($CH_2OCH_3\times2$), 60.7 ($CHOCH_3$), 73.7 ($CH_2\times2$), 74.6 (COH), 87.7 ($CHCOH$), 91.9, 93.1, 94.3 ($C_{Cr}H$), 104.1, 104.9, 106.4 ($C_{Cr}C$), 239.4 ppm ($C{\equiv}O\times3$); MS (EI): *m*/*z* (%): 404 (72) [M^+], 373 (13) [M^+-OCH_3], 356 (3) [M^+-OCH_3-OH], 345 (5) [$M^+-(CH_3)_2COH$], 320 (34) [M^+-3CO], 289 (4) [$M^+-3CO-OCH_3$], 258 (6) [$M^+-3CO-2OCH_3$], 228 (15) [$M^+-3CO-2CH_2OCH_3-2H$], 210 (27) [$M^+-Cr(CO)_3-(CH_3)_2COH+H$], 200 (12) [$M^+-3CO-OCH_3-(CH_3)_2COH-2CH_3$], 178 (100) [$M^+-Cr(CO)_3-(CH_3)_2COH-OCH_3$]; elemental analysis calcd (%) for $C_{18}H_{24}CrO_7$ (404.09): C 53.46, H 5.98; found: C 53.40, H 6.06.

(+)-(*R*,*R*,*R*)-Tricarbonyl[1,3,5-tris(1-methoxy-3-hydroxy-propyl)benzene]chromium(0) (+)-26: *n*-Butyllithium (2.40 mL, 2.50 M in hexanes, 6.0 mmol) was added dropwise to a stirred solution of diamine (+)-**13** (1.260 g, 3.00 mmol) in dry THF (24 mL) at −78 °C. The solution was allowed to warm to room temperature over a period of 30 min and then recooled to −78 °C before a solution of heat-gun-dried lithium chloride (0.127 g, 3.00 mmol) in THF (8 mL) was added through a cannula. The reaction mixture was stirred for a further 5 min, then a precooled solution (−78 °C) of complex **19** (0.346 g, 1.00 mmol) in THF (8 mL) was introduced dropwise through a short cannula. Stirring was continued for a period of 60 min before a cooled solution (−78 °C) of ethylene oxide (2.5 mL, 50.0 mmol) in THF (2.5 mL) was added through a short cannula. Immediately after the addition of epoxide, $BF_3{\cdot}OEt_2$ complex (0.76 mL, 6.0 mmol) was added in one portion leading to a colour change of solution from red to yellow. The reaction mixture was then stirred for 1.5 h at −78 °C, MeOH (2 mL) was then added and the solvent was removed in vacuo. Purification of the residue by flash column chromatography (silica gel; ethyl acetate/methanol 99:1→95:5) afforded (+)-**26** as a yellow oil which solidified upon standing (0.330 g, 69 %). R_f = 0.50 (silica gel; ethyl acetate/methanol 9:1). Enantiomeric excess was determined by HPLC analysis (Chiralpak AD, *n*-hexane/propan-2-ol 80:20, 0.5 mL min^{-1}, 330 nm); *S*,*S*,*S* enantiomer t_r = 20.6 min (minor); *R*,*R*,*R* enantiomer t_r = 23.0 min (major): 93 % *ee*. $[\alpha]_D^{20}$ = +96 (c = 0.018 in $CHCl_3$); m.p. 112–114 °C; IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3250 (OH) 1963 (C≡O), 1887 cm^{-1} (C≡O); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.90–1.93 (m, 3H; $CHHCH_2OH\times3$), 1.96–1.99 (m, 3H; $CHHCH_2OH\times3$), 2.36 (s, 3H; $OH\times3$), 3.60 (s, 9H; $OCH_3\times3$), 3.79 (s, 6H, $CHHCH_2OH\times3$), 4.25–4.29 (m, 3H; $CHCH_2CH_2OH\times3$), 5.55 ppm (s, 3H; $C_{Cr}H\times3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.3 ($CH_2CH_2OH\times3$), 58.9 ($OCH_3\times3$), 59.7 ($CH_2OH\times3$), 79.9 ($CHOCH_3\times3$), 89.7 ($C_{Cr}H\times3$), 109.2 ($C_{Cr}CH\times3$), 232.8 ppm ($C{\equiv}O\times3$); MS (EI): *m*/*z* (%): 478 (2) [M^+], 402 (6) [$M^+-CH_2CH_2OH-OCH_3$], 332 (13) [$M^+-2CO-2CH_2CH_2OH$], 310 (7) [$M^+-CH_3OCH_2CH_2CH_2OH-CH_3CH_2OH-CH_3OH$], 297 (100) [$M^+-2CH_3OCH_2CH_2CH_2OH-H$], 270 (27) [$M^+-CO-2CH_3OCH_2CH_2CH_2OH$], 265 (38) [$M^+-2CH_3OCH_2CH_2CH_2OH-CH_3OH-H$]; HRMS (EI): *m*/*z* calcd for $C_{21}H_{30}CrO_9$: 478.1295; found: 478.1276.

