Tricarbonylpyridinechromium Complexes: Stereoselective Alkylations and Aldol-type Reactions involving α-Carbanions Derived from η-Tricarbonyl(2-alkylpyridine)chromium Complexes

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Reaction of tricarbonyl(η-2-alkylpyridine)chromium(0) complexes with lithium diisopropylamide at −40 °C generates the resonance stabilised carbanions at the α-position which undergo completely stereoselective electrophilic quench with alkyl halides to generate the corresponding α-branched tricarbonyl(η-2-alkylpyridine)chromium(0) complexes. These complexes can then be subjected to nucleophilic additions with methyllithium followed by methyl iodide quench to afford the tricarbonyl-(η-*exo*-6-alkyl-1,2-dimethyl-1,2-dihydropyridine)chromium(0) complexes. Treatment of the resonance stabilised α-carbanion derived from tricarbonyl(η-2-ethylpyridine)chromium(0) with the non-enolisable aldehydes benzaldehyde or pivalaldehyde affords the *erythro*-aldol-type products with complete control of stereochemistry at both the newly formed α- and carbinol centres. X-Ray crystal structures of *SR*(*RS*)-tricarbonyl[η-*exo*-1,2-dimethyl-6-(2-pent-4-enyl)-1,2-dihydropyridine)-chromium(0) and *RSS*(*SRR*)-tricarbonyl[*erythro*-2-η-(2-pyridyl)-1-phenylpropanol]chromium(0) are reported.

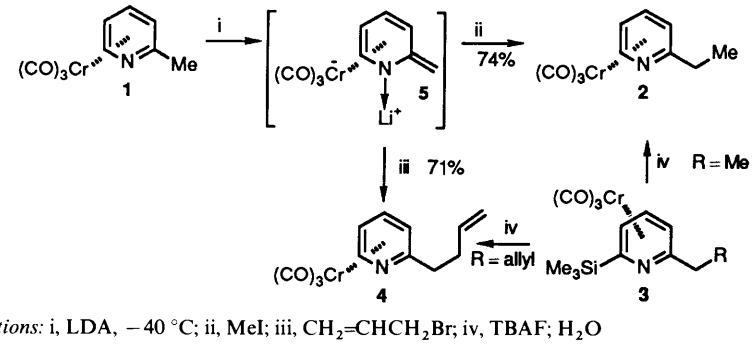
In tricarbonylarenechromium complexes the electron-withdrawing nature of the tricarbonylchromium moiety results in increased acidities of aryl[1] and benzylic[2] protons and an increased propensity towards nucleophilic additions.[3] We have reported previously new methodology which permitted access to a variety of tricarbonyl(η-pyridine)chromium(0) complexes and consequently allowed the reactivity of such complexes to be investigated. We recently described the ready nucleophilic additions between tricarbonyl(η-pyridine)chromium(0) complexes and alkyllithium reagents to afford, after electronic quench, tricarbonyl(η-*exo*-2-alkyl-1,2-dihydropyridine)chromium(0) complexes.[4] Tricarbonyl(alkylarene)chromium complexes bearing a substituent *ortho* to the alkyl group are chiral and the alkylation reactions of derived benzylic carbanions have been shown to proceed with high stereoselectivities.[5] Tricarbonyl(η-2-alkylpyridine)chromium(0) complexes are also chiral and we describe here their α-deprotonation with lithium diisopropylamide and the stereoselective alkylation and aldol-type reactions of the thus formed anions. Part of this work has been previously communicated.[6]

Results and Discussion

Treatment of a 5 molar excess of lithium diisopropylamide with tricarbonyl(η-2-methylpyridine)chromium(0) **1** in tetrahydrofuran at −40 °C resulted in the initial yellow colour of the solution becoming very deep red. After 2 h an excess of methyl iodide was added to the solution causing it to lighten in colour considerably. Warming to room temperature, filtration through alumina and evaporation of the solvent afforded a yellow gum. ^{1}H NMR spectroscopic analysis of the product revealed it to be tricarbonyl(η-2-ethylpyridine)chromium(0) **2**, crystallisation of which gave yellow crystals in 74% yield, identical with those prepared from desilylation of tricarbonyl(η-6-ethyl-2-trimethylsilylpyridine)chromium(0) **3** (R = Me).[7] Repetition of the reaction, but this time using allyl bromide as the quenching agent resulted in an oil on work-up. This was shown to be tricarbonyl[η-2-(but-3-enyl)pyridine]chromium(0) **4**, again identical with the product prepared previously from **3** (R = allyl).[7] The intermediate in these reactions is presumed to be anion **5** whereby the negative charge is delocalised onto the tricarbonylchromium fragment.[5] In neither case was there any evidence for ring deprotonation, the base deprotonating only the methyl side chain (Scheme 1).

Interestingly, when ethyl iodide was used as an electrophile, starting complex **1** was recovered and no product formed. Presumably, in this case use of ethyl iodide did not give the alkylated product due to base-catalysed elimination of hydrogen iodide being a competing reaction.

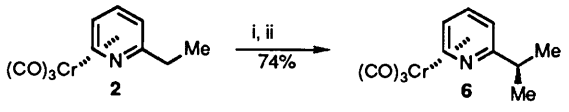
Of interest was the generation of the α-anion derived from tricarbonyl(η-2-alkylpyridine)chromium(0) complexes where the methyl group of complex **1** was replaced by some other alkyl group. For complexes bearing a methylene substituent at C-2 the methylene protons are diastereotopic, with the result that deprotonation/alkylation reactions can give rise to the possibility of forming two epimers at this position. Thus, it was of interest to see if any stereocontrol could be introduced at this centre by the presence of the sterically



Scheme 1 *Reagents and conditions:* i, LDA, −40 °C; ii, MeI; iii, CH_2=$CHCH_2Br$; iv, TBAF; H_2O

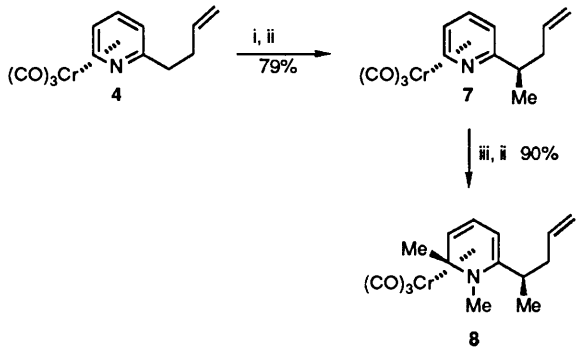
demanding tricarbonylchromium group and the adjacent heteroatom.

Treatment of tricarbonyl(η-2-ethylpyridine)chromium(0) **2** with 5 equiv. of lithium diisopropylamide at −40 °C by reverse addition* resulted (as in the case for complex **1**) in a dark red solution. After 2 h methyl iodide was added and the solution allowed to warm to room temperature with the resultant formation of a yellow–brown solution. Filtration through alumina and evaporation of the solvents gave a yellow gum. ^{1}H NMR spectroscopy showed four contiguous ring protons between δ 6.62 and 5.21 along with a 1 H septet at 2.83 due to the methine proton of the isopropyl group and two distinct doublets at δ 1.32 and 1.27, characteristic of the two diastereotopic methyl groups. A molecular ion at *m/z* 257 allowed assignment of the compound as tricarbonyl(η-2-isopropylpyridine)chromium(0) **6** (Scheme 2). This new compound was fully characterised.



Scheme 2 *Reagents and conditions:* i, LDA, −40 °C; ii, MeI

The above result indicates that complexes bearing 2-alkyl substituents can be deprotonated at the α-site if there is a methyl or other alkyl group present. Treatment of tricarbonyl[η-2-(but-3-enyl)pyridine]chromium(0) **4** with lithium diisopropylamide by reverse addition as before created a dark solution which was quenched with methyl iodide. Evaporation of the solvent, extraction of the residue with dichloromethane and evaporation of the extract afforded a yellow oil. ^{1}H NMR analysis of the latter crude product revealed the presence of a similar peak pattern to that of starting complex **4** but that there was only one α-proton in the mixture and a single methyl doublet at δ 1.27. The ^{1}H NMR spectrum of complex **7** was consistent with only a single diastereoisomer being produced, by removal of one of the α-protons with quenching of the anion away from the tricarbonylchromium moiety to give **7**. Complex **7** was purified by chromatography, as an oil, and was full characterised.



