Remote stereocontrol as a synthetic strategy: diastereoselective annulations on an arene tricarbonylchromium template †

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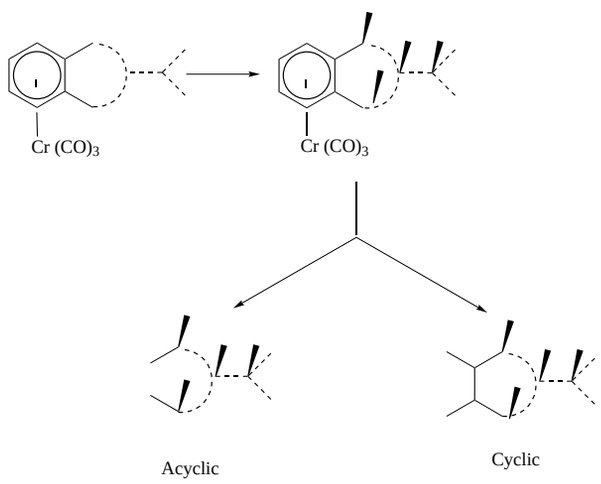
Stereoselective annulations on $Cr(CO)_3$ complexed tetralone and benzosuberone§ derivatives have been achieved. Diastereomeric products are shown to be related by an epimerisable chiral centre. An unusually facile de-ethoxycarbonylation has been observed.

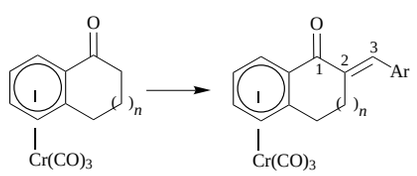
Introduction

Metal complexation to one face of an aromatic ring in arene tricarbonylchromium complexes permits excellent stereocontrol in reactions at aromatic,[1] benzylic[2] as well as homobenzylic[3] positions, where the reagent approaches preferentially from the face opposite to the metal (*anti*-addition). In suitably designed substrates and reactions, such steric bias can be transmitted to reaction centres even three carbons away from the complexed arene ring[4] thereby extending the scope of stereoselective synthesis on such metal templates. A lone exception to this general trend is a *syn*-selective cyclopropanation of a 2-arylidene-1-tetralone-$Cr(CO)_3$ complex by dimethylsulfoxonium methylide.[5] Otherwise, a *syn*-addition is observed only if the reagent is delivered from the metal.[6] With the availability of optically pure starting complexes and methods for obtaining them,[7] enantioselective synthesis of various target molecules has now been achieved.[8] One can now conceptually integrate such methodologies into tailored approaches to multi-functionalised aliphatic or alicyclic structures as depicted in Scheme 1.

As a step towards this goal, we present the results of ring annulations to an extended π-system anchored on tricarbonylchromium to examine the extent of diastereocontrol at different stereogenic centres in the products.[9] During this investigation an unusually facile de-ethoxycarbonylation of a β-keto ester intermediate was observed.



Scheme 1



1 $n = 1$ **2a–c**

3 $n = 2$ **4a,b**

Ar	*n*	Product	Yield%
4-CH_3-C_6H_4	1	**2a**	95
C_6H_5	1	**2b**	97
4-OCH_3-C_6H_4	1	**2c**	97
4-CH_3-C_6H_4	2	**4a**	92
C_6H_5	2	**4b**	89

Scheme 2

Results and discussion

Tricarbonylchromium complexes of 2-arylidene-1-tetralone (**2a**–**c**) and 2-arylidene-1-benzosuberone (**4a,b**) were selected for initial explorations (Scheme 2). They offer the following advantages: (a) the rigid structural framework of this complex would allow immediate stereochemical correlation, and, (b) a planar π-system extending beyond the periphery of the fused cyclohexenone ring would facilitate *exo*-addition of nucleophiles at C-3. These complexes were prepared in excellent yields from the parent tetralone and benzosuberone tricarbonylchromium complexes (**1** and **3**) by condensation with pertinent aromatic aldehydes,[10] and were obtained as dark red, crystalline solids. The singlet around 7.50–8.00 ppm due to the olefinic proton in all the arylidene derivatives confirmed their (*E*)-stereochemistry.[11]

Conjugate addition of dimethyl malonate

In the first set of experiments, dimethyl malonate was added as a nucleophile. With complexes (**2a,b**), the conjugate addition of dimethyl malonate was carried out in NaOMe–MeOH at room temperature.[12] Each substrate furnished a diastereomerically pure product, whose structure was formulated as a cyclic enol ester (Scheme 3) based on spectral and microanalytical data.

The products **5a,b** were obtained as yellow, microcrystalline solids after crystallisation from dichloromethane–light petroleum. In addition to the intense IR absorptions at 1980 and 1900 cm^{-1} corresponding to Cr–CO groups, characteristic absorptions at 1770 and 1730 cm^{-1} indicated the presence of two carbonyl functions. The region of two ^{13}C NMR signals at 167.2 and 162.6 ppm suggested that these could be esters or lactones. The ^1H NMR spectra of the products showed the methylene protons of the tetralone ring as multiplets at 2.05–2.20, 2.35–2.70, 2.70–2.95 ppm. The singlet at 3.75 ppm was due to the CO_2CH_3 group. The signals at 3.85 and 4.15 ppm were due to the proton on the carbon flanked by the carbonyl groups and the benzylic proton respectively. The complexed aromatic ring

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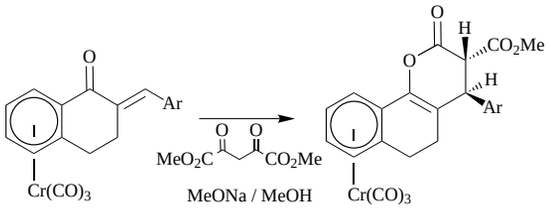
§ Tetralone refers to 1,2,3,4-tetrahydronaphthalene-1-one and benzosuberone refers to 6,7,8,9-tetrahydro-5*H*-benzocycloheptene-5-one.