(+)-(*R*,*R*,*R*)-Tricarbonyl[1,3,5-tris(1-diphenylphosphino-1-methoxymethyl)benzene]chromium(0) ((+)-28): *n*-Butyllithium (1.49 mL, 2.50 M in

hexanes, 3.7 mmol) was added dropwise to a stirred solution of diamine (+)-**13** (0.208 g, 1.86 mmol) in dry THF (100 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature over 30 min and was recooled to −78 °C before a solution of heat-gun-dried lithium chloride (0.080 g, 1.86 mmol) in THF (10 mL) was added through a cannula. The reaction mixture was stirred for a further 5 min, then a precooled solution (−78 °C) of complex **19** (0.208 g, 0.60 mmol) in THF (10 mL) was introduced dropwise through a short cannula. Stirring was continued for a period of 60 min before chlorodiphenylphosphine (0.99 mL, 5.4 mmol) was added in one portion. The reaction mixture was then stirred for 1 h at −78 °C followed by a further 2 h at −40 °C; MeOH (2 mL) was then added and the solvent was removed in vacuo. Purification of the resulting residue by flash column chromatography (silica gel; hexane/diethyl ether 99:1→90:10) afforded (+)-**28** as a yellow solid (0.253 g, 47 %). R_f = 0.40 (silica gel; hexane/diethyl ether 9:1). Enantiomeric excess was determined by HPLC analysis (Chiralcel OD-H, *n*-hexane/propan-2-ol 99.6:0.4, 1.0 mL min^{-1}, 330 nm); *S*,*S*,*S* enantiomer t_r = 12.5 min (minor); *R*,*R*,*R* enantiomer t_r = 20.6 min (major): = 95 % *ee*. $[\alpha]_D^{20}$ = +227 (*c* = 0.0067 in $CHCl_3$); m.p. 155–157 °C; IR (CH_2Cl_2): ν_{max} = 1967 (C≡O), 1882 cm^{-1} (C≡O); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.43 (s, 9H; OCH_3×3), 4.75 (d, *J* = 4.7 Hz, 3H; C*H*PPh$_2$×3), 5.54 (s, 3H; $C_{Cr}H$×3), 7.28–7.40 (m, 24H; $C_{Ar}H$×3), 7.46–7.51 ppm (m, 6H; $C_{Ar}H$×3); ^{31}P NMR (202 MHz, $CDCl_3$): δ = 13.38 ppm (*P*Ph$_2$×3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 61.0 (O*C*H$_3$×3), 83.6 (d, *J* = 23.6 Hz, *C*HPPh$_2$×3), 89.8 (d, *J* = 10.4 Hz, C_{Cr}H×3), 107.2 (d, *J* = 19.4 Hz, C_{Cr}CH×3), 128.3–128.5 (m, C_{Ar}), 128.9, 129.5 (C_{Ar}), 132.2 (d, *J* = 15.3 Hz, C_{Ar}), 133.2 (d, *J* = 19.4 Hz, C_{Ar}), 135.2 (d, *J* = 20.0 Hz, C_{Ar}), 135.9 (d, *J* = 14.7 Hz, C_{Ar}), 233.6 ppm (*C*≡O×3); MS (FAB): *m*/*z* (%): 898 (72) [M^+], 814 (100) [M^+−3CO], 629 (38) [M^+−3CO−PPh$_2$]; elemental analysis calcd (%) for $C_{51}H_{45}CrO_6P_3$ (898.83): C 68.15, H 5.05; found: C 68.15, H 4.93.