Scheme 3 *Reagents and conditions:* i, LDA, −40 °C; ii, MeI; iii, MeLi, −78 °C

At this stage, although a single diastereoisomer had been produced, nothing could be ascertained concerning its stereochemistry. X-Ray crystal structure analysis of **7** was out of the question, due to its physical nature. Treatment of **7** with methyllithium at −78 °C followed by addition of methyl iodide by the method described previously[4] gave a red solution which

* Addition of lithium diisopropylamide to solutions of tricarbonyl(η-2-alkylpyridine)chromium(0) complexes in the normal sense results in the formation of intractable material. This may be due to the resulting anion attacking undeprotonated material to give polymeric chains of dihydropyridine complexes. If the concentration of undeprotonated complex is kept to a minimum, this is avoided.

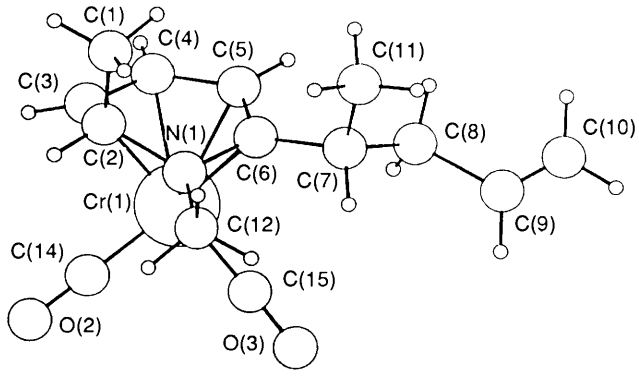
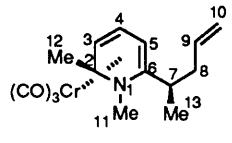


Fig. 1 The molecular structure of *SR(RS)*-tricarbonyl[*exo*-1,2-dimethyl-6-(pent-4-en-2-yl)-1,2-dihydropyridine]chromium(0) **8** as determined by X-ray crystallography

Table 1 Fractional atomic coordinates for *SR(RS)*-tricarbonyl[*exo*-1,2-dimethyl-6-(pent-4-en-2-yl)-1,2-dihydropyridine]chromium(0) **8**

Atom	*x/a*	*y/b*	*z/c*
Cr(1)	0.068 00(7)	0.090 15(4)	−0.037 03(5)
N(1)	−0.138 5(4)	0.071 9(2)	0.047 9(3)
C(1)	−0.187 5(7)	0.136 5(4)	0.238 5(4)
C(2)	−0.124 0(5)	0.154 6(3)	0.122 8(4)
C(3)	0.042 7(6)	0.175 4(3)	0.121 5(4)
C(4)	0.141 1(5)	0.102 5(4)	0.136 0(4)
C(5)	0.091 0(5)	0.009 0(3)	0.116 4(4)
C(6)	−0.050 2(5)	−0.007 6(3)	0.070 3(3)
C(7)	−0.115 0(5)	−0.105 0(3)	0.055 4(4)
C(8)	0.006 7(6)	−0.178 8(3)	0.029 2(7)
C(9)	−0.060 2(9)	−0.268 5(5)	−0.033 1(7)
C(10)	−0.067(1)	−0.342 1(6)	0.007(1)
C(11)	−0.198 3(7)	−0.131 5(4)	0.161 1(6)
C(12)	−0.287 5(5)	0.061 9(3)	−0.001 4(4)
C(13)	0.261 6(5)	0.096 1(3)	−0.083 2(4)
C(14)	0.011 1(5)	0.195 4(3)	−0.113 4(4)
C(15)	0.043 0(6)	0.020 4(3)	−0.162 7(4)
O(1)	0.384 8(4)	0.098 2(3)	−0.116 8(4)
O(2)	−0.031 7(5)	0.261 4(3)	−0.160 0(4)
O(3)	0.036 1(5)	−0.021 4(3)	−0.244 8(3)

Table 2 Selected bond and torsional angles (°) for *SR(RS)*-tricarbonyl-[*exo*-1,2-dimethyl-6-(pent-4-en-2-yl)-1,2-dihydropyridine]chromium(0) **8** (using systematic atom numbering)



8

C(6)–N(1)–C(2)	118.2(3)	C(5)–C(4)–C(3)	119.1(4)
C(3)–C(2)–N(1)	103.5(3)	C(6)–C(5)–C(4)	120.5(4)
C(4)–C(3)–C(2)	118.5(4)	C(5)–C(6)–N(1)	116.4(4)

N(1)–C(6)–C(7)–C(13)	−85.1
C(11)–N(1)–C(6)–C(5)	179.5
C(11)–N(1)–C(2)–C(3)	−155.7
C(11)–N(1)–C(2)–C(12)	80.6
C(13)–C(7)–C(6)–C(5)	88.2
C(12)–C(2)–C(3)–C(4)	75.5

was shown by ^{1}H NMR spectroscopy to be the tricarbonyl(η-1,2-dihydropyridine)chromium(0) complex **8** resulting from attack of methyllithium at the vacant 6-position. The spectrum contained, as well as the four contiguous ring protons, an *N*-methyl singlet at δ 2.71, doublets at δ 1.25 and 0.60 corresponding to the α-methyl and *exo*-ring-methyl group derived from attack by the methyllithium. Work-up and

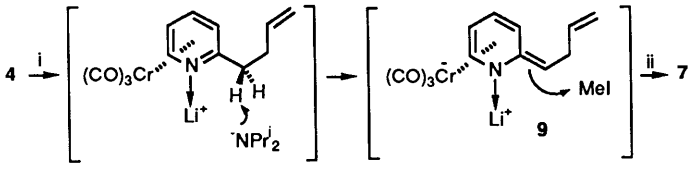


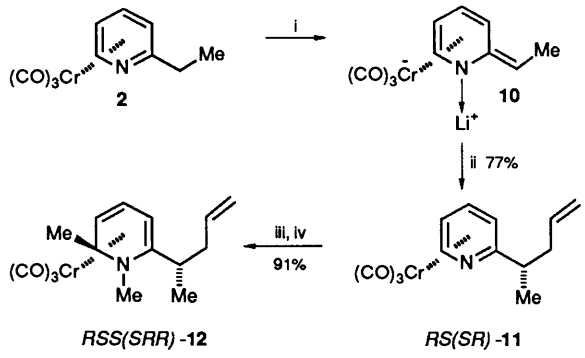
Fig. 2 *Reagents and conditions:* i, LDA, −40 °C; ii, MeI

crystallisation gave **8** in 9% yield which was fully characterised including elemental analysis (Scheme 3). A single crystal suitable for an X-ray structure determination was obtained by three recrystallisations of complex **8** from dichloromethane–heptane. Fig. 1 shows the X-ray crystal structure of *SR*(*RS*)-tricarbonyl[*exo*-1,2-dimethyl-6-(pent-4-enyl-2-yl)-1,2-dihydropyridine]chromium(0). Table 1 lists the final atomic coordinates for **8** and selected bond angles and torsional angles are given in Table 2.

The structure of **8** clearly shows that the four carbon atoms C(3)–C(6) of the diene system and the nitrogen atom lie in a plane above the tricarbonylchromium moiety and that the distances between these five atoms and the chromium atom are approximately the same, whilst the tetrahedral carbon atom C-2 is displaced above this plane away from the tricarbonylchromium unit. The *exo*-nature of the addition of methyllithium to the pyridine complex **7** is apparent and is consistent with alkyllithium reagents approaching, as expected,[8] away from the sterically demanding tricarbonylchromium unit. Although completely stereoselective nucleophilic additions to tricarbonyl(η-pyridine)chromium(0) complexes has been reported this provides the first unambiguous assignment of the *exo* stereochemistry.

The stereochemistry about the α-site is consistent with deprotonation of **4** to generate the *E*-anion **9** which is subsequently methylated from the face away from the bulky tricarbonylchromium. Formation of the anion **9** is consistent with coordination of the nitrogen atom of the pyridine ring to the lithium diisopropylamide with the sterically demanding butenyl side chain lying *anti*- to the pyridine nitrogen. This places the two diastereotopic methylene protons in different steric environments, with the *exo*-proton away from the tricarbonylchromium unit being the only one of the two which is accessible to the relatively bulky lithium diisopropylamide. The result of this is the generation of the anion **9**, which due to its exocyclic double bond nature, is stereochemically rigid at −40 °C. Quenching with methyl iodide results in attack of the electrophile from the unhindered face of **9** to afford the methylated complex *RR*(*SS*)-tricarbonyl[η-2-(pent-4-en-2-yl)pyridine]chromium(0) **7**.* This is shown in Fig. 2.