2a,**b** **5a**,**b**

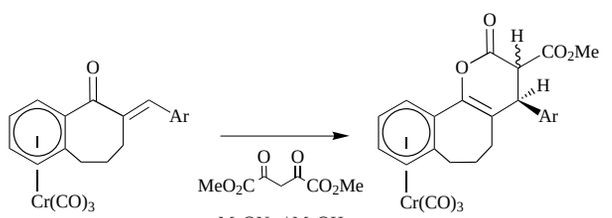
Complex	Product	Yield%
2a	**5a**	89
2b	**5b**	88

Scheme 3

protons appeared at 5.25–5.35, 5.40–5.50 and 5.85 ppm as two multiplets and a doublet respectively. The aromatic protons appeared at the expected positions at 7.10 and 7.15 ppm as two doublets. The two sets of mutually coupled, downfield aliphatic doublets at 4.15 and 3.85 ppm were assigned to the pair of contiguous methine protons. The relative stereochemistry at those two centres was determined to be *trans* by correlating the coupling constants of these signals with dihedral angles measured from Drieding models of the organic ligand.

In the light of the preceding nitromethane addition,[13] the conjugate addition was believed to have occurred stereoselectively from the *exo*-face, and the stereochemistry of that centre (C-3) was fixed accordingly. The relative stereochemistry of complexes **5a,b** shown in Scheme 3, therefore, assumes preferential *exo*-protonation of the β-keto ester enolate.

The reaction conditions using NaOMe–MeOH was expected to provide the thermodynamic product. It was gratifying to note that a single diastereomer was obtained in this reaction even when the new stereogenic centre was four carbons away from the complexed aromatic ring. However, from the two analogous benzosuberone derivatives (**4a**–**b**), two diastereomeric enol lactones were obtained (Scheme 4).



4a,**b** **6a**,**b**

Complex	Product	Yield% [a]
4a	**6a**	78
4b	**6b**	84

[a] Mixture of isomers

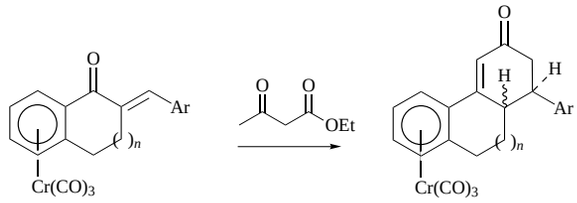
Scheme 4

For complexes **4a,b**, the reaction was almost instantaneous (complete within 15 min whilst tetralone analogues **2a,b** required 1.5 to 2 h), accompanied by a dramatic change in the colour of the solution from red to yellow. The isomer ratio (6 : 1) was deduced from the relative integration of well-resolved peaks in the ^{1}H NMR spectra. Separation of diastereoisomers by chromatography was not possible because the compounds decomposed on a silica column. The relative stereochemistry of the major isomers was believed to be the same as the enol lactones **5a**–**b**. The minor isomers then differ in the relative configuration at the carbon adjacent to the carbonyl function only.[14]

Robinson annulation with ethyl acetoacetate

Use of ethyl acetoacetate as a nucleophile resulted in an efficient Robinson annulation (Scheme 5).

On stirring with ethyl acetoacetate in the presence of potassium *tert*-butoxide in *tert*-butyl alcohol and THF (1 : 5 v/v) at room temperature for 8–12 h, both sets of complexes (**2a**–**c** and **4a**,**b**) afforded a pair of diastereomeric products in excellent combined yield, and the isomers were separated by flash chromatography. While spectral features were generally consistent with the expected structures, absence of the CO_2Et group was evident in all products.



2a–c *n* = 1 **7a–c** and **8a–c**
4a,**b** *n* = 2 **9a**,**b** and **10a**,**b**

Complex	*n*	Product	Yield%
2a	1	**7a + 8a**	78 (78:22)
2b	1	**7b + 8b**	73 (76:24)
2c	1	**7c + 8c**	84 (79:21)
4a	2	**9a + 10a**	78 (73:27)
4b	2	**9b + 10b**	81 (71:29)

Scheme 5

Equilibration of the major diastereomeric product with DBU–CH_2Cl_2 for both cases resulted in a diastereomeric mixture within 2 h. The products were separated by chromatography and their diastereomeric ratio was found to be same as that obtained in the original reaction. This indicated that the products were epimeric at the allylic center. Therefore, the addition of the nucleophile at carbon-3 must have occurred stereoselectively in an *anti*-fashion, *i.e.* the $Cr(CO)_3$ group was effective in blocking one face of the enone moiety.

The ^{1}H NMR spectrum of the major isomer, **7a**, showed the tetralone ring methylenes, the methylene protons of the newly constructed six-membered ring and the allylic proton as two sets of multiplets at 1.72–1.80 and 2.85–3.05 ppm. The benzylic methine appeared as a multiplet at 3.05 ppm. The aromatic protons of the complexed ring appeared as two doublets and two triplets between 5.15 and 5.85 ppm. The olefinic proton of the cyclohexenone system appeared as a singlet at 6.55 ppm. The aromatic ring protons appeared at the expected position centred at 7.20 ppm.

For the minor product, **8a**, the ^{1}H NMR spectrum was characteristically different. The methylene protons of the tetralone and the newly constructed enone system along with the allylic and the benzylic protons showed up as three sets of multiplets at 1.50–1.65, 1.85–2.00 and 2.65–2.95 ppm. The complexed aromatic ring protons appeared as a doublet, triplet and a multiplet at 5.92, 5.60 and 5.25 ppm respectively. The olefinic proton appeared as a singlet at 6.50 ppm, the aromatic protons appeared at their expected positions.

The ^{1}H NMR spectrum of the major diastereomer for the benzosuberone series **9a** major isomer showed complex multiplets at 1.65–2.05, 2.40–2.64 and 2.65–3.05 ppm corresponding to the methylene protons of the benzosuberone ring as well as the cyclohexenone ring and the allylic proton. The benzylic proton appeared further downfield as a quartet at 3.35 ppm. The complexed aromatic ring protons appeared as a triplet, doublet and a multiplet at 5.43, 5.35 and 5.14 ppm respectively. The olefinic proton appeared as a singlet at 6.30 ppm. The rest of the protons appeared at their expected places.