(+)-(*R*,*R*,*R*)-1,3,5-Tris[1-(boronatodiphenylphosphino)-1-methoxymethyl)]benzene ((+)-29): A BH_3·THF complex (1.56 mL, 1.00 M solution in THF, 1.6 mmol) was added dropwise, under an inert atmosphere, to a stirred solution of triphosphine (+)-**28** (0.350 g, 0.39 mmol) in THF (30 mL). Stirring was continued for 1.5 h at room temperature and then the solvent was removed in vacuo. The resulting residue was then redissolved in DCM (100 mL) before being stirred in an open vessel and in the presence of air and light. After stirring for 18 h no more chromium-containing species were detected (by TLC) and the green reaction mixture was concentrated to give a residue which was purified by flash column chromatography (silica gel; hexane/ethyl acetate 3:1) to afford (+)-**29** as a white solid (0.301 g, 97 %). R_f = 0.20 (silica gel; hexane/ethyl acetate 4:1). $[\alpha]_D^{20}$ = +109 (*c* = 0.015 in $CHCl_3$); m.p. 114–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.70 (s, 9H; BH_3×3), 2.99 (s, 9H; OCH_3×3), 4.90 (d, *J* = 5.4 Hz, 3H; C*H*PPh$_2$×3), 6.83 (d, *J* = 1.6 Hz, 3H; $C_{Ar}H$×3), 7.37–7.49 (m, 18H; $C_{Ar}H$), 7.63–7.76 ppm (m, 12H; $C_{Ar}H$); ^{31}P NMR (202 MHz, $CDCl_3$): δ = 25.60 ppm (*P*Ph$_2$×3); ^{11}B NMR (160 MHz, $CDCl_3$): δ = −40.04 ppm (*B*H$_3$×3); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 58.5 (O*C*H$_3$×3), 82.5 (d, *J* = 43.5 Hz, *C*HPPh$_2$×3), 125.3 (d, *J* = 53.2 Hz, C_{Ar}), 128.3 (d, *J* = 10.4 Hz, C_{Ar}H), 128.5 (d, *J* = 10.3 Hz, C_{Ar}H), 128.6 (C_{Ar}), 130.9, 131.5 (C_{Ar}H), 132.7 (d, *J* = 8.6 Hz, C_{Ar}H), 134.3 (C_{Ar}), 134.7 ppm (d, *J* = 8.7 Hz, C_{Ar}H); MS (FAB): *m*/*z* (%): 804 (14) [M^+(^{11}B×3)], 803 (22) [M^+(^{11}B×2, ^{10}B×1)], 789 (10) [M^+−BH$_3$], 775 (4) [M^+−2BH$_3$], 745 (12) [M^+−2BH$_3$−OCH$_3$], 701 (13) [M^+−3BH$_3$−OCH$_3$−2CH$_3$], 671 (6) [M^+−3BH$_3$−3OCH$_3$+H], 605 (8) [M^+−BH$_3$−PPh$_2$], 591 [M^+−2BH$_3$−PPh$_2$] (11), 577 (8) [M^+−3BH$_3$−PPh$_2$], 561 (8) [M^+−2BH$_3$−PPh$_2$−OCH$_3$], 547 (29) [M^+−3BH$_3$−PPh$_2$−OCH$_3$]; elemental analysis calcd (%) for $C_{48}H_{54}B_3O_3P_3$ (804.36): C 71.68, H 6.77; found: C 71.65, H 6.73.

(+)-(*R*,*R*,*R*)-Tricarbonyl[1,3,5-tris(1-methoxy-2-(3-pyridyl)ethyl)benzene]chromium(0) ((+)-30)

Preparation of 3-(bromomethyl)pyridine: A 250 mL flask containing a stirrer bar and fitted with a reflux condenser was placed under an inert atmosphere of nitrogen. The flask was charged with 3-(bromomethyl)pyridine hydrobromide (3.26 g, 12.9 mmol), powdered potassium carbonate (7.13 g, 51.6 mmol) and anhydrous toluene (78 mL). The reaction mixture was stirred vigorously for 45 min at room temperature, 45 min at 40 °C, 45 min at 50 °C, 45 min at 65 °C, 45 min at 80 °C and 30 min at 90 °C. The solution was then allowed to cool to room temperature over a period of 40 min.