The epimer of complex **7** was prepared as follows. Deprotonation of tricarbonyl(η-2-ethylpyridine)chromium(0) **2** in the normal fashion gave the resonance stabilised anion **10**. Treatment of this anion with allyl bromide gave, on work-up and chromatography, a single yellow band which was evaporated to provide a yellow oil. ^{1}H NMR analysis of this product revealed the presence of peaks which were, in general, similar to those of complex **7**, but the methyl doublet at δ 1.27 was completely absent and was replaced by a similar doublet at δ 1.31. This led to the assignment of the product as being *RS*(*SR*)-tricarbonyl[η-2-(pent-4-en-2-yl)pyridine]chromium(0) **11**,* the epimer to complex **7**, formed completely stereoselectively in 77% yield, as a yellow oil which could not be crystallised. The formation of this diastereoisomer is consistent with deprotonation of complex **2** to give the anion **10** with the β-methyl group positioned in a plane *anti*- to the nitrogen of the pyridine ring by analogy with anion **9**. Subsequently, complex **11** was treated with methyllithium followed by methyl iodide to afford exclusively the corresponding tricarbonyl(η-1,2-dihydropyridine)chromium(0) complex **12**, as a red solid in 90% yield (Scheme 4). Crystallisation from dichloromethane–hexane gave red needles, which were fully characterised. The ^{1}H NMR spectrum of this dihydropyridine complex was similar to that of the complex **8** except that the *N*-methyl singlet appeared at δ 2.71, the α-methyl group was at δ 1.36 and the *exo*-methyl group on the ring was a δ 0.61 showing the differing relative stereochemistry in this complex compared to that of its diastereoisomer **8**.



Scheme 4 *Reagents and conditions:* i, LDA, −40 °C; ii, CH_2=CH-CH_2Br; iii, MeLi, −78 °C; iv, MeI

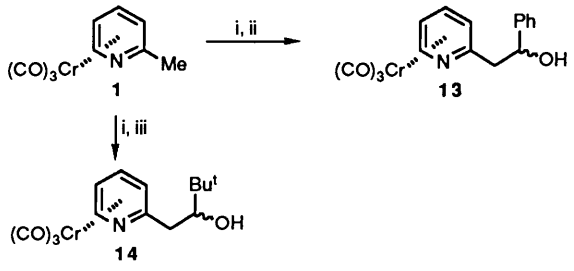
The above results show that the anions derived from tricarbonyl(η-2-alkylpyridine)chromium(0) complexes are stereochemically rigid under the reaction conditions employed, quenching with the electrophile generating a single epimer at the newly formed α-chiral centre. It was thus of interest to generate these anions as before but this time employ a prochiral electrophile in order to allow the possibility of forming a β-chiral centre stereoselectively. The obvious choice for such a reaction would be an aldehyde in an aldol-type condensation with anions such as **5** and **10**.

The aldol reaction, which involves the nucleophilic attack of an enolate species onto a carbonyl group, is perhaps the most fundamental carbon–carbon bond-forming reaction. The scope and stereochemical aspects of this reaction have been exhaustively reviewed.[9,10]

Generation of the anion **5** from **1** as before at −40 °C, followed by cooling the resultant dark solution to −78 °C and the addition of an excess of benzaldehyde resulted in the solution rapidly becoming light brownish yellow. Addition of methanol, warming to room temperature, filtration of the solution through alumina and evaporation of the solvent gave a yellow solid. The ^{1}H NMR spectrum of this product showed the presence of two sets of peaks in the ratio 67:33, along with a little recovered starting material. Features of this spectrum

* There are no formal rules for assignment of the configuration of tricarbonyl(pyridine)chromium(0) complexes. The configuration of the N-atoms using the normal priority rules unambiguously defines the configuration and this convention is used throughout. For a description of the Cahn-Ingold-Prelog notation as applied to chiral metallocenes see K. Schlögl, *Top. Stereochem.*, 1967, **1**, 39. Where a tricarbonyl(pyridine)chromium(0) complex has a chiral alkyl side chain, the nitrogen atom of the pyridine ring has priority, and the ordering of the substituents around this nitrogen atom is such that the lone pair has least priority. The stereochemistry due to the ring is noted first, then the relative stereochemistry within the alkyl side-chain. In the case of dihydropyridine complexes the stereochemistry of the tetrahedral carbon atoms on the ring at the 2-position is noted first before the chirality at the side chain. The use of the term *exo* in conjunction with the defined stereochemistry of the tetrahedral ring carbon and the side chain of dihydropyridine complexes renders the planar chirality of the ring redundant, and for clarity is omitted. In all cases the stereochemistry is denoted as drawn in the text, the other enantiomer being placed in brackets, *e.g. SR*(*RS*).

included the presence of four contiguous complexed ring protons and a 5 H multiplet at δ 7.44–7.30 indicative of a phenyl group. Also present were sets of apparent doublets at δ 3.04 and 2.96 together with a minor set at δ 3.09 and 2.91, corresponding to the two sets of diastereoisomeric methylene protons and broad 1 H resonances at δ 5.17 and 5.14 also in the ratio 67:33. Another broad resonance at δ 3.50 suggested that a hydroxy group was present. This was confirmed by a broad band in the IR region at 3400 cm^{-1} along with bands at 1991 and 1920 cm^{-1} due to the tricarbonylchromium unit. This led to the assignment of the product as a 67:33 mixture of the two diastereoisomers of the complex **13** formed by attack of the anion **5** on benzaldehyde to generate the aldol-type product (Scheme 5). Chromatography failed to separate the two diastereoisomers, as did attempts at fractional crystallisation. Thus, although the mixture was fully characterised, including by elemental analysis, the stereochemistry of the major diastereoisomer could not be assigned.

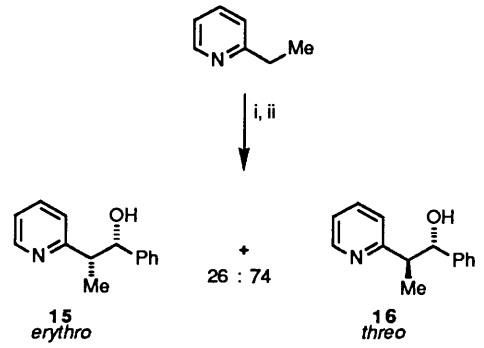


Scheme 5 *Reagents and conditions:* i, LDA, −40 °C; ii, PhCHO; iii, Bu^{t}CHO

The reaction was repeated, but instead of using benzaldehyde, pivalaldehyde was employed. This resulted again in the aldol product, this time as a 55:45 mixture of the two possible diastereoisomers of complex **14** which could not be separated (Scheme 5). The ^{1}H NMR spectrum of the major component contained four contiguous ring protons along with two mutually coupled 1 H resonances at δ 4.01 and 1.69 corresponding to the CH(OH) protons and a 9 H singlet at 0.98 due to the *tert*-butyl group. The minor component was similar in its ^{1}H NMR spectrum, except that the CH(OH) protons had resonances at δ 3.86 and 1.86, and the *tert*-butyl resonance appeared at 0.99. The stereochemistry of the major diastereoisomer could not be assigned but, as before, the mixture was fully characterised. All attempts to repeat this reaction using enolisable aldehydes such as acetaldehyde resulted only in the re-isolation of starting complex **1**, presumably due to the basic nature of the anion **5** derived from **1**.

The reactions described above had the possibility of forming only one chiral centre β- to the ring in the product, however, utilising tricarbonyl(η-2-ethylpyridine)chromium(0) **2** in these types of reactions allows the formation of two such centres both α- and β- to the ring. Furthermore, it was expected that the extra methyl group would perhaps create greater stereocontrol, as it has been found that propionate enolates are more steroselective in aldol reactions than their acetate counterparts.[11]

Reaction of uncomplexed 2-ethylpyridine with lithium diisopropylamide followed by quenching with benzaldehyde has been reported in the literature[12] as affording a 1:3 mixture of the *erythro*- and *threo*- aldol-type products **15** and **16**. The predominance of the *threo*-isomer was explained by invoking a six-membered closed transition state where both the phenyl and methyl group are sitting equatorially, giving the major diastereoisomer **16**. The minor product **15** was accounted for by considering the methyl group to be axial in the transition state, which is sterically less favourable.[12] For a description of this and a comparison with the complexed pyridine derivative *vide infra*. This reaction was repeated and identical results were obtained to those reported (Scheme 6). The two diastereo-



Scheme 6 *Reagents and conditions:* i, LDA, −40 °C; ii, PhCHO

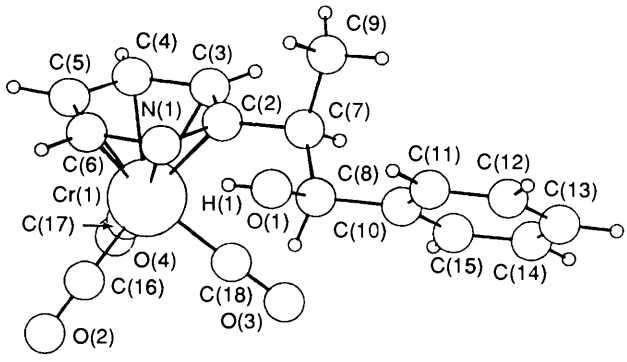
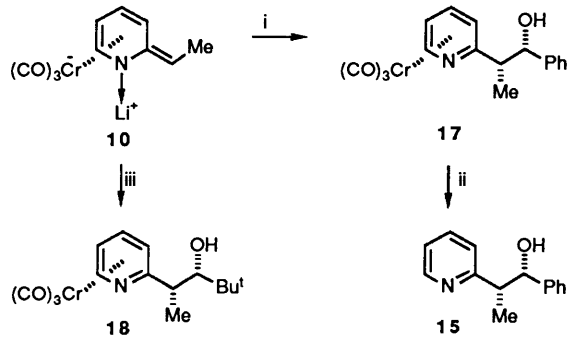


Fig. 3 The molecular structure of *RSS*(*SRR*)-tricarbonyl[*erythro*-2-η-(2-pyridyl)-1-phenylpropanol]chromium(0) **17** as determined by X-ray crystallography

isomers **15** and **16** could be separated by flash chromatography and isolated pure. The ^{1}H NMR data for these compounds were in good agreement with those reported previously.