The corresponding minor diastereomer, **10a**, displayed characteristically different patterns in the ^{1}H NMR spectrum. The pattern of the multiplets due to the methylene protons appearing at 1.80–2.05, 2.40–2.55 and 2.65–3.02 ppm were quite different in the set of minor diastereomers, the quartet due to the benzylic proton shifted upfield by only 0.15 ppm (3.20 ppm) when compared with the same signal of the major isomer **9a** (3.35 ppm). The patterns of the complexed aromatic ring

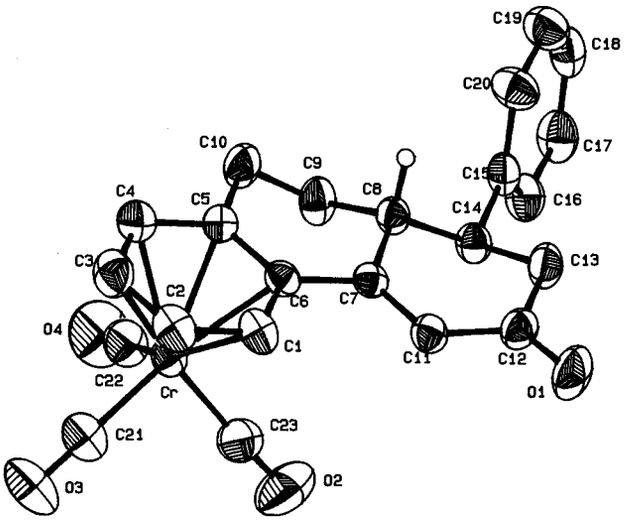


Fig. 1 X-Ray crystal structure of **7b**

protons appeared as a triplet, a doublet and a multiplet at 5.45, 5.34 and 5.10 ppm respectively. The singlet due to the olefinic proton appeared as expected at 6.25 ppm. The signals due to the aromatic protons appeared at their expected positions at 6.85 and 7.20 ppm.

In the tetralone series, the ^{1}H NMR signal due to the olefinic proton appeared at 6.55 ppm (for the minor isomer) and 6.50 ppm (for the major isomer) as a broad singlet. The pattern of complexed aromatic protons was different for the two diastereoisomers. For the major isomer, the four protons appeared as four distinct signals. In the spectrum of the minor diastereoisomer, three signals were observed—two signals overlap to form a complex two-proton multiplet. The major isomers (**9a,b**) of the benzosuberone series, however, presented some variations from this general trend (*vide infra*).

The relative configuration of the major isomer was established from the crystal structure of a representative complex, **7b**. As anticipated in this isomer, the acidic allylic proton was oriented *anti* with respect to the metal (Fig. 1).

Certain differences in the nature of products obtained from tetralone and benzosuberone derivatives deserve mention. While annulated products **7a**–**c** and **8a**–**c** were all red, crystalline solids, there was a distinct difference in colour between the major and the minor stereoisomers (**9a,b** and **10a,b** respectively) of the benzosuberone series; the major isomers were yellow and the minor isomers were red solids. Another difference concerns the relative polarity of the major and minor isomers in a series; in the tetralone series (**7a**–**c** and **8a**–**c**), the major stereoisomers were more polar than the minor ones; in the benzosuberone derivatives (**9a,b** and **10a,b**), the major isomers were less polar than the minor isomers. A third difference is related to the chemical shift of the *peri* proton of the complexed aromatic ring in different complexes. Normally, this is the most deshielded among the complexed aromatic protons owing to the anisotropy of the neighbouring, coplanar π-bond of the enone, as observed for complexes **7a**–**c** and **8a**–**c**. This also holds good for the minor isomers **10a,b** in the benzosuberone derivatives. But the typical, deshielded doublet of this *peri* proton is absent in the spectra of the major isomers (**9a,b**). The yellow colour of this last set of complexes and the relative shielding of the *peri* protons suggested a disruption of coplanarity of the extended π-framework and consequent breach of conjugation of the enone function with the complexed aromatic ring in these complexes. Analysis of the X-ray crystal structure of **9a** confirmed such a structural distortion (Fig. 2).

The dihedral angle between the plane containing the complexed aromatic ring and the plane of the enone system was 66°. Since metal-complexation does not distort the planarity of an aromatic ring, the observed deviation of planarity of the

