Regioselective Nucleophilic Additions to Tricarbonyl(η^6-arene)chromium(0) complexes: Electronic *versus* Chelation Control

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Regioselective addition of t-butyl-lithium to tricarbonyl(η^6-benzyl alcohol)chromium(0) proceeds to give tricarbonyl(η^6-5-methylene-6-*exo*-t-butylcyclohexa-1,3-diene)chromium(0), which can be isomerised to tricarbonyl(η^6-*o*-t-butyltoluene)chromium(0). Repetition of the reaction on tricarbonyl(η^6-1-phenethanol)chromium(0) gives regio- and stereo-selectively the corresponding 5-ethylidene complex.

The regioselective lithiation of arenes possessing a heteroatom substituent either directly attached to the arene ring[1] or in a benzylic position[2] has been widely studied. The successful application of this methodology to the synthesis of substituted arene systems has stimulated interest in the behaviour of the corresponding tricarbonyl(η^6-arene)chromium(0) complexes. The electron-withdrawing metal moiety renders the aromatic protons more acidic *via* stabilisation of the carbanion formed on deprotonation[3,4] and increases the susceptibility of the ring towards nucleophilic attack.[5] For example, additions of carbanions to tricarbonyl(η^6-benzene)chromium(0) (**1**) generates an intermediate tricarbonyl(η^5-6-*exo*-alkylcyclohexadienyl)chromium(0) anion which on oxidation or protonation generates the corresponding uncomplexed substituted arenes or cyclohexadienes respectively.[6,7] Thus, tricarbonyl(η^6-benzene)chromium(0) (**1**) reacts with the dithiane anion (**2**) to give, following iodine oxidation, (**3**) in excellent yield Scheme 1).[8]

Our interest focussed on the possibility of chelation-controlled nucleophilic addition of carbanions to tricarbonyl-(η^6-arene)chromium(0) complexes possessing a benzylic heteroatom function. Part of this work has been previously communicated.[9]

Results and Discussion

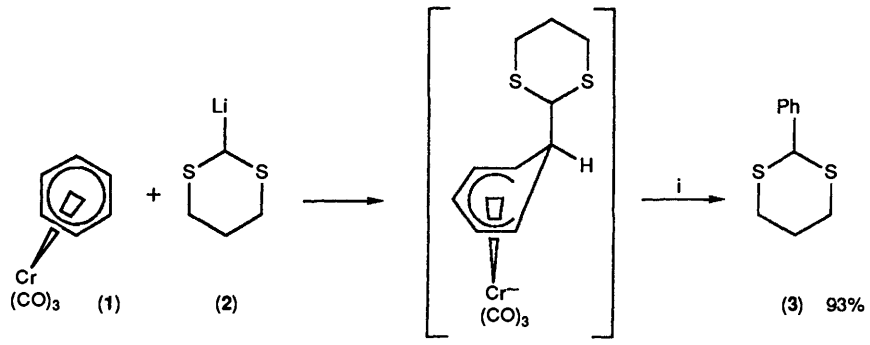
Thermolysis of benzyl alcohol and hexacarbonylchromium(0) in a 10:1 mixture of dibutyl ether and THF gave tricarbonyl(η^6-benzyl alcohol)chromium(0) (**4**) in 81% yield. Treatment of a THF solution of complex (**4**) at −78 °C with at least 2 equivalents of t-butyl-lithium resulted in an immediate colour change from yellow to orange. Allowing the orange solution to warm to room temperature before quenching generated, after chromatography, a red compound in moderate yield. The novel red compound was identified as tricarbonyl(η^6-5-methylene-6-*exo*-t-butylcyclohexa-1,3-diene)chromium(0) (**5**). The ^{1}H NMR spectrum of complex (**5**) contained a multiplet splitting pattern characteristic of the four contiguous protons of a co-ordinated cyclohexa-1,3-diene system together with singlets δ 4.13 (1 H), 3.73 (1 H), and 0.74 (9 H) indicative of *exo*-methylene and t-butyl groups respectively. Selected decoupling experiments allowed the spectrum to be fully assigned. Decoupling of the doublet of doublets δ 1.57 resulted in the collapse of the doublet of triplets δ 2.94 to a doublet; decoupling of the doublet of triplets δ 2.94 resulted in collapse of the doublet of doublets δ 1.57 to a singlet and simplification of the multiplet δ 5.28–5.25. Lastly, decoupling of the doublet δ 4.49 resulted in collapse of the multiplet δ 5.61–5.59 to a doublet. These experiments established that the two downfield multiplets δ 5.61–5.59 and δ 5.28–5.25 were assignable to the central protons, 3-H and 2-H respectively, of the cyclohexadiene system, whilst the doublet of triplets δ 2.94 and the doublet 4.49 were assignable to the terminal protons, 1-H and 4-H respectively, of the cyclohexadiene system. The doublet of doublets δ 1.57 was assigned to 6-H. IR absorptions (1 980, 1 900, and 1 880 cm^{-1}) and a molecular ion [*m*/*z* 284 (M^+)] in the mass spectrum indicated that the tricarbonylchromium(0) unit was still present. The assignment of complex (**5**) was confirmed by elemental microanalysis and subsequently by an X-ray crystal structure