Repetition of the reaction utilising complex **2** (Scheme 7) gave, after quenching the dark enolate **10** with benzaldehyde, a deep yellow–brown solution. Filtration of this solution through alumina and evaporation gave a yellow gum. The ^{1}H NMR spectrum of this product showed the presence of a 5 H multiplet at δ 7.41–7.26 along with four contiguous ring protons between δ 6.61 and 5.21. A single doublet of quartets at δ 2.99 along with an associated 3 H doublet at δ 1.18 suggested the formation of essentially a single diastereoisomeric product by 300 MHz ^{1}H NMR. The formation of the aldol-type product was supported by a band at 3400 cm^{-1} in the IR spectrum. From this data it was however impossible to assign the stereochemistry of the product. Repeated recrystallisation of the product from dichloromethane–hexane gave single crystals suitable for X-ray crystallographic analysis. Fig. 3 shows the X-ray crystal structure of *RSS*(*SRR*)-tricarbonyl[*erythro*-2-η-(2-pyridyl)-1-phenylpropanol]chromium(0) **17**. Table 3 lists the final atomic coordinates for **17** and selected bond angles and torsional angles are given in Table 4.

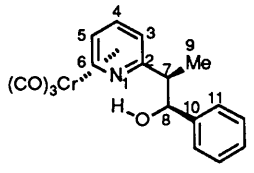


Scheme 7 *Reagents and conditions:* i, PhCHO; ii, O_2, *hν*; iii, Bu^{t}CHO

Table 3 Fractional atomic coordinates for *RSS*(*SRR*)-tricarbonyl-[*erythro*-2-η-(2-pyridyl)-1-phenylpropanol]chromium(0) **17**

Atom	*x/a*	*y/b*	*z/c*
Cr(1)	−0.215 61(3)	−0.145 72(6)	−0.114 34(4)
N(1)	−0.217 9(2)	−0.128 5(3)	−0.290 5(2)
O(1)	−0.099 2(2)	−0.287 7(3)	−0.371 4(3)
H(1)	−0.118(4)	−0.208(7)	−0.357(5)
O(2)	−0.078 2(2)	0.106 7(3)	0.009 1(3)
O(3)	−0.253 6(2)	−0.154 9(3)	0.101 1(2)
O(4)	−0.084 3(2)	−0.410 4(3)	0.000 8(2)
C(2)	−0.249 7(2)	−0.279 8(4)	−0.277 6(2)
C(3)	−0.320 6(2)	−0.298 3(4)	−0.238 7(3)
C(4)	−0.360 3(2)	−0.157 1(5)	−0.213 1(3)
C(5)	−0.330 0(2)	−0.001 7(5)	−0.231 6(3)
C(6)	−0.258 3(2)	0.005 9(4)	−0.267 3(3)
C(7)	−0.210 3(2)	−0.429 2(4)	−0.313 0(2)
C(8)	−0.111 5(2)	−0.410 1(4)	−0.297 5(3)
C(9)	−0.269 0(3)	−0.472 8(6)	−0.436 8(3)
C(10)	−0.074 7(2)	−0.570 9(4)	−0.320 0(3)
C(11)	−0.054 7(2)	−0.594 9(4)	−0.417 7(3)
C(12)	−0.021 0(3)	−0.744 2(5)	−0.435 7(3)
C(13)	−0.006 5(2)	−0.869 8(5)	−0.358 1(3)
C(14)	−0.027 0(3)	−0.846 2(5)	−0.260 6(3)
C(15)	−0.059 7(2)	−0.697 3(5)	−0.241 9(3)
C(16)	−0.130 4(2)	0.010 5(4)	−0.040 6(3)
C(17)	−0.241 0(2)	−0.150 2(4)	0.016 3(3)
C(18)	−0.133 8(2)	−0.307 9(4)	−0.045 1(3)

Table 4 Selected bond angles and torsional angles (°) for *RSS*(*SRR*)-tricarbonyl[*erythro*-2-η-(2-pyridyl)-1-phenylpropanol]chromium(0) **17** (using systematic atom numbering)



17

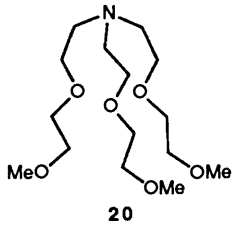
C(6)–N(1)–C(2)	118.0(3)	C(5)–C(4)–C(3)	118.9(3)
C(3)–C(2)–N(1)	121.7(3)	C(6)–C(5)–C(4)	118.3(3)
C(4)–C(3)–C(2)	119.1(3)	C(5)–C(6)–N(1)	123.8(3)

N(1)–C(2)–C(7)–C(8)	31.4
N(1)–C(2)–C(7)–C(9)	−94.1
C(2)–C(7)–C(8)–O(1)	−65.4
C(2)–C(7)–C(8)–C(10)	172.3
C(9)–C(7)–C(8)–C(10)	−63.9
C(7)–C(8)–C(10)–C(11)	108.9

The results of the X-ray determination on **17** clearly show the *erythro*-[13] stereochemistry of the two contiguous α- and β-chiral centres of the aldol-type product, in contrast to the stereochemistry of the major product obtained in the parallel reaction with uncomplexed material. The planar nature of the complexed pyridine ring is also evident, the tricarbonylchromium tripod sitting below the centroid of the almost regular hexagon. In the solid state the β-hydroxy group hydrogen bonds to the pyridine nitrogen [2.17(5) Å]. The single diastereoisomeric product **17** was fully characterised, including elemental analysis. Exposure of an ether solution of the product obtained in this last reaction to air and sunlight resulted, after filtration from the chromium residues and evaporation of solvent a colourless gum. ^{1}H NMR analysis of this product revealed it to be the *erythro*-diasteroisomer **15** identical with an authentic sample prepared by the literature method[12] (Scheme 6). This confirms the original literature stereochemical assignment, which had been deduced from ^{1}H NMR data, of the major diastereoisomer derived from the uncomplexed reaction.

The reaction was repeated this time using pivalaldehyde as the electrophile (Scheme 7), and again a single diasteroisomeric product was obtained. This exhibited along with the four contiguous ring protons in the ^{1}H NMR spectrum, a single methyl doublet at δ 1.35 and a single Bu^t singlet at δ 1.05, identifying the complex as the aldol type product **18**. The relative stereochemistry was assigned as being the same as that of the related complex **17**. Attempts to repeat these reactions on enolisable aldehydes only met with recovered starting complex **2**, as in the case of the anion **5** derived from complex **1**, showing the somewhat basic nature of the anion **10**.