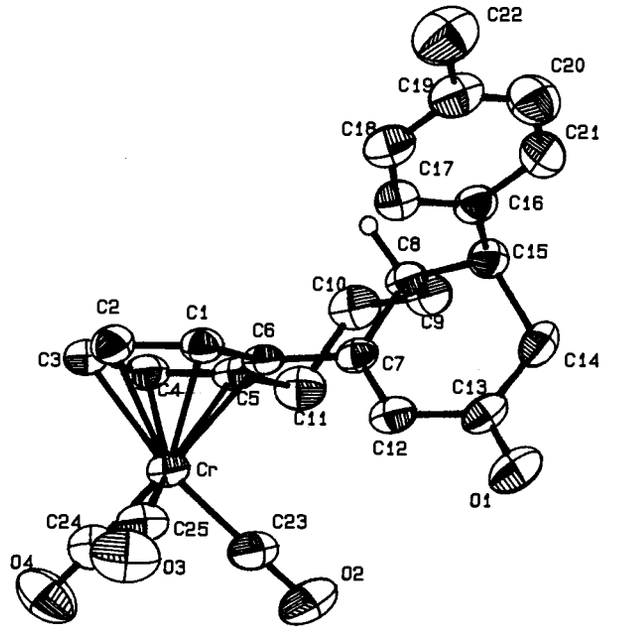


Fig. 2 X-Ray crystal structure of **9a**

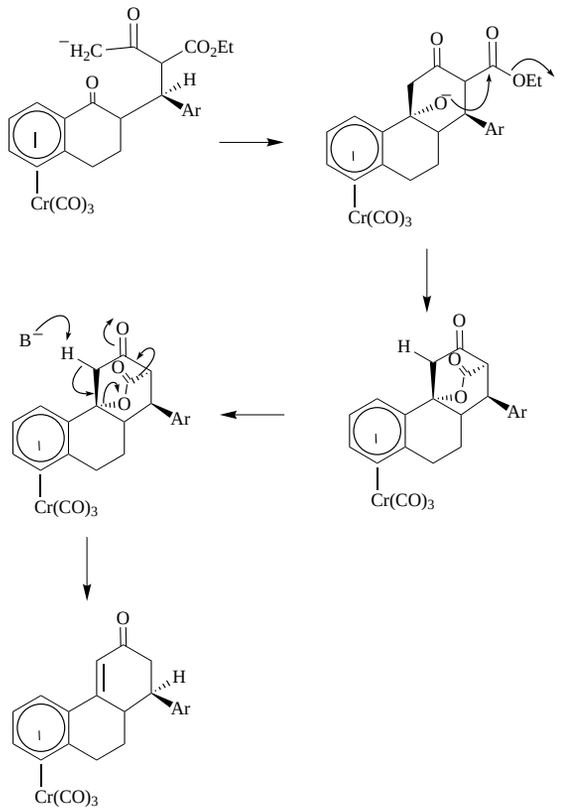
extended π-system is probably a consequence of the steric effects associated with ring fusion.

The de-ethoxycarbonylation that accompanied annulation is rather unusual. De-ethoxycarbonylation has usually been a twostep process where hydrolysis of the ester precedes decarboxylation. In a recently developed and widely-used procedure, sodium chloride in moist DMSO at temperatures higher than 100 °C has been shown to effect de-ethoxycarbonylation in a one-pot operation.[15] In the annulation reaction described above, de-ethoxycarbonylation was observed to be a rapid reaction at room temperature. No intermediate could be traced by monitoring the reaction every thirty minutes by TLC, only spots due to the substrates **2a** or **4a** and corresponding isomeric products could be seen. This would imply that both the Michael addition and aldol condensation yielded reactive species which were transformed to the end-products rapidly. A rapid and spontaneous de-ethoxycarbonylation can therefore be explained in terms of the stereochemical uniqueness of these metal-complexed substrates and intermediates. It is possible that the aldol cyclization produced an *endo* carbinol which intramolecularly lactonized with expulsion of an ethoxide ion. In the presence of a strong base like *tert*-butoxide, deprotonation at the methylene group next to the ketone would trigger a cascade involving elimination and decarboxylation to generate an enolate in the end (Scheme 6).

These steps are probably facile due to the presence of a sterically bulky $Cr(CO)_3$ group crowding the *endo*-face of the molecule. When uncomplexed 2-benzylidene-1-tetralone was treated with ethyl acetoacetate under similar conditions, about 50% of the starting material persisted even after 48 h and a series of spots were seen on the TLC plate indicating a slow progress of many competing pathways.

Conclusion

Exclusive *anti*-addition [with respect to the $Cr(CO)_3$ moiety] by two different nucleophiles to a site three carbons away from the complexed aromatic ring has been realised in reactions of complexed tetralone and benzosuberone derivatives. The products of annulation reactions are obtained as diastereomers due to the presence of enolizable protons as shown by equilibration studies. The diastereomers, in most instances, were chromatographically separated and characterized. In one series of such diastereomers of the annulated product, the extended conjugation was found to be disrupted by non-coplanarity of the enone



Scheme 6

chromophore with the complexed aromatic ring. Annulation by ethyl acetoacetate was marked by an unusually facile *in situ* de-ethoxycarbonylation of a 1,3-dicarbonyl intermediate. Further elaboration of these functional derivatives to specific target molecules is under progress.

Experimental

All reactions were performed under an inert atmosphere of argon, using freshly distilled, degassed solvents. Infrared spectra were recorded on a Perkin-Elmer 599B spectrometer in chloroform. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm relative to tetramethylsilane as internal reference and *J* values are given in Hz. Elemental analyses were carried out on a Carlo-Erba 1100 automatic analyzer by Dr. S. Y. Kulkarni and his group at NCL. Melting points were determined in open capillary tubes on a Thermonik Campbell melting point apparatus and are uncorrected. Light petroleum refers to the fraction with bp 60–80 °C.

6,7,8,9-Tetrahydro-5*H*-benzocyclohepten-5-one

Ethyl propane-1,1,3,3-tetracarboxylate was prepared from diethyl malonate and formaldehyde in the presence of diethylamine. The tetracarboxylate was hydrolyzed by 1:1 aqueous HCl to afford glutaric acid which was converted to the corresponding anhydride. Friedel–Crafts acylation of this anhydride with benzene yielded the δ-keto phenylvaleric acid. Clemmenson reduction of the acid followed by PPA cyclization afforded the desired benzocyclohepten-5-one.

Tricarbonyl(1-oxo-1,2,3,4-tetrahydronaphthalene)chromium(0) 1 and tricarbonyl(5-oxo-6,7,8,9-tetrahydro-5*H*-benzocycloheptene)chromium(0) 3¶

To a solution of the organic ligand (48 mmol) in *n*-dibutyl ether (100 ml), $Cr(CO)_6$ (3 g, 13.7 mmol) and THF (5 ml) were added and the reaction mixture was heated under reflux at 140 °C (oil bath temp.). After 12 h, the reaction mixture was allowed to cool to room temperature and filtered through Celite. The filtrate was refrigerated to provide a red crystalline solid and unreacted $Cr(CO)_6$ (400 mg). The chromium complex was dissolved in benzene while the $Cr(CO)_6$ remained insoluble. Concentration of the benzene solution provided the complex **1** or **3** (57 to 60%), based on consumed $Cr(CO)_6$.

General method for the preparation of enones (2a–c) and (4a,b)

A solution of aromatic aldehyde (2.64–5.34 mmol) and complex **1** or **3** (1.76–3.56 mmol) in ethanol (10 ml) was cooled in an ice–salt bath. An ethanolic solution of KOH (1.76–3.56 mmol in 10 ml ethanol) was added dropwise *via* syringe. The reaction was monitored by TLC. After complete disappearance of the starting material the reaction mixture was worked up to provide orange to red solid products **2a**–**c** or **4a,b**. The crude products were washed with light petroleum (3 × 20 ml) and recrystallized from dichloromethane–light petroleum ether to afford analytically pure complexes.