Table 1. Atomic co-ordinates for complex (**5**) with estimated standard deviations in parentheses.

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cr(1)	0.219 54(5)	0.115 64(6)	0.607 87(6)
C(1)	0.195 6(3)	0.218 3(4)	0.453 9(4)
C(2)	0.131 2(3)	0.186 8(4)	0.510 0(4)
C(3)	0.116 3(3)	0.076 1(4)	0.517 7(5)
C(4)	0.104 8(3)	0.034 6(5)	0.618 1(5)
C(5)	0.112 7(3)	0.100 8(5)	0.707 5(4)
C(6)	0.119 6(3)	0.207 1(5)	0.694 5(4)
C(7)	0.095 8(3)	0.257 8(4)	0.592 8(4)
C(8)	0.007 3(3)	0.287 3(5)	0.580 8(4)
C(9)	−0.012 0(4)	0.367 0(5)	0.666 4(5)
C(10)	−0.048 1(4)	0.196 3(6)	0.592 3(6)
C(11)	−0.003 2(4)	0.335 5(5)	0.471 2(5)
C(12)	0.283 9(3)	0.045 7(4)	0.515 0(5)
C(13)	0.269 4(4)	0.030 9(5)	0.706 0(5)
C(14)	0.288 0(4)	0.221 8(5)	0.648 4(5)
O(1)	0.323 6(3)	−0.003 8(4)	0.461 8(4)
O(2)	0.304 9(3)	−0.021 5(4)	0.761 2(4)
O(3)	0.328 0(3)	0.287 4(4)	0.673 3(5)
H(1)	0.208 0(3)	0.293 2(4)	0.446 6(4)
H(2)	0.230 2(3)	0.165 7(4)	0.419 8(4)

Table 2. Selected torsional angles (°) for complex (**5**).

C(1)–C(2)–C(3)–C(4)	128.1
C(2)–C(3)–C(4)–C(5)	−3.7
C(3)–C(4)–C(5)–C(6)	9.9
C(4)–C(5)–C(6)–C(7)	18.1
C(5)–C(6)–C(7)–C(2)	−44.7
C(6)–C(7)–C(2)–C(3)	−79.1
C(10)–C(8)–C(7)–C(2)	64.6
C(10)–C(8)–C(7)–C(6)	−57.8
C(1)–C(2)–Cr(1)–C(12)	−49.4
C(1)–C(2)–Cr(1)–C(14)	55.4
H(2)–C(1)–C(2)–C(3)	0.2



Scheme 1. *Reagents:* i, I_2.