The origin of the high degree of stereocontrol in these aldol-type reactions may now be addressed. The lack of selectivity for the lithium anion **5** can be accounted for by consideration of the fact that, in common with the enolates derived from methyl ketones, the reactivity is increased due to the presence of sterically undemanding hydrogen atoms. This increased reactivity has the effect of lowering any selectivity for the reaction, hence the low selecivity observed in the reaction of the anion **5** with the aldehydes as described earlier. The question of the transition state for the remarkable degree of stereocontrol in the reaction of the anion **10** with non-enolisable aldehydes now arises. In the reaction of the anion derived from 2-ethylpyridine with benzaldehyde, the predominance of the *threo*-product **16** was explained by invoking a six-membered closed-chair transition state **19** with the phenyl group of the benzaldehyde and the methyl group of the ethyl side-chain of the pyridine ring equatorial.[12] In order to show that a six-membered closed-transition state was likely to be in operation, in accord with the literature explanation, the reaction was repeated but this time the complexing agent TDA-1 **20** (see Fig. 4) was added before the addition of the benzaldehyde. This reagent is known to form very stable 1:1 complexes with Li^+ ions[14] and so addition of the reagent should have the effect of altering the selectivity of any reaction under chelation control by Li^+. Thus, prior addition of **20** to the reaction mixture followed by warming to 0 °C, re-cooling, and addition of benzaldehyde resulted in the selectivity of the addition reducing to give a 43:57 ratio of *erythro*- to *threo*-products **15** and **16**. This lends support to the closed transition state for this reaction.[12]



20

Fig. 4 TDA-1 **20**

Due to the electron-withdrawing nature of the tricarbonylchromium moiety the likelihood of chelation control in a six-membered transition in the reaction of the anion **10** with benzaldehyde is remote and here it would be better to invoke an alternative open transition state.[15] This was tested by repeating the reaction, but this time before the aldehyde was added the anion was treated with an excess of TDA-1 **20**. Work-up as before gave a yellow gum which was exposed without further purification, as an ether solution, to air and sunlight. ^{1}H NMR analysis of the crude reaction mixture revealed that only *erythro*-diastereoisomer **15** was present. That TDA-1 had no effect on the stereochemical outcome of the reaction indicates that a chelated transition state is perhaps unlikely to be involved. As in the case of the reaction with tricarbonyl(η-2-methylpyridine)-chromium(0) **1**, where the negative charge of the anion **5** would be withdrawn into the tricarbonylchromium moiety, an open transition state would seem most appropriate for anion **10**.

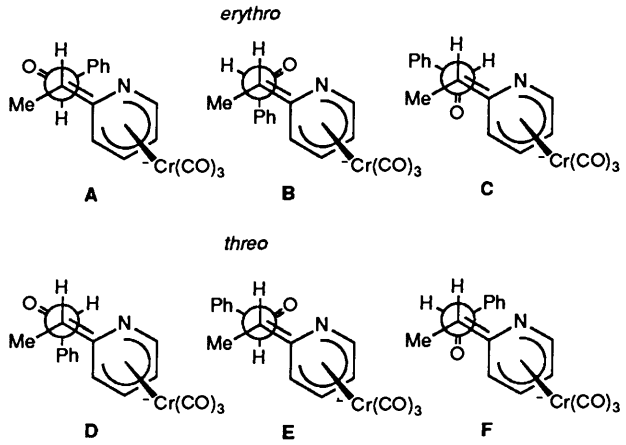


Fig. 5 Possible transition states for the reaction of the anion **10** with benzaldehyde.

The Newman projections of the six most likely open transition states can be drawn out showing the possible orientations of the anion **10** to benzaldehyde, leading to the *erythro*- and *threo*-products, and are shown in Fig. 5. Out of these six transition states, **B** and **E** where the carbonyl of the benzaldehyde is adjacent to the nitrogen of the pyridine ring are disfavoured on dipole–dipole repulsion arguments, also in **B** there is steric repulsion between the pyridine ring and phenyl ring of the benzaldehyde. Transition states **A**, **D** and **F** can also be discounted due to the bad steric interactions between these two moieties. Out of this, only **C**, which leads to the observed isomer, is favoured because the phenyl ring is *anti*- to the pyridine ring and the carbonyl is away from the pyridine nitrogen. The nature of aggregation in various lithium enolates has been extensively studied,[16] but the nature of the enolates derived from both tricarbonyl(η-2-methylpyridine)chromium-(0) **1** and tricarbonyl(η-2-ethylpyridine)chromium(0) **2** was beyond the scope of this study.

Conclusion

It has been shown that deprotonation of the α-protons of 2-alkyl substituted pyridine tricarbonylchromium complexes can be effected with lithium diisopropylamide and that in the case of the anion derived from tricarbonyl(η-2-ethylpyridine)-chromium(0) **2** the stereochemistry is controlled, resulting in the production of single diastereoisomers on quenching with electrophiles. The geometry of this anion **10** was elucidated from X-ray crystallographic evidence relating to the derived alkylation and aldol-type products. In the case of aldol-type reactions, there was little stereocontrol where tricarbonyl(η-2-methylpyridine)chromium(0) **1** was employed, but with tricarbonyl(η-2-ethylpyridine)chromium(0) **2** the control was complete. The relative stereochemistry within the side chain was shown to be *erythro*- by X-ray crystallography, and comparison of the ^{1}H NMR data of the decomplexed products with those of samples prepared by the literature procedure showed the previous assignment of stereochemistry of these compounds to be correct.

Experimental

General.—All reactions and purifications involving organometallic reagents were carried out under an atmosphere of nitrogen using vacuum line and Schlenk tube techniques [17] and all solvents were deoxygenated. For reactions with organic materials, no special conditions were used unless otherwise stated. All solvents were removed under reduced pressure. Tetrahydrofuran and ether were distilled from sodium benzophenone ketyl under nitrogen and dichloromethane was distilled from calcium hydride under nitrogen. Light petroleum refers to the fraction boiling in the range 40–60 °C and hexane between 67–70 °C. Butyllithium was used as a 1.4 mol dm^{-3} solution in hexane and lithium diisopropylamide as a 1.5 mol dm^{-3} solution in cyclohexane. All other reagents were used as received or purified by standard methods.[18] Flash chromatography was performed on silica gel (43–60 μm) under a positive nitrogen pressure. Alumina used in filtrations was deactivated grade V.

^{1}H NMR spectra were recorded in deuteriochloroform unless otherwise stated on a Brüker WH 300 at 300.13 MHz spectrometer. IR spectra were obtained as chloroform solutions in 0.1 mm cells on a Perkin-Elmer 781 instrument calibrated against polystyrene (1601 cm^{-1}) unless otherwise stated and for clarity only salient, characteristic peaks are noted. Mass spectra were obtained on a V.G. Micromass ZAB 1F instrument using electron impact or chemical ionization techniques. M.p.s were obtained on a Gallenkamp hot-stage melting-point apparatus and are uncorrected. Elemental analyses were obtained by the Dyson Perrins analytical department.

Complexes **1**, **2** and **4** were prepared as previously described.[7]

General Procedure for Alkylation of Tricarbonyl(η-2-alkylpyridine)chromium(0) Complexes with Lithium Diisopropylamide and Alkyl Halides.—To lithium diisopropylamide (*ca.* 5 equiv.) in tetrahydrofuran (10 ml) at −40 °C was added the relevant tricarbonyl(η-2-alkylpyridine)chromium(0) complex in tetrahydrofuran (5 ml) dropwise *via* a cannula over a period of 1 h, resulting in the production of a dark brown solution. The solution was stirred (−40 °C; 1 h) and then the relevant alkyl halide added (*ca.* 5 equiv.) and the solution allowed to warm (20 °C) resulting in a yellow-brown solution. Solvent was evaporated, the residue extracted (dichloromethane, 2 × 10 ml), filtered through alumina, and the solvent evaporated to give the crude product as an oil or gum. This was further purified by flash chromatography, eluting with a light petroleum–ether solvent system to afford the alkylated complex. Further purification by recrystallisation was carried out where required.

Methylation of tricarbonyl(η-2-methylpyridine)chromium(0). **1**. To lithium diisopropylamide (1.45 ml, 2.2 mmol) was added tricarbonyl(η-2-methylpyridine)chromium(0) **1** (100 mg, 0.437 mmol) followed by electrophilic quench with methyl iodide (0.5 ml, excess) according to the general procedure. Work-up (eluent: 1:2) and recrystallisation from isopentane gave tricarbonyl(η-2-ethylpyridine)chromium(0) **2** (78 mg, 74%), identical with the previously prepared sample.[7]

Allylation of tricarbonyl(η-2-methylpyridine)chromium(0) **1**. To lithium diisopopylamide (1.3 ml, 2.0 mmol) was added tricarbonyl(η-2-methylpyridine) chromium(0) **1** (70 mg, 0.305 mmol) followed by electrophilic quench with allyl bromide (0.5 ml, excess) according to the general procedure. Work-up (eluent 1:1) gave tricarbonyl[η-2-but-3-enyl)pyridine]-chromium(0) **4** as an oil (58 mg, 71%), identical the previously prepared sample.[7]

Methylation of tricarbonyl(η-2-ethylpyridine)chromium(0) **2**. To lithium diisopropylamide (1.45 ml, 2.2 mmol) was added tricarbonyl(η-2-ethylpyridine)chromium(0) **2** (50 mg, 0.205 mmol) followed by electrophilic quench with methyl iodide (0.5 ml, excess) according to the general procedure. Work-up (eluent: 3:2) and recrystallisation from isopentane gave *tricarbonyl(η-2-isopropylpyridine)chromium(0)* **6** (39 mg, 74%); m.p. 75 °C (decomp.); ν_{max}/cm^{-1} 1989 and 1918 (CO); δ_H 6.62 (1 H, br d, *J* 3.7, 6-H), 5.67 (1 H, dt, *J* 1.5 and 6.5, 4-H), 5.26 (1 H, d, *J* 6.5, 3-H), 5.21 (1 H, m, 5-H), 2.83 (1 H, sep, *J* 6.9, C*H*Me$_2$), 1.32 (3 H, d, *J* 6.9, CH*Me*$_2$), 1.27 (3 H, d, *J* 6.9,

$CHMe_2$); *m/z* 257 (M^+) (Found: C, 51.6; H, 4.3; N, 5.7. $C_{11}H_{11}CrNO_3$ requires C, 51.4; H, 4.4; N, 5.45%).