Tricarbonyl[(2*E*)-1-oxo-2(*p*-tolylmethylidene)-1,2,3,4-tetrahydronaphthalene]chromium(0) 2a. Orange solid (mp 164–165 °C) (Found: C, 65.79; H, 4.37; $C_{21}H_{16}O_4Cr$ requires C, 65.63; H, 4.20%); ν_{max}/cm^{-1} 1980, 1910 (br), 1660 and 1600; δ_H(200 MHz; $CDCl_3$) 2.40 (s, 3H), 2.56–2.58 (m, 1H), 2.59–3.15 (m, 2H), 3.25–3.50 (m, 1H), 5.20 (d, 1H, *J* 7), 5.40 (t, 1H, *J* 6), 5.70 (t, 1H, *J* 6), 6.30 (d, 1H, *J* 7), 7.27 (d, 2H), 7.38 (d, 2H), 7.85 (s, 1H); δ_C(50.3 MHz; $CDCl_3$) 21.2, 25.5, 27.0, 84.6, 89.8, 91.4, 94.2, 114.6, 129.1, 129.8, 130.0, 131.3, 132.1, 138.3, 139.2, 185.7, 230.9.

Complex 2b. Red solid (mp 150–151 °C) (Found: C, 65.19; H, 4.15; $C_{20}H_{14}O_4Cr$ requires C, 65.04; H, 3.79%); ν_{max}/cm^{-1} 1980, 1920 (br), 1660 and 1620; δ_H(200 MHz; $CDCl_3$) 2.50–2.80 (m, 1H), 2.85–3.15 (m, 2H), 3.20–3.40 (m, 1H), 5.15 (d, 1H, *J* 7), 5.40 (t, 1H, *J* 6), 5.65 (t, 1H, *J* 6), 6.25 (d, 1H, *J* 7), 7.30–7.55 (br s, 5H), 7.85 (s, 1H); δ_C(50.3 MHz; $CDCl_3$) 25.4, 26.9, 89.6, 89.8, 91.4, 93.9, 94.2, 114.7, 128.3, 128.8, 129.9, 132.1, 134.9, 138.0, 185.7, 230.8.

Complex 2c. Red solid (mp 154–155 °C) (Found: C, 62.91; H, 4.37; $C_{21}H_{16}O_5Cr$ requires C, 63.00; H, 4.03%); ν_{max}/cm^{-1} 1980, 1920 (br), 1660 and 1620; δ_H(200 MHz; $CDCl_3$) 2.62–2.75 (m, 1H), 2.85–3.15 (m, 2H), 3.2–3.35 (m, 1H), 3.85 (s, 3H), 5.15 (d, 1H, *J* 7), 5.40 (t, 1H, *J* 6), 5.65 (t, 1H, *J* 6), 6.25 (d, 1H, *J* 7), 6.95 (d, 2H, *J* 9), 7.45 (d, 2H, *J* 9), 7.85 (s, 1H); δ_C(50.3 MHz; $CDCl_3$) 25.5, 26.8, 55.1, 89.6, 89.8, 91.4, 94.2, 113.9, 114.6, 127.5, 130.0, 131.9, 138.0, 160.2, 185.5, 230.9.

Tricarbonyl[(2*E*)-5-oxo-6-(*p*-tolylmethylidene)-6,7,8,9-tetrahydro-5*H*-benzocycloheptene]chromium(0) 4a. Orange solid (mp 165–166 °C) (Found: C, 65.56; H, 4.74; $C_{22}H_{18}O_4Cr$ requires C, 66.32; H, 4.56%); ν_{max}/cm^{-1} 1980, 1920 (br), 1660 and 1620; δ_H(200 MHz; $CDCl_3$) 2.00–2.35 (m, 3H), 2.40 (s, 3H), 2.56–2.65 (m, 1H), 2.70–2.95 (m, 1H), 3.02–3.15 (m, 1H), 5.08 (d, 1H, *J* 7), 5.25 (t, 1H, *J* 6), 5.58 (t, 1H, *J* 6), 6.15 (d, 1H, *J* 7), 7.20 (d, 2H, *J* 9), 7.38 (d, 2H, *J* 9), 7.75 (s, 1H); δ_C(50.3 MHz; $CDCl_3$) 21.2, 25.2, 26.3, 32.4, 88.1, 90.6, 95.4, 98.08, 102.1, 109.8, 114.5, 127.8, 131.7, 134.5, 139.3, 160.7, 194.7, 231.6.

Complex 4b. Red solid (mp 160 °C) (Found: C, 65.22; H, 4.46; $C_{21}H_{16}O_4Cr$ requires C, 65.62; H, 4.20%); ν_{max}/cm^{-1} 1980, 1920 (br), 1660 and 1620; δ_H(200 MHz; $CDCl_3$) 2.00–2.50 (m, 3H), 2.56–2.70 (m, 1H), 2.75–2.95 (m, 1H), 3.00–3.15 (m, 1H), 5.10 (d, 1H, *J* 7), 5.25 (t, 1H, *J* 6), 5.58 (t, 1H, *J* 6), 6.15 (d, 1H, *J* 7), 7.35–7.65 (m, 5H), 7.75 (s, 1H); δ_C(50.3 MHz; $CDCl_3$) 25.2, 27.2, 32.4, 88.0, 90.5, 95.4, 98.0, 101.4, 109.9, 128.9, 129.2, 129.7, 135.4, 136.8, 139.6, 194.7, 231.5.

General procedure for the addition of dimethyl malonate to complexes 2a,b and 4a,b

Dimethyl malonate (1.58 g, 12 mmol) was added to NaOMe (276 mg, 12 mmol of Na in 5 ml of methanol) at 0 °C. After 10

¶ IUPAC names are given for complexes **1** and **3**. Representative examples of each series derived from them are also given.

min, the complexed substrate **2a,b/4a,b** (1.2 mmol) was added as a solid followed by diethyl ether (15 ml). After 10 min, the reaction was allowed to warm to room temperature and stirred for 2–3.5 h. After completion, the reaction was worked up by evaporating the solvent, washing with water and extracting with dichloromethane. Crystallization from dichloromethane–light petroleum yielded yellow microcrystals.