*Preparation of complex (+)-**30***: *n*-Butyllithium (2.08 mL, 2.50 M in hexanes, 5.2 mmol) was added dropwise to a stirred solution of diamine (+)-**13** (1.186 g, 2.82 mmol) in dry THF (50 mL) at −78 °C under an inert atmosphere of nitrogen. The solution was then allowed to warm to room temperature over a period of 30 min. The resulting deep red solution was recooled to −78 °C and a solution of heat-gun-dried lithium chloride (0.110 g, 2.60 mmol) in THF (16 mL) was added dropwise through a cannula. The reaction mixture was stirred for a further 5 min, then a precooled (−78 °C) solution of complex **19** (0.300 g, 0.87 mmol) in THF (10 mL) was introduced dropwise through a short cannula. After stirring the orange solution at −78 °C for a period of 60 min, 3-(bromomethyl)-pyridine (prepared as above) was added through a cannula and the resulting yellow solution was stirred for 2 h at −78 °C. MeOH (3 mL) was then added and the solvent removed in vacuo. Purification of the residue by flash column chromatography (silica gel; ethyl acetate/methanol 4:1 and then silica gel; chloroform/methanol 9:1) afforded (+)-**30** as a yellow solid (0.45 g, 84 %). R_f = 0.38 (silica gel; ethyl acetate/methanol 4:1); $[\alpha]_D^{20}$ = +36 (*c* = 0.0067 in $CHCl_3$); m.p. 104–106 °C; IR (CH_2Cl_2): ν_{max} = 1965 (C≡O), 1889 (C≡O), 1592 (C=N), 1575 cm^{-1} (C=N); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.74 (dd, *J* = 6.5, 14.0 Hz, 3H; CHC*H*HPy×3), 2.89 (dd, *J* = 4.0, 14.0 Hz, 3H; CHCH*H*Py×3), 3.46 (s, 9H; OCH_3×3), 4.08 (dd, *J* = 4.0, 6.5 Hz, 3H; C*H*CH$_2$Py×3), 5.13 (s, 3H; $C_{Cr}H$×3), 7.26 (dd, *J* = 4.5, 7.5 Hz, 3H; $C_{Py}H$×3), 7.47 (d, *J* = 7.5 Hz, 3H; $C_{Py}H$×3), 8.30 (d, *J* = 1.5 Hz, 3H; $C_{Py}H$×3), 8.49 ppm (dd, *J* = 1.5, 4.5 Hz, 3H; $C_{Py}H$×3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.5 (CH*C*H$_2$×3), 58.7 (O*C*H$_3$×3), 81.1 (*C*HCH$_2$×3), 88.5 (C_{Cr}H×3), 108.5 (C_{Cr}×3), 123.2 (C_{Py}H×3), 132.3 (C_{Py}×3), 137.4, 148.1, 150.9 (C_{Py}H×3), 232.5 ppm (*C*≡O×3); MS (EI): *m*/*z* (%): 619 (4) [M^+], 535 (40) [M^+−3CO], 483 (60) [M^+−3CO−Cr], 391 (100) [M^+−3CO−Cr−CH$_2$Py]; elemental analysis calcd (%) for $C_{33}H_{33}CrN_3O_6$ (619.18): C 63.97, H 5.37, N 6.78; found: C 63.98, H 5.31, N 6.72.