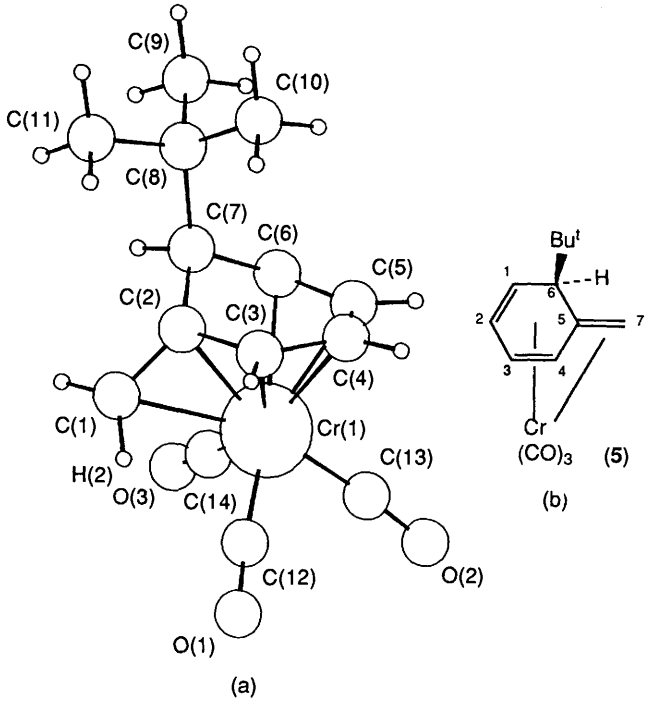


Figure 1. (a) X-Ray crystal structure of tricarbonyl(η^6-5-methylene-6-*exo*-t-butylcyclohexa-1,3-diene)chromium(0) (**5**); (b) systematic numbering scheme.

analysis performed on a single crystal of compound (**5**) grown from a saturated pentane solution (Figure 1).

Atomic co-ordinates and selected torsional angles for the structure are presented in Tables 1 and 2 above.* The most important feature arising from Figure 1 is the η^6-co-ordination of the ligand to the metal atom; co-ordination of the *exo*-methylene group to the chromium results in puckered geometry of the cyclohexa-1,3-diene moiety. The 6-t-butyl group is approximately perpendicular to the plane of the cyclohexa-1,3-diene system.

Repetition of the reaction but with addition of methyl iodide prior to quenching with methanol, warming to room temperature, and evaporation gave a red oil.

Chromatography afforded starting material and a less polar red compound which was crystallised to give red needles of complex (**5**). None of the *ortho* alkylated benzyl alcohol complex, an authentic sample of which had been prepared, could be detected by ^{1}H NMR spectroscopy.

Formation of the triene (**5**) is consistent with initial formation of the alkoxide (**6**) followed by regioselective chelation-controlled *ortho* addition of the carbanion from the *exo* face giving the dianion (**7**). Protonation of (**7**) on addition of methanol followed by loss of the benzylic oxygen substituent *via* neighbouring group participation from the chromium atom would generate the observed triene (**5**) (Scheme 2).

This regioselective *ortho* addition contrasts with the reported nucleophilic additions to tricarbonyl(η^6-anisole)chromium(0)[10] and tricarbonyl(η^6-α,α,α-trifluorotoluene)chromium(0)[11] which occur predominantly in the *meta* and *para* positions respectively. The absence of the expected *ortho* alkylated benzyl alcohol complexes in the reaction of tricarbonyl(η^6-benzyl alcohol)chromium(0) (**4**) with t-butyl-lithium at −78 or 20 °C in the presence of methyl iodide contrasts with the regioselective *ortho* lithiation of free benzyl alcohol reported by Seebach[12] and illustrates the increased susceptibility of tricarbonyl(η^6-arene)chromium(0) complexes towards nucleophilic attack.