Tricarbonyl{(3*R,4*R**)-3-methoxycarbonyl-2-oxo-4-phenyl-3,4,4a,5,6,10b-hexahydro-2*H*-benzo[*h*]chromene}chromium(0) 5a.** Yellow solid (mp 170–172 °C) (Found: C, 61.80; H, 4.35; $C_{25}H_{20}O_7Cr$ requires C, 61.99; H, 4.16%); ν_{max}/cm^{-1} 1970, 1900, 1770 and 1740; δ_H(200 MHz; $CDCl_3$) 2.05–2.20 (m, 1H), 2.30 (s, 3H), 2.35–2.70 (m, 2H), 2.70–2.95 (m, 1H), 3.75 (s, 3H), 3.85 (d, 1H, *J* 6.3), 4.15 (d, 1H, *J* 6.3), 5.25–5.35 (m, 2H), 5.40–5.50 (m, 1H), 5.85 (d, 1H, *J* 6), 7.10 (d, 2H, *J* 9), 7.15 (d, 2H, *J* 9); δ_C(50.3 MHz; $CDCl_3$) 20.9, 24.6, 26.2, 45.0, 53.0, 54.0, 86.8, 90.9, 91.2, 92.2, 96.2, 106.5, 115.3, 127.5, 129.9, 133.3, 138.0, 140.7, 162.6, 167.2, 232.7.

Complex 5b. Yellow solid (mp 188–189 °C) (Found: C, 61.07; H, 3.76; $C_{24}H_{18}O_7Cr$ requires C, 61.28; H, 3.86%); ν_{max}/cm^{-1} 1970, 1900, 1770 and 1740; δ_H(200 MHz; $CDCl_3$) 2.05–2.30 (m, 1H), 2.35–2.70 (m, 2H), 2.75–3.00 (m, 1H), 3.85 (s, 3H), 3.90 (d, 1H, *J* 5), 4.20 (d, 1H, *J* 5), 5.30–5.60 (m, 3H), 5.90 (d, 1H, *J* 6), 7.20–7.50 (m, 5H); δ_C(50.3 MHz; $CDCl_3$) 24.7, 26.2, 45.5, 53.0, 53.9, 86.7, 90.9, 91.1, 92.2, 96.1, 106.5, 115.1, 127.7, 128.2, 129.3, 136.5, 140.9, 162.5, 167.2, 232.6.

Tricarbonyl(3-methoxycarbonyl-2-oxo-4-phenyl-2,3,4,4a,5,6,7,11b-octahydro[6,7]cyclohepta[*b*]pyran)chromium(0) 6a. Yellow solid (Found: C, 62.70; H, 4.76; $C_{26}H_{22}O_7Cr$ requires C, 62.65; H, 4.45%); ν_{max}/cm^{-1} 1970, 1900, 1770 and 1740; δ_H(200 MHz; $CDCl_3$) 2.00–2.20 (m, 2H), 2.30–2.70 (m, 6H), 2.85 (m, 1H), 3.90 (s, 3H), 4.00 (d, 1H, *J* 5), 4.25 (d, 1H, *J* 5), 4.30 (s, 1H), 5.40 (m, 2H), 5.60 (t, 1H, *J* 7), 5.95 (d, 1H, *J* 6), 6.05 (d, 1H, *J* 6), 7.30 (br s, 4H); δ_C(50.3 MHz; $CDCl_3$) 21.2, 29.2, 29.5, 30.8, 31.0, 33.1, 33.3, 46.9, 47.5, 53.3, 53.8, 54.1, 54.3, 88.9, 89.4, 92.1, 92.3, 92.5, 93.2, 93.7, 100.6, 112.5, 112.7, 120.4, 120.4, 120.8, 127.4, 127.6, 130.3, 134.4, 138.4, 141.8, 162.9, 167.6, 232.4, 232.7.

Complex 6b. Yellow solid (Found: C, 61.83; H, 4.38; $C_{25}H_{20}O_7Cr$ requires C, 61.99; H, 4.16%); ν_{max}/cm^{-1} 1970, 1900, 1770 and 1740; δ_H(200 MHz; $CDCl_3$) 1.80–2.00 (m, 2H), 2.15–2.30 (m, 2H), 2.40–2.50 (m, 1H), 2.60–2.75 (m, 1H), 3.75 (s, 6H), 3.85 (d, 1H, *J* 5), 4.10 (d, 1H, *J* 5), 4.25 (s, 1H), 5.25 (m, 2H), 5.40 (t, 1H, *J* 7), 5.80 (d, 1H, *J* 6), 5.90 (d, 1H), 6.90–7.45 (m, 5H); δ_C(50.3 MHz; $CDCl_3$) 29.7, 30.2, 31.2, 31.5, 33.4, 33.6, 47.1, 47.5, 53.4, 54.0, 54.3, 54.6, 88.9, 89.4, 92.3, 92.6, 92.7, 93.4, 93.8, 100.7, 112.8, 113.0, 120.6, 120.7, 121.2, 127.5, 127.7, 130.4, 134.5, 138.6, 141.9, 162.9, 167.8, 232.7, 233.1.

General method for annulation of complexes 2a–c using ethyl acetoacetate

Ethyl acetoacetate (260 mg, 2 mmol) was added to Bu^{t}OK (10 mmol of K in 1 ml of *tert*-butyl alcohol) at 0 °C. After 10 min, the complexed substrate **2a–c** (1 mmol) was added as solid followed by THF (5 ml). The reaction was monitored by TLC, and was found to reach completion in 8–12 h. After completion, solvent was removed under reduced pressure, the reaction mixture washed with water and extracted using dichloromethane (3 × 20 ml). The diastereomers were separated using chromatography (gradient elution, 10% ethyl acetate–90% light petroleum to 40% ethyl acetate–60% light petroleum). The less polar fraction provided the minor isomer while the major isomer was contained in the polar fraction.