(+)-(*R*,*R*,*R*)-1,3,5-Tris[1-methoxy-2-(3-pyridyl)ethyl]benzene ((+)-31): Ceric ammonium nitrate (1.042 g, 1.90 mmol) was added to a solution of complex (+)-**30** (0.588 g, 0.95 mmol) in MeOH (15 mL). The resulting mixture was stirred at room temperature for 1 h. The reaction mixture was neutralized by addition of a saturated potassium carbonate solution and extracted with dichloromethane (2×20 mL). The combined extracts were washed with brine (2×10 mL), dried ($MgSO_4$) and then concentrated in vacuo to afford the crude product. Purification of the crude product by flash column chromatography (silica gel; ethyl acetate/acetone/triethylamine 6:3:1) afforded (+)-**31** as a colourless oil (0.367 g, 76 %); R_f = 0.35 (silica gel; ethyl acetate/acetone/triethylamine 6:3:1); $[\alpha]_D^{20}$ = +15 (*c* = 0.002 in CH_2Cl_2); IR (KBr pellet): $\tilde{\nu}_{max}$ = 1592 (C=N), 1575 cm^{-1} (C=N); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.79 (dd, *J* = 6.0, 14.0 Hz, 3H; CHC*H*HPy×3), 3.01 (dd, *J* = 7.0, 14.0 Hz, 3H; CHCH*H*Py×3), 3.15 (s, 9H; OCH_3×3), 4.24 (t, *J* = 6.5 Hz, 3H; C*H*CH$_2$Py×3), 6.89 (s, 3H; $C_{Ar}H$×3), 7.16 (dd, *J* = 4.5, 7.0 Hz, 3H; $C_{Py}H$×3) 7.35 (d, *J* = 7.0 Hz, 3H; $C_{Py}H$×3), 8.24 (s, 3H; $C_{Py}H$×3), 8.42 ppm (d, *J* = 4.5 Hz, 3H; $C_{Py}H$×3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.9 (CH*C*H$_2$×3), 57.2 (O*C*H$_3$×3), 84.3 (*C*HCH$_2$×3), 122.9 (C_{Py}H×3), 124.5 (C_{Ar}H×3), 133.4 (C_{Py}×3), 137.4 (C_{Py}H×3), 141.4 (C_{Ar}×3), 148.1, 151.1 ppm (C_{Py}H×3); MS (EI): *m*/*z* (%): 484 (19) [M^++H], 483 (67) [M^+], 391 (100) [M^+−CH$_2$Py]; elemental analysis calcd (%) for $C_{30}H_{33}N_3O_6$ (483.25): C 74.51, H 6.87, N 8.68; found: C 74.50, H 7.00, N 8.69.

(+)-(*R*,*R*,*R*)-[1,3,5-Tris(1-methoxy-2-(3-pyridyl)ethyl)benzene]ruthenium dihexafluorophosphate ((+)-32): A mixture of ligand (+)-**31** (0.100 g, 0.21 mmol) and $RuCl_3$ (0.215 g, 0.11 mmol) were refluxed in 5 mL of ethylene glycol for 20 min. The solution was cooled to room temperature, water added (5 mL) and a precipitate was formed upon addition of a concentrated aqueous NH_4PF_6 solution (2 mL). The green precipitate was filtered off, washed with water (10 mL) and dried under reduced pressure. The residue was purified via crystallization from dichloromethane/methanol/hexane (1:0.25:3) to afford (+)-**32** as a yellow crystalline solid (0.074 g, 46 %). $[\alpha]_D^{20}$ = +26 (*c* = 0.0047 in $CHCl_3$); m.p. 240 °C (decomp); UV/Vis spectrum (CH_3CN): λ_{max} (ε) = 368 (67060), 246 nm (103063); IR (KBr pellet): $\tilde{\nu}_{max}$ = 1483 (C=N), 1430 cm^{-1} (C=N); ^{1}H NMR (500 MHz,

CD_3CN): $\delta = 2.21$ (t, $J = 13.0$ Hz, 3H; CHC*H*HPy × 3 A), 2.30 (dd, $J = 4.0$, 13.0 Hz, 3H; CHC*H*HPy × 3 B), 3.09 (s, 9H; OCH_3 × 3 A), 3.28 (dd, $J = 4.0$, 13.0 Hz, 3H; CHCH*H*Py × 3 A and B), 3.39 (s, 9H; OCH_3 × 3 B), 4.23 (dd, $J = 4.0$, 13.0 Hz, 3H; C*H*CH_2Py × 3 A), 4.63 (t, $J = 4.0$ Hz, 3H; C*H*CH_2Py × 3 B), 6.35 (s, 6H; $C_{Py}H$ × 3 A and B), 6.47 (s, 3H; $C_{Ar}H$ × 3 B), 6.67 (s, 3H; $C_{Ar}H$ × 3 A), 7.18–7.27 (m, 12H; $C_{Py}H$ × 6 A and B), 7.81 (d, $J = 7.0$ Hz, 3H; $C_{Py}H$ × 3 A or B), 7.92 ppm (d, $J = 7.0$ Hz, 3H; $C_{Py}H$ × 3 A or B); ^{13}C NMR (125 MHz, CD_3CN): $\delta = 39.7$ (CHCH_2 × 3 B), 41.6 (CHCH_2 × 3 A), 56.6 (OCH_3 × 3 A), 57.6 (OCH_3 × 3 B), 81.0 (*C*HCH_2 × 3 B), 85.0 (CHCH_2 × 3 A), 122.3 (C_{Py}H × 3 A and B), 127.1 (C_{Ar}H × 3 A and B), 127.7, 128.5 (C_{Py}H × 3 A and B), 137.3, 138.0 (C_{Py} × 3 A and B), 140.5, 141.7 (C_{Py}H × 3 A and B), 141.0, 141.6 (C_{Ar} × 3 A and B) 152.9, 153.1, 155.5 ppm (C_{Py}H × 3 A and B); MS (FAB$^+$): *m*/*z* (%): 1213 (19) [$M^+ - PF_6$], 1068 (22) [$M^+ - 2PF_6$], 584 (82) [$M^+ - 2PF_6 - C_{30}H_{33}N_3O_3$], 484 (12) [$M^+ - 2PF_6 - C_{30}H_{33}N_3O_3$], 73 (100) [$C_3H_6OCH_3^+$]; elemental analysis calcd (%) for [$C_{60}H_{66}N_6O_6Ru$]-$(PF_6)_2 \cdot 2CH_2Cl_2$ (1528.05): C 48.72, H 4.61, N 5.49; found: C 48.81, H 4.64, N 5.48.