Methylation of tricarbonyl[η-2-(*but*-3-*enyl*)*pyridine*]-*chromium*(0) **4**. To lithium diisopropylamide (1.45 ml, 2.2 mmol) was added tricarbonyl[η-2-(but-3-enyl)pyridine]chromium(0) **4** (100 mg, 0.372 mmol) followed by electrophilic quench with methyl iodide (0.5 ml, excess) according to the general procedure. Work-up (eluent: 2:1) gave RR(SS)-*tricarbonyl*[2-(*pent*-4-*en*-2-*yl*)*pyridine*]*chromium*(0) **7** as a yellow oil (77 mg, 79%); ν_{max}/cm^{-1} 1985 and 1913 (CO); δ_H 6.60 (1 H, br d, *J* 4.0, 6-H), 5.80 (1 H, m, CH=CH_2), 5.61 (1 H, t, *J* 6.2, 4-H), 5.23 (2 H, m, 3-H and 5-H), 5.08–5.01 (2 H, m, CH=CH_2), 2.75 [2 H, sex, *J* 6.8, C*H*(Me)CH_2], 2.50–2.21 [2H, m, CH(Me)CH_2] and 1.27 (3 H, d, *J* 6.8, CH*Me*); *m/z* 284 (M^+ + 1) (Found: C, 55.4; H, 4.3. $C_{13}H_{13}CrNO_3$ requires C, 55.1; H, 4.6%).

SR(RS)-*Tricarbonyl*[exo-1,2-*dimethyl*-6-(*pent*-4-*en*-2-*yl*)-1,2-*dihydropyridine*]*chromium*(0) **8**.—*RR*(*SS*)-Tricarbonyl[2-(pent-4-en-2-yl)pyridine]chromium(0) **7** (50 mg, 0.176 mmol) in tetrahydrofuran (10 ml) at −78 °C was treated with methyllithium (0.2 ml, 0.2 mmol) and the mixture stirred (1 h). Methyl iodide (0.1 ml, excess) was added, the solution allowed to warm (20 °C) and solvent evaporated to give a red residue. Extraction (dichloromethane, 2 × 10 ml) and evaporation gave on chromatography (eluent 1:1) **8** which recrystallised as orange–red blocks from isopentane (49 mg, 90%); m.p. 121 °C (decomp.); ν_{max}/cm^{-1} 1960, 1881 and 1844 (CO); δ_H 5.91 (1 H, m, CH=CH_2), 5.49 (1 H, d, *J* 5.8, 5-H), 5.16 (3 H, m, CH=CH_2 and 4-H), 3.94 (1 H, t, *J* 5.8, 3-H), 3.50 (2 H, m, C*H*(Me)CH_2 and 2-H), 2.71 (3 H, s, N-Me), 2.41–2.20 [2 H, m, CH(Me)CH_2], 1.25 (3 H, d, *J* 6.5, CH*Me*) and 0.60 (3 H, d, *J* 6.4, 2-Me); *m/z* 314 (M^+ + 1) (Found: C, 57.4; H, 6.2; N, 4.5. $C_{15}H_{19}CrNO_3$ requires C, 57.5; H, 6.1; N, 4.5%). Three recrystallisations of this compound from dichloromethane–heptane gave single crystals of two distinct morphologies, one of which was suitable for X-ray cryatal structure determination.

Crystal data for compound **8**. $C_{15}H_{19}CrNO_3$, M = 313.32, orthorhombic, $P = 2_12_12_1$ (No. 19), a = 8.914(1), b = 14.252(2), c = 12.047(9) Å (from least squares fitting of setting angles for 25 reflections $21.5 \leq \theta \leq 39.5°$), V = 1534 Å^3, Z = 4, D_x = 1.357 g cm^{-3}, Cu-Kα radiation, orange triangular prismatic crystal 0.4 × 0.4 × 0.3 mm (base × height × depth), μ = 62.84 cm^{-1}, crystal sealed in Lindemann glass capillary.

Data collection and processing. Data were collected on a CAD-4F diffractometer in ω:2 θ mode, $0 < 2\theta \leq 150°$, ($-3 \leq h \leq 11$, $-4 \leq k \leq 17$, $-15 \leq l \leq 15$). 5267 Reflections measured, 2875 unique (R_{merge} = 0.036, Friedel pairs were not merged) of which 2295 were observed ($I \geq 3\sigma I$). No significant variation in intensity of 3 check reflections was observed.

Structure solution and refinement. The structure was solved by heavy atom methods[19] which yielded coordinates for all non-hydrogen atoms except C(9) and C(10). Refinement of the model was undertaken using the CRYSTALS program package.[20] Difference electron density consistent with two partially occupied sites for each of C(9) and C(10) was observed but refinement of a disordered model was unsatisfactory, these atoms being best described by single sites with large thermal parameters. The short C(9)–C(10) bond length 1.16(1) Å is a consequence of this treatment. Full matrix least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for each H-atom type [with the exception of those bonded to C(9) and C(10)] was continued until convergence, the H-atom coordinates were geometrically calculated. A Flack enantiopole[21] was also included in the refinement and converged to a value of 0.42(1), this is attributed to merohedral twinning [the presence of both (+) and (−) crystals with the twin operator being inversion]. An empirical absorption correction[22] based on θ was applied (min. 0.834, max. 1.277) and 4-term Chebychev polynomial weighting scheme was employed. At convergence R = 0.045, R_w = 0.053 for 189 parameters [$R = \Sigma w|\Delta|(\Sigma wF_o)^{-1}$, $R_w = \Sigma w\Delta_i^2(\Sigma wF_{o_i}^2)^{-1}$].

Allylation of tricarbonyl(η-2-*ethylpyridine*)*chromium*(0) **2**.—To lithium diisopropylamide (1.45 ml, 2.2 mmol) was added tricarbonyl(η-2-ethylpyridine)chromium(0) **2** (50 mg, 0.205 mmol) followed by electrophilic quench with allyl bromide (0.5 ml, excess) according to the general procedure. Work-up (eluent 1:1) gave RS(SR)-*tricarbonyl*[2-(*pent*-4-*en*-2-*yl*)-*pyridine*]*chromium*(0) **11** as a yellow oil (48 mg, 77%); ν_{max}/cm^{-1} 1984 and 1913 (CO); δ_H 6.62 (1 H, br d, *J* 4.0, 6-H), 5.76 (1 H, m, CH=CH_2), 5.66 (1 H, dt, *J* 1.4 and 6.5, 4-H), 5.24 (1 H, d, *J* 6.5, 3-H), 5.20 (1 H, m, 5-H), 5.06–5.00 (2 H, m, CH=CH_2), 2.77 [2 H, m, C*H*(Me)CH_2], 2.49 [1 H, m, CH(Me)CH_2], 2.26 [1 H, m, CH(Me)CH_2] and 1.31 [3 H, d, *J* 7.0, CH(*Me*)CH_2]; *m/z* 284 (M^+ + 1) (Found: C, 55.2; H, 4.3. $C_{13}H_{13}CrNO_3$ requires C, 55.1; H, 4.6%).

SS(RR)-*Tricarbonyl*[exo-1,2-*Dimethyl*-6-(*pent*-4-*en*-2-*yl*)-1,2-*dihydropyridine*]*chromium*(0) **12**.—*RS*(*SR*)-Tricarbonyl[2-(pent-4-en-2-yl)pyridine]chromium(0) **11** (50 mg, 0.176 mmol) was treated with methyllithium (0.2 ml, 0.2 mmol) and the mixture stirred (1 h). Methyl iodide (0.1 ml, excess) was added, the solution allowed to warm (20 °C) and the solvent evaporated to give a red residue. Extraction (dichloromethane, 2 × 10 ml) of the latter and evaporation of the extract gave, on chromatography (eluent 1:1) of the residue, **12** which was recrystallised as orange–red blocks from isopentane (50 mg, 91%); m.p. 116 °C (decomp.); ν_{max}/cm^{-1} 1951, 1872 and 1840 (CO); δ_H 5.84 (1 H, m, CH=CH_2), 5.53 (1 H, dd, *J* 1.5 and 5.7, 5-H), 5.18–5.10 (3 H, m, CH=CH_2 and 4-H), 3.84 (1 H, m, 3-H), 3.51 [2 H, m, C*H*(Me)CH_2 and 2-H], 2.74 (3 H, s, N-Me), 2.38 [1 H, m, CH(Me)CH_2], 2.19 [1 H, m, CH(Me)CH_2], 1.36 [3 H, d, *J* 6.5, CH(*Me*)CH_2], 0.61 (3 H, d, *J* 6.4, 2-Me); *m/z* 314 (M^+ + 1) (Found: C, 57.1; H, 6.2; N, 4.2. $C_{15}H_{19}CrNO_3$ requires C, 57.5; H, 6.1; N, 4.5%).