Tricarbonyl[3-oxo-1-(*p*-tolyl)-1,2,3,9,10,10a-hexahydrophenanthrene]chromium(0) 7a. Red solid (mp 166 °C) (Found: C, 67.67; H, 4.42; $C_{24}H_{20}O_4Cr$ requires C, 67.92; H, 4.75%); ν_{max}/cm^{-1} 1990, 1920 (br), 1680 and 1620; δ_H(200 MHz; $CDCl_3$) 1.72–1.80 (m, 1H), 2.37 (s, 3H), 2.85–3.05 (m, 4H), 3.05 (m, 1H), 5.20 (d, 1H, *J* 7), 5.40 (t, 1H, *J* 6), 5.55 (t, 1H, *J* 6), 5.80 (d, 1H, *J* 7), 6.55 (s, 1H), 7.20 (m, 4H); δ_C(50.3 MHz; $CDCl_3$) 21.2, 27.1, 28.2, 41.4, 45.3, 47.2, 89.5, 90.1, 91.6, 94.2, 97.7, 112.3, 120.0, 127.6, 129.9, 137.3, 138.8, 154.9, 198.2, 232.2.

Complex 8a. Red solid (mp 212 °C, decomp.) (Found: C, 67.81; H, 4.77; $C_{24}H_{20}O_4Cr$ requires C, 67.92; H, 4.75%); ν_{max}/cm^{-1} 1990, 1920 (br), 1680 and 1620; δ_H(200 MHz; $CDCl_3$) 1.50–1.65 (m, 1H), 1.85–2.00 (m, 2H), 2.40 (s, 3H), 2.65–2.95 (m, 5H), 5.25 (m, 2H, *J* 6), 5.60 (t, 1H, *J* 6), 5.92 (d, 1H, *J* 7), 6.50 (s, 1H), 7.20 (m, 4H); δ_C(50.3 MHz; $CDCl_3$) 21.2, 26.0, 29.3, 42.6, 45.4, 47.2, 89.5, 90.5, 92.1, 93.4, 95.5, 111.4, 121.9, 127.5, 129.7, 137.1, 138.7, 155.2, 197.8, 231.9.

Complex 7b. Red solid (mp 184 °C) (Found: C, 67.04; H, 3.90; $C_{23}H_{18}O_4Cr$ requires C, 67.31; H, 4.42%); ν_{max}/cm^{-1} 1990, 1920 (br), 1680 and 1620; δ_H(200 MHz; $CDCl_3$) 1.72–1.80 (m, 1H), 2.37 (s, 3H), 2.85–3.05 (m, 4H), 3.05 (m, 1H), 5.20 (d, 1H, *J* 7), 5.40 (t, 1H, *J* 6), 5.55 (t, 1H, *J* 6), 5.80 (d, 1H, *J* 7), 6.55 (s, 1H), 7.25–7.55 (m, 5H); δ_C(50.3 MHz; $CDCl_3$) 21.2, 27.1, 28.2, 41.4, 45.3, 47.2, 89.5, 90.1, 91.7, 94.2, 97.7, 112.3, 120.0, 127.6, 129.8, 137.3, 138.8, 154.9, 198.3, 232.2.

Complex 8b. Red solid (mp 230 °C, decomp.) (Found: C, 66.90; H, 4.01; $C_{23}H_{18}O_4Cr$ requires C, 67.31; H, 4.42%); ν_{max}/cm^{-1} 1990, 1920 (br), 1680 and 1620; δ_H(200 MHz; $CDCl_3$) 1.25–1.50 (m, 2H), 1.90 (m, 1H), 2.50–3.00 (m, 5H), 5.25 (m, 2H, *J* 7), 5.60 (t, 1H, *J* 6), 5.90 (d, 1H, *J* 7), 6.50 (s, 1H), 7.25–7.45 (m, 5H); δ_C(50.3 MHz; $CDCl_3$) 27.4, 28.5, 41.6, 45.5, 46.8, 89.7, 90.5, 91.9, 94.8, 95.3, 112.5, 114.7, 126.4, 128.7, 134.1, 154.9, 159.2, 198.5, 232.9.

Complex 7c. Red solid (mp 166–167 °C) (Found: C, 65.23; H, 4.92; $C_{24}H_{20}O_5Cr$ requires C, 65.45; H, 4.58%); ν_{max}/cm^{-1} 1990, 1920 (br), 1680 and 1620; δ_H(200 MHz; $CDCl_3$) 1.55–1.35 (m, 1H), 1.75–1.85 (m, 1H), 2.50–2.85 (m, 4H), 3.05 (m, 1H), 3.85 (s, 3H), 5.20 (d, 1H, *J* 7), 5.40 (t, 1H, *J* 6), 5.55 (t, 1H, *J* 6), 5.85 (d, 1H, *J* 7), 6.55 (s, 1H), 6.95 (d, 2H), 7.20 (d, 2H); δ_C(50.3 MHz; $CDCl_3$) 26.1, 29.3, 42.9, 45.6, 46.9, 55.4, 89.4, 90.5, 92.0, 93.8, 95.5, 111.3, 114.5, 122.0, 128.6, 133.8, 155.1, 159.0, 197.8, 231.9.

Complex 8c. Red solid (mp 199 °C) (Found: C, 65.03; H, 4.29; $C_{24}H_{20}O_5Cr$ requires C, 65.45; H, 4.58%); ν_{max}/cm^{-1} 1990, 1920 (br), 1680 and 1620; δ_H(200 MHz; $CDCl_3$) 1.25–1.50 (m, 1H), 1.85–2.00 (m, 2H), 2.55–3.00 (m, 5H), 3.85 (s, 3H), 5.25 (m, 1H), 5.65 (t, 1H, *J* 6), 5.90 (d, 1H, *J* 7), 6.50 (s, 1H), 6.95 (d, 2H, *J* 9), 7.20 (d, 2H, *J* 9); δ_C(50.3 MHz; $CDCl_3$) 27.1, 28.2, 41.7, 45.4, 46.8, 55.5, 89.4, 90.0, 91.6, 94.2, 94.7, 112.4, 114.6, 126.0, 128.7, 133.8, 154.9, 159.1, 198.3, 232.8.