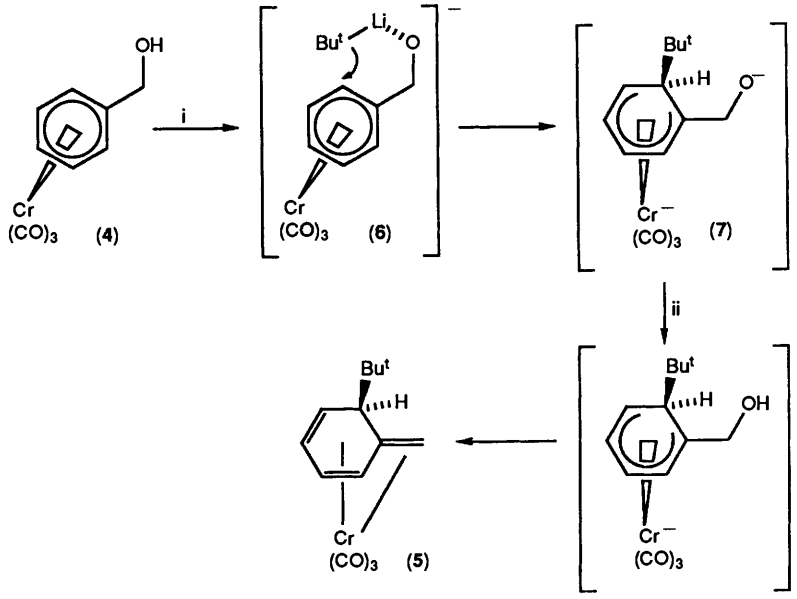
The triene complexes were found to undergo rearrangement when heated in protic solvents. On warming a red methanolic solution of the triene (**5**), a yellow solution was obtained. Work-up gave tricarbonyl(η^6-*o*-t-butyltoluene)chromium(0) (**8**) as a yellow powder (Scheme 3).

This isomerisation could also be achieved using acidic methanol but prolonged warming with methanol containing a catalytic amount of methoxide resulted in extensive decomposition and none of the desired complex (**8**). The use of deuteriomethanol gave the α-monodeuteriated complex (**9**). These results are consistent with initial protonation/deuteriation of the triene (**5**) followed by deprotonation at C-6 (Scheme 4).

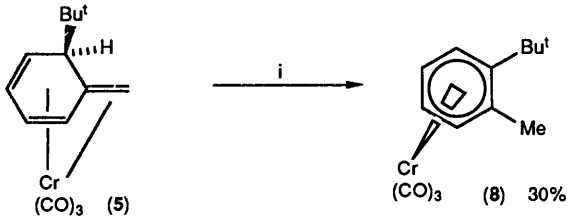
The treatment of tricarbonyl(η^6-benzyl alcohol)chromium(0) (**4**) with at least 2 equiv. of methyl-lithium–TMEDA, butyl-lithium, or phenyl-lithium gave the corresponding red triene complexes (**10**), (**11**), and (**12**) respectively (Scheme 5). Complexes (**10**) and (**11**) were unstable however and chromatography resulted in isomerisation to the fully aromatic complexes (**13**) and (**14**) respectively. Complex (**13**) was identical in all respects with an authentic sample synthesised from thermolysis of hexacarbonylchromium(0) and *o*-xylene (**16**). The stable triene (**12**) afforded red crystals from pentane. The ^{1}H NMR spectrum of complex (**12**) exhibited similar features to that of triene (**5**). Singlets at δ 4.36 and 3.79 were assigned to the *exo*-methylene group whilst the proton at the phenyl substituted carbon C-6 appeared as a doublet δ 2.47. Methanol treatment of triene (**12**) gave the fully aromatic complex (**15**) in 33% overall yield.

Decomposition of (**13**) and (**15**) by exposure of diethyl ether solutions to the air and sunlight gave *o*-xylene (**16**) and *o*-methylbiphenyl (**17**) identical in all respects with authentic samples.

* Thermal parameters and other bond lengths and angles are available on request from the Cambridge Crystallographic Data Centre. See Instructions for Authors (1990), *J. Chem. Soc., Perkin Trans. I*, 1990, Issue 1.



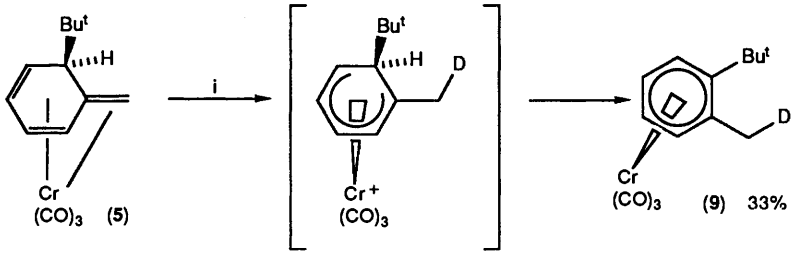
Scheme 2. *Reagents:* i, 2 Bu^{t}Li; ii, H^+.