Table 1. Crystal data, data collection and refinement parameter for compounds (+)-**20**, (+)-**28** and (+)-**32**.

	(+)-**20**	(+)-**28**	(+)-**32**
formula	$C_{18}H_{24}CrO_6$	$C_{51}H_{45}CrO_6P_3$	$C_{60}H_{66}N_6O_6RuPF_6 \cdot 2CH_2Cl_2$
M_r	388.37	898.78	1528.05
colour/habit	yellow platy needles	yellow plates	yellow shards
T [K]	293	293	173
crystal system	triclinic	ortho-rhombic	monoclinic
space group	$P1$ (no. 1)	$P2_12_12_1$ (no 19)	$P2_1$ (no. 4)
a [Å]	7.176(2)	11.497(5)	10.5334(5)
b [Å]	10.628(4)	17.024(8)	18.2106(8)
c [Å]	13.043(4)	23.651(10)	17.6404(9)
α [°]	102.081(14)	90	90
β [°]	91.33(3)	90	90.877(4)
γ [°]	101.31(3)	90	90
V [Å^3]	951.7(5)	4629(3)	3383.4(3)
Z	2	4	2
ρ_{calcd} [g cm^{-3}]	1.355	1.290	1.500
radiation	$Cu_{K\alpha}$	$Cu_{K\alpha}$	$Mo_{K\alpha}$
μ [mm^{-1}]	5.203	3.403	0.524
reflns measured	3415	4388	21626
reflns observed [$\lvert F_o \rvert > 4\sigma(\lvert F_o \rvert)$]	2719	3294	20273
$2\theta_{max}$ [°]	128	130	66
parameters	452	479	838
R_1^+	0.0694	0.0601	0.1075
R_1^-	0.0784	0.0928	0.1091
Flack parameter x^+	0.04(3)	0.000(14)	0.11(4)
Flack parameter x^-	0.96(3)	n/a	0.89(4)
R_1/wR_2	0.069/0.170	0.060/0.149	0.108/0.182

X-ray crystallography: Table 1 provides a summary of the crystalllographic data for compounds (+)-**20**, (+)-**28** and (+)-**32**. Data was collected on a Bruker P4 diffractometer. CCDC-273326 ((+)-**20**), CCDC-246809 ((+)-**28**) and CCDC-264307 ((+)-**32**) 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.