General Procedure for Reaction of Tricarbonyl(η-2-*alkylpyridine*)*chromium*(0) *Complexes with Lithium Diisopropylamide and Aldehydes*.—To lithium diisopropylamide (*ca.* 5 equiv.) in tetrahydrofuran (10 ml) at −40 °C was added the relevant tricarbonyl(η-2-alkylpyridine)chromium(0) complex in tetrahydrofuran (5 ml) dropwise *via* a cannula over a period of 1h, resulting in the production of a dark brown solution. The solution was stirred (−40 °C; 1 h), cooled (−78 °C) and then the relevant aldehyde added (*ca.* 5 equiv.). The solution was allowed to warm (20 °C) and methanol (0.5 ml) added resulting in a yellow-brown solution. Solvent was evaporated, the residue extracted (dichloromethane, 2 × 10 ml), filtered through alumina and the solvent evaporated to give the crude product as an oil or gum. This was further purified by flash chromatography, eluting with a light petroleum–ether solvent system to afford the corresponding β-hydroxy complex. Further purification by recrystallisation was carried out where required.

Treatment of tricarbonyl(2-*methylpyridine*)*chromium*(0) **1** *with lithium diisopropylamide and benzaldehyde*. To lithium diisopropylamide (0.7 ml, 1.05 mmol) was added tricarbonyl(2-methylpyridine)chromium(0) **1** (60 mg, 0.262 mmol) followed by electrophilic quench with benzaldehyde at −78 °C (0.5 ml, excess) according to the general procedure. Work-up (eluent 1:2) and recrystallisation from dichloromethane–hexane gave *tricarbonyl*[2-η-(2-*pyridyl*)-1-*phenylethanol*]*chromium*(0) **13** as a 67:33 mixture of diastereoisomers (45 mg, 51%); m.p. 141 °C (decomp.); ν_{max}/cm^{-1} 3400 (OH), 1983 and 1910 (CO); δ_H(major isomer) 7.44–7.30 (5 H, m, Ph), 6.62 (1 H, d, *J* 4.0,

6-H), 5.67 (1 H, dd, *J* 1.8 and 6.7, 4-H), 5.25 (1 H, dd, *J* 4.0 and 6.5, 5-H), 5.20 (1 H, d, *J* 6.5, 3-H), 5.17 (1 H, br, CH_2CHOH), 3.50 (1 H, br s, CH_2CHOH), 3.04 (1 H, app d, *J* 9.3, CH_2CHOH) and 2.96 (1 H, app d, *J* 1.6, CH_2CHOH); δ_H(minor isomer) 7.44–7.30 (5 H, m, Ph), 6.62 (1 H, d, *J* 4.0, 6-H), 5.67 (1 H, dt, *J* 1.4 and 6.5, 4-H), 5.25 (1 H, dd, *J* 4.0 and 6.5, 5-H), 5.20 (1 H, d, *J* 6.5, 3-H), 5.14 (1 H, br, CH_2CHOH), 3.50 (1 H, br s, CH_2CHOH), 3.09 (1 H, app d, *J* 9.3, CH_2CHOH) and 2.91 (1 H, app d, *J* 1.6, CH_2CHOH); *m/z* 336 ($M^+ + 1$)(Found: C, 57.4; H, 3.8; N, 4.2. $C_{16}H_{13}CrNO_4$ requires C, 57.3; H, 3.9; N, 4.2%). Further elution (ether) gave recovered starting complex **1** (12 mg, 20%).

Treatment of tricarbonyl(2-methylpyridine)chromium(0) **1** *with lithium diisopropylamide and pivalaldehyde.* To lithium diisopropylamide (2 ml, 3 mmol) was added tricarbonyl(2-methylpyridine)chromium(0) **1** (140 mg, 0.61 mmol) followed by electrophilic quench with pivaldehyde at −78 °C (0.5 ml, excess) according to the general procedure. Work-up (eluent 1:2) and recrystallisation from dichloromethane–hexane gave *tricarbonyl*[1-(2-*pyridyl*)-3,3-*dimethylbutan*-2-*ol*]*chromium*(0) **14** as a 55:45 mixture of diastereoisomers (88 mg, 46%); m.p. 126 °C (decomp.); ν_{max}/cm^{-1} 3400 (OH), 1988 and 1921 (CO); δ_H(major isomer) 6.56 (1 H, d, *J* 1.9, 6-H), 5.95 (1 H, dd, *J* 1.9 and 6.7, 5-H), 5.25 (1 H, d, *J* 6.7, 4-H), 5.20 (1 H, d, *J* 6.7, 3-H), 4.01 (1 H, d, *J* 3.3, CH_2CHOH), 2.42 (2 H, s, CH_2CHOH), 1.69 (1 H, s, CH_2CHOH) and 0.98 (9 H, s, Bu^t); δ_H(minor isomer) 6.84 (1 H, d, *J* 1.8, 6-H), 5.61 (1 H, dd, *J* 1.8 and 6.6, 5-H), 5.20 (1 H, d, *J* 6.7, 3-H), 5.18 (1 H, d, *J* 6.6, 4-H), 3.86 (1 H, d, *J* 3.3, CH_2CHOH), 2.41 (2 H, s, CH_2CHOH), 1.86 (1 H, s, CH_2CHOH) and 0.99 (9 H, s, Bu^t); *m/z* 316 ($M^+ + 1$) (Found: C, 53.2; H, 5.3; N, 4.15. $C_{14}H_{17}CrNO_4$ requires C, 53.3; H, 5.4; N, 4.4%). Further elution (ether) gave recovered starting complex **1** (45 mg, 32%).

Erythro- *and* threo-2-(2-*Pyridyl*)-1-*phenylpropanol* **15** *and* **16**.[9]—2-Ethylpyridine (468 mg, 4.38 mmol) in tetrahydrofuran (20 ml) was added to lithium diisopropylamide (3.3 ml, 5 mmol) in tetrahydrofuran (10 ml) at −78 °C and the mixture stirred (0.5 h) resulting in a deep red solution. Benzaldehyde (1.05 ml, 4.92 mmol) was added and the mixture allowed to warm (20 °C) to give a pale yellow solution. This was washed with aqueous Na_2CO_3 (20 ml), the aqueous phase extracted (ether, 2 × 10 ml) and the extract dried (K_2CO_3) and evaporated to give a yellow oil. Distillation of this afforded a 1:3 mixture of **15** and **16** as an oil (646 mg, 69%); b.p. 210 °C at 0.1 mmHg. The mixture was subjected to flash chromatography (eluent light petroleum–ether, 5:1) to afford on evaporation of solvent *erythro*-2-(2-pyridyl)-1-phenylpropanol **15** as a white solid (101 mg, 11%); m.p. 50 °C; δ_H 8.53 (1 H, d, *J* 4.9, py-2-H), 7.66–7.11 (8 H, m, Ar-H), 5.87 [1 H, s, C(Me)HCHO*H*], 5.22 [1 H, d, *J* 2.6, C(Me)HCHOH], 3.14 [1 H, dq, *J* 2.6 and 7.1, C(Me)*H*CHOH] and 1.16 [3 H, d, *J* 7.1, C(*Me*)HCHOH]; *m/z* 214 {lit.,[9] δ_H 8.57–7.07 (9 H, Ar-H), 5.20 [1 H, d, *J* 3, C(Me)HC*H*OH], 5.17 [1 H, s, C(Me)HCHO*H*], 3.13 [1 H, dq, *J* 3 and 7.5, C(Me)*H*CHOH], 1.14 (3 H, d, *J* 7.5, C(*Me*)HCHOH]}. Evaporation of the major fraction gave *threo*-2-(2-pyridyl)-1-phenylpropanol **16** as a white solid (316 mg, 34%); m.p. 53 °C; δ_H 8.47 (1 H, d, *J* 4.9, py-2-H), 7.55–6.98 (8 H, m, Ar-H), 5.39 [1 H, s, C(Me)HCHO*H*], 4.93 [1 H, d, *J* 6.0, C(Me)HC*H*OH], 3.20 [1 H, qu, *J* 6.9, C(Me)*H*CHOH] and 1.34 [3 H, d, *J* 7.0, C(*Me*)HCHOH]; *m/z* 214 {lit.,[9] δ_H 8.50–6.90 (9 H, Ar-H), 5.30 [1 H, s, C(Me)HCHO*H*], 4.90 [1 H, d, *J* 3, C(Me)HC*H*OH], 5.17 [1 H, s, C(Me)HCHO*H*], 3.17 [1 H, dq, *J* 7.0, C(Me)*H*CHOH] and 1.27 (3 H, d, *J* 7.5 C(*Me*)HCHOH]}.