Scheme 3. *Reagents:* i, H^+.

addition of carbanions to tricarbonyl(η^6-benzyl alcohol)-chromium(0) (**4**) and to elucidate further aspects of the mechanism, the tricarbonylchromium(0) complexes of racemic 1-phenethanol and diphenylmethanol were prepared. Thermolysis of hexacarbonylchromium(0) with each of the arenes, gave the corresponding complexes (**21**) and (**22**). In the case of diphenylmethanol, a small quantity of the bistricarbonyl-chromium(0) complex (**23**) was isolated (Scheme 8).

The presence of a chiral centre in the side-chain of complexes (**21**) and (**22**) renders the two *ortho* positions diastereotopic.



Scheme 4. *Reagents:* i, CD_3OD.

Semmelhack has shown that intermediates resulting from nucleophilic addition to tricarbonyl(η^6-arene)chromium(0) complexes may be oxidatively trapped with iodine to give the ring substituted arene complex.[6-8] For example, treatment of tricarbonyl(η^6-benzene)chromium(0) (**1**) with t-butyl-lithium followed by iodine oxidation of the resulting intermediate, gives t-butylbenzene (**18**) in 97% yield (Scheme 6).

To confirm that dianions of the type (**7**) (Scheme 2) are intermediates on the reaction pathway, tricarbonyl(η^6-benzyl alcohol)chromium(0) (**4**) in THF at −78 °C was treated with phenyl-lithium and allowed to warm to room temperature whereupon a characteristic red solution was observed. The solution was cooled to −78 °C and iodine was added; the mixture was then warmed to room temperature and stirred for 12 h to give, after work-up, *o*-biphenylmethanol (**19**). A minor product was also isolated; ^{1}H NMR and IR spectroscopic data were consistent with the corresponding aldehyde (**20**) which is presumably formed by iodine-mediated oxidation of the alcohol (**19**) (Scheme 7).

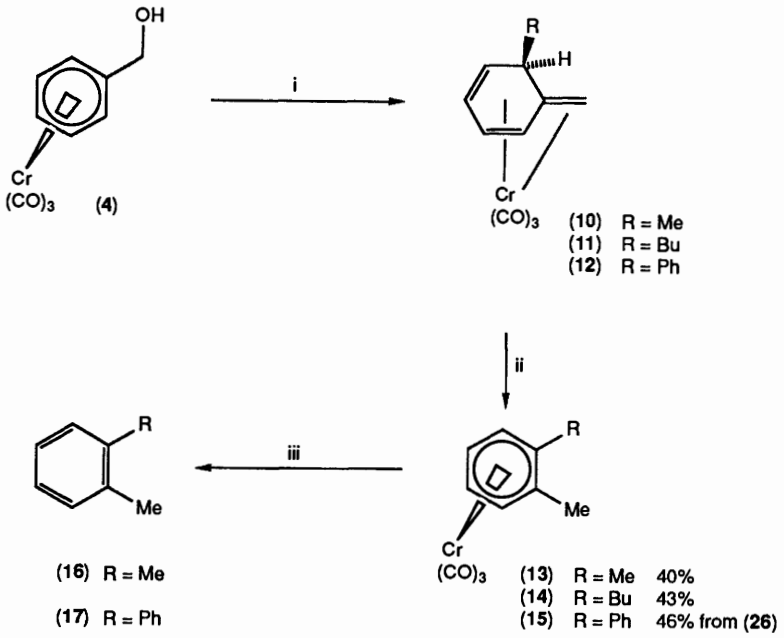
In order to examine the generality of the regioselective *ortho*

Previous work has shown that treatment of tricarbonyl[η^6-(*S*)-α-methylbenzyldimethylamine