[1] a) C. Moberg, *Angew. Chem.* **1998**, *110*, 260–281; *Angew. Chem. Int. Ed.* **1998**, *37*, 248–268, and references therein; b) M. Czugler, E. Weber, L. Párkányi, P. P. Korkas, P. Bombicz, *Chem. Eur. J.* **2003**, *9*, 3741–3747, and references therein.
[2] P. Wyatt, H. Eley, J. Charmant, B. J. Daniel, A. Kantacha, *Eur. J. Org. Chem.* **2003**, 4216–4226.
[3] M. T. Powell, A. M. Porte, J. Reibenspies, K. Burgess, *Tetrahedron* **2001**, *57*, 5027–5038.
[4] M. J. Burk, R. L. Harlow, *Angew. Chem.* **1990**, *102*, 1511–1513; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1462–1464.
[5] T. R. Ward, L. M. Venanzi, A. Albinati, F. Lianza, T. Gerfin, V. Gramlich, G. M. R. Tombo, *Helv. Chim. Acta* **1991**, *74*, 983–988.
[6] M. J. Baker, P. G. Pringle, *J. Chem. Soc. Chem. Commun.* **1993**, 314–316.
[7] See, for example, a) W. A. Nugent, *J. Am. Chem. Soc.* **1992**, *114*, 2768–2769; b) F. Di Furia, G. Licini, G. Modena, R. Motterle, W. A. Nugent, *J. Org. Chem.* **1996**, *61*, 5175–5177; c) M. Bonchio, G. Licini, F. Di Furia, S. Mantovani, G. Modena, W. A. Nugent, *J. Org. Chem.* **1999**, *64*, 1326–1330.
[8] H. Lütjens, P. Knochel, *Tetrahedron: Asymmetry* **1994**, *5*, 1161–1162.
[9] G. Bringmann, R-M. Pfeifer, C. Rummey, K. Hartner, M. Breuning, *J. Org. Chem.* **2003**, *68*, 6859–6863.
[10] T. Fang, D-M. Du, S-F. Lu, J. Xu, *Org. Lett.* **2005**, *7*, 2081–2084.
[11] a) W. N. Lipscomb, N. Sträter, *Chem. Rev.* **1996**, *96*, 2375–2433; b) C. Dro, S. Bellemin-Laponnaz, R. Welter, L. H. Gade, *Angew. Chem.* ***2004***, *116*, 4579–4582; *Angew. Chem. Int. Ed.* **2004**, *43*, 4479–4482; c) B. D. Ward, S. Bellemin-Laponnaz, L. H. Gade, *Angew. Chem.* **2005**, *117*, 1696–1699; *Angew. Chem. Int. Ed.* **2005**, *44*, 1668–1671.
[12] a) S-G. Kim, K-H. Kim, Y. K. Kim, S. K. Shin, K. H. Ahn, *J. Am. Chem. Soc.* **2003**, *125*, 13819–13824; b) S-G. Kim, K-H. Kim, J. Jung, S. K. Shin, K. H. Ahn, *J. Am. Chem. Soc.* **2002**, *124*, 591–596.
[13] E. L. M. Cowton, S. E. Gibson, M. J. Schneider, M. H. Smith, *Chem. Commun.* **1996**, 839–840.
[14] M. P. Castaldi, S. E. Gibson, M. Rudd, A. J. P. White, *Angew. Chem.* **2005**, *117*, 3498–3501; *Angew. Chem. Int. Ed.* **2005**, *44*, 3432–3435.
[15] K. Bambridge, M. J. Begley, N. S. Simpkins, *Tetrahedron Lett.* **1994**, *35*, 3391–3394.
[16] a) S. M. Dimick, S. C. Powell, S. A. McMahon, D. N. Moothoo, J. H. Naismith, E. J. Toone, *J. Am. Chem. Soc.* **1999**, *121*, 10286–10296; b) W. P. Cochrane, P. L. Pauson, T. S. Stevens, *J. Chem. Soc. C* **1968**, 630–632.
[17] Although triether **18** is produced as a minor product in alkyne trimerization reactions, it has not been fully characterized to date. a) P. H. M. Budzelaar, H. J. Alberts-Jansen, J. Boersma, G. J. M. van der Kerk, *Polyedron* **1982**, *1*, 563–566; b) P. Diversi, L. Ermini, G. Ingrosso, A. Lucherini, *J. Organomet. Chem.* **1993**, *447*, 291–298; c) H.-Y. Rhyoo, B. Y. Lee, H. K. B. Yu, Y. K. Chung, *J. Mol. Catal.* **1994**, *92*, 41–49; d) P. Le Floch, F. Mathey, *Organometallics* **1996**, *15*, 2713–2719; e) K. Tanaka, K. Toyoda, A. Wada, K. Shirasaka, M. Hirano, *Chem. Eur. J.* **2005**, *11*, 1145–1156.
[18] H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056–2075; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021.
[19] D. F. Shriver, M. A. Drzdzon, *The Manipulation of Air Sensitive Compounds*, Wiley, Chichester, **1986**.
[20] W. G. Kofron, L. M. Baclawski, *J. Org. Chem.* **1976**, *41*, 1879–1880.

Received: August 23, 2005
Published online: November 9, 2005