Treatment of tricarbonyl(2-ethylpyridine)chromium(0) **2** *with lithium diisopropylamide and benzaldehyde.* To lithium diisopropylamide (0.7 ml, 1.05 mmol) was added tricarbonyl(2-ethylpyridine)chromium **2** (50 mg, 0.205 mmol) followed by electrophilic quench with benzaldehyde at −78 °C (0.5 ml, excess) according to the standard procedure. Work-up (eluent 1:2) and recrystallisation from dichloromethane–hexane gave RSS(SRR)-*tricarbonyl*[erythro-2-η-(2-*pyridyl*)-1-*phenylpropanol*]*chromium*(0) **17** as yellow prisms (58 mg, 81%); m.p. 138–141 °C (decomp.); ν_{max}/cm^{-1} 3400 (OH), 1982 and 1918 (CO); δ_H 7.41–7.26 (5 H, m, Ph), 6.61 (1 H, d, *J* 4.0 Hz, 6-H), 5.68 (1 H, dt, *J* 1.1 and 6.7, 4-H), 5.30 [2 H, m, C(Me)HC*H*OH, 5-H], 5.21 (1 H, d, *J* 6.7, 3-H), 3.85 [1 H, br s, C(Me)HCHO*H*], 2.99 [1 H, dq, *J* 1.8 and 7.2, C(Me)*H*CHOH], and 1.18 [3 H, d, *J* 7.2, C(*Me*)HCHOH]; *m/z* 350 ($M^+ + 1$) (Found: C, 58.35; H, 4.3; N, 4.0. $C_{17}H_{15}CrNO_4$ requires C, 58.5; H, 4.3; N, 4.0%).

Five recrystallisations of this compound from dichloromethane–heptane gave single crystals upon which the X-ray crystal determination was carried out.

Crystal data for compound **17**. $C_{17}H_{15}CrNO_4$, *M* 349.31, monoclinic, $P2_1/a$ (No. 14), a = 16.157(2) b = 8.163(2) c = 12.554(1) Å, β = 111.654(9)° (from least squares fitting of setting angles for 24 reflections $22.5 \leq \theta \leq 33°$), V = 1539 Å^3, Z = 4, D_x = 1.508 g cm^{-3}, Cu-K_α radiation, yellow tabular crystals, 0.5 × 0.4 × 0.2 mm, μ = 63.83 cm^{-1} crystal sealed in Lindemann glass capillary.

Data collection and processing. Data were collected on a CAD-4F diffractometer in ω:2θ mode $O < 2\theta \leq 150°$ ($-1 \leq h \leq 20$, $-1 \leq k \leq 10$, $-14 \leq l \leq 14$). 3976 Reflections measured, 3116 unique (R_{merge} = 0.035) of which 2129 were observed ($I \geq 3\sigma I$). No significant variation in intensity of 3 check reflections was observed. An absorption correction (min. 3.88, max. 11.62) based on azimuthal scans was applied.[23]

Structure solution and refinement. The structure was solved by heavy atom methods[19] which yielded coordinates for all non-hydrogen atoms. Evidence of all hydrogen atoms was observed in subsequent difference electron density maps. Full-matrix least-squares refinement[20] of positional and anisotropic thermal parameters for the non-hydrogen atoms, positional parameters for the hydrogen atom of the hydroxo group and isotropic thermal parameters for each H-atom type was continued to convergence. H-Atom coordinates [except H(1)] were geometrically calculated and a 4-term Chebychev polynomial weighting scheme was employed. At convergence R = 0.045, R_w = 0.050 for 216 parameters [R,R_w as for **8**].

Decomplexation of RSS(SRR)-*Tricarbonyl*[erythro-2-η-(2-*pyridyl*)-1-*phenylpropanol*]*chromium*(0) **17**.—*RSS*(*SRR*)-Tricarbonyl[*erythro*-2-η(2-pyridyl)-1-phenylpropanol]chromium(0) **17** (30 mg, 0.086 mmol) was dissolved in ether (30 ml) and the solution exposed to air and sunlight (7 h) to give in a colourless solution and a green brown precipitate. Filtration of this solution through Celite and evaporation of the solvent gave *erythro*-2-(2-*pyridyl*)-1-*phenylpropanol* **15** (18 mg, 95%), identical with an authentic sample.

Treatment of Tricarbonyl(2-ethylpyridine)chromium(0) **2** *with Lithium Diisopropylamide and Pivalaldehyde.*—To lithium diisopropylamide (0.7 ml, 1.05 mmol) was added tricarbonyl(2-ethylpyridine)chromium(0) **2** (50 mg, 0.205 mmol) followed by electrophilic quench with pivalaldehyde at −78 °C (0.5 ml, excess) according to the standard procedure. Work-up (eluent 1:2) and recrystallisation from ispentane gave RSR(SRS)-*tricarbonyl*[erythro-2-(2-*pyridyl*)-2,4,4-*trimethylpentan*-3-*ol*]-*chromium*(0) **18** as yellow prisms (51 mg, 76%); m.p. 118–120 °C (decomp.); ν_{max}/cm^{-1} 3400 (OH), 1978 and 1911 (CO); δ_H 6.55 (1 H, dd, *J* 1.3 and 4.5, 6-H), 5.67 (1 H, dt, *J* 1.3 and 6.4, 4-H), 5.23 (2 H, m, 3-H and 5-H), 3.70 [1 H, d, *J* 3.9, C(Me)HCHO*H*], 3.01 [1 H, q, *J* 7.2, C(Me)*H*CHOH], 2.86 [1 H, d, *J* 3.9, C(Me)HC*H*OH], 1.35 [3 H, d, C(*Me*)HCHOH] and 1.05 (9 H,

s, Bu^t); *m/z* 330 ($M^+ + 1$) (Found: C, 54.6; H, 6.1; N, 4.0. $C_{15}H_{19}CrNO_4$ requires C, 54.7; H, 5.8; N, 4.25%).

Reaction of 2-Ethylpyridine with Lithium Diisopropylamide and Benzaldehyde in the Presence of TDA-1 **20**.—2-Ethylpyridine (235 mg, 2.19 mmol) in tetrahydrofuran (10 ml) was added to lithium diisopropylamide (1.65 ml, 2.5 mmol) in tetrahydrofuran (10 ml) at −78 °C and the mixture stirred (0.5 h) resulting in a deep red solution. TDA-1 **20** (0.2 ml, 6.0 mmol) was added, the solution warmed briefly and then re-cooled. Benzaldehyde (0.5 ml, 2.34 mmol) was added and the mixture allowed to warm (20 °C) to give a pale yellow solution. The latter was washed with aqueous Na_2CO_3 (20 ml), the aqueous phase extracted (ether, 2 × 10 ml) and the extract dried (K_2CO_3) and evaporated to give a yellow oil which was shown by ^{1}H NMR spectroscopy to be a 43:57 mixture of *erythro*-2-(2-pyridyl)-1-phenylpropanol **15** and *threo*-2-(2-pyridyl)-1-phenylpropanol **16**.

Treatment of Tricarbonyl(2-ethylpyridine)chromium(0) **2** *with Lithium Diisopropylamide and Benzaldehyde in the Presence of* TDA-1 **20** *and Subsequent Decomplexation*.—To lithium diisopropylamide (0.7 ml, 1.05 mmol) was added tricarbonyl(2-ethylpyridine)chromium **2** (50 mg, 0.205 mmol) followed by TDA-1 **20** (0.61 ml, 2.1 mmol); the mixture was warmed briefly and then re-cooled prior to electrophilic quench with benzaldehyde at −78 °C (0.5 ml, excess) according to the general procedure. Work-up (eluent ether) gave *RSS*(*SRR*)-tricarbonyl[*erythro*-2-(η-2-pyridyl)-1-phenylpropanol]-chromium(0) **17** which was not purified further, but exposed as an ether solution to air and sunlight (7 h). This gave a colourless solution with a green brown precipitate. Filtration of this solution through Celite and evaporation of solvent gave *erythro*-2-(2-pyridyl)-1-phenylpropanol **15** (37 mg, 85%), identical with an authentic sample.

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