General method for annulation of complexes 4a,b using ethyl acetoacetate

Ethyl acetoacetate (260 mg, 2 mmol) was added to Bu^{t}OK (10 mmol of K in 1 ml of *tert*-butyl alcohol) at 0 °C. After 10 min, the complexed substrate **4a,b** (1 mmol) was added as a solid followed by THF (5 ml). The reaction was monitored by TLC, and was found to be complete in 8–12 h. After completion of the reaction, the solvent was removed under reduced pressure, the reaction mixture washed with water and extracted using dichloromethane (3 × 20 ml). The diastereomers were separated using chromatography (gradient elution, 10% ethyl acetate–90% light petroleum to 40% ethyl acetate–60% light petroleum). The less polar fraction provided the yellow coloured major isomer while the red coloured minor isomer was contained in the polar fraction.

Tricarbonyl(2-oxo-4-phenyl-3,4,4a,5,6,7-hexahydro-2*H*-dibenzo[*a*,*c*]cycloheptene)chromium(0) 9a. Yellow solid (mp 154 °C) (Found: C, 68.00; H, 4.79; $C_{25}H_{22}O_4Cr$ requires C, 68.49; H, 5.06%); ν_{max}/cm^{-1} 1990, 1920, 1680, 1620; δ_H(200 MHz; $CDCl_3$) 1.65–2.05 (m, 4H), 2.33 (s, 3H), 2.40–2.64 (m, 1H), 2.64–3.05 (m, 4H), 3.35 (q, 1H, *J* 10), 5.14 (m, 2H), 5.35 (d, 1H, *J* 6), 5.43 (t, 1H, *J* 7), 6.30 (s, 1H), 7.10 (m, 4H); δ_C(50.3 MHz; $CDCl_3$) 21.1, 24.7, 31.3, 33.0, 42.0, 45.4, 45.6, 87.6, 90.9, 94.5, 96.2, 110.7, 111.3, 127.2, 129.6, 130.2, 136.8, 139.7, 161.0, 168.0, 198.0, 232.5.

Complex 10a. Red solid (mp 194 °C) (Found: C, 67.99; H,

4.68; $C_{25}H_{22}O_4Cr$ requires C, 68.49; H, 5.06%); ν_{max}/cm^{-1} 1990, 1920, 1680, 1620; δ_H(200 MHz; $CDCl_3$) 1.80–2.05 (m, 4H), 2.40–2.55 (m, 1H), 2.65–3.02 (m, 4H), 3.20 (q, 1H, *J* 10), 3.81 (s, 3H), 5.10 (m, 2H), 5.34 (d, 1H, *J* 7), 5.45 (t, 1H, *J* 6), 6.25 (s, 1H), 6.85 (d, 2H, *J* 9), 7.20 (d, 2H, *J* 9).

Complex 9b. Yellow solid (mp 162 °C) (Found: C, 67.40; H, 4.64; $C_{24}H_{20}O_4Cr$ requires C, 67.92; H, 4.75%); ν_{max}/cm^{-1} 1990, 1920, 1680, 1620; δ_H(200 MHz; $CDCl_3$) 1.82–2.10 (m, 4H), 2.45–2.60 (m, 1H), 2.70–3.05 (m, 4H), 3.40 (q, 1H, *J* 10), 5.13 (m, 2H), 5.35 (d, 1H, *J* 7), 5.45 (t, 1H, *J* 6), 6.30 (s, 1H), 7.15–7.63 (m, 5H); δ_C(50.3 MHz; $CDCl_3$) 24.4, 31.1, 32.8, 41.5, 45.0, 45.6, 87.3, 90.7, 94.2, 95.9, 110.5, 110.9, 127.0, 128.1, 128.7, 129.9, 142.4, 160.7, 197.6, 231.9.

Complex 10b. Red solid (mp 189 °C) (Found: C, 67.55; H, 4.39; $C_{24}H_{20}O_4Cr$ requires C, 67.92; H, 4.75%); ν_{max}/cm^{-1} 1990, 1920, 1680, 1620; δ_H(200 MHz; $CDCl_3$) 1.80–2.05 (m, 4H), 2.40–2.55 (m, 1H), 2.65–3.02 (m, 4H), 3.35 (q, 1H, *J* 10), 3.81 (s, 3H), 5.10 (m, 2H), 5.34 (d, 1H, *J* 7), 5.45 (t, 1H, *J* 7), 6.25 (s, 1H), 6.85 (d, 2H, *J* 9), 7.20 (d, 2H, *J* 9).

Crystal data for 7b

Intensity data were collected on a Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å).‖ Crystal data are as follows: $C_{23}H_{18}O_4Cr$, M = 410.37, monoclinic, space group $P2_1/c$, $a = 11.607(2)$, b = 12.281(2), $c = 13.419(3)$ Å, $\beta = 99.22(2)°$, $V = 1888.1(6)$ Å^3, $Z = 4$, $F(000) = 848$, $D_x = 1.444$, red coloured tablet 0.1 × 0.3 × 0.4 mm, μ(Mo-Kα) = 0.633 mm^{-1}. A total of 2924 reflections were collected by the ω–2θ scan technique. The structure was solved by direct methods using SHELXL-93 and refined by full matrix least-squares. Non-hydrogen atoms were refined with anisotropic thermal parameters. The final R and wR factors were 0.0351 and 0.0935 respectively for 2764 observed reflections [$I > 2\sigma(I)$].

Crystal data for 9a

Intensity data were collected on a Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). Crystal data are as follows: $C_{25}H_{22}O_4Cr$, M = 438.44, monoclinic, space group $P2_1/a$, $a = 11.763(2)$, b = 14.485(2), $c = 12.296(3)$ Å, $\beta = 106.72(3)°$, $V = 2109.3(10)$ Å^3, $Z = 4$, $F(000) = 912$, $D_x = 1.381$, red coloured tablet 0.2 × 0.4 × 0.7 mm, μ(Mo-Kα) = 0.571 mm^{-1}. A total of 3252 reflections were collected by the ω–2θ scan technique. The structure was solved by direct methods using SHELXL-93 and refined by full matrix least-squares. Non-hydrogen atoms were refined with anisotropic thermal parameters. The final R and wR factors were 0.0572 and 0.1642 respectively, for 3097 observed reflections [$I > 2\sigma(I)$]. For both **7b** and **9a** the structures were solved using NRCVAX[16] with structure refinement using SHELXL-93.[17] Hydrogen atoms were located by a difference Fourier and were held fixed during refinement.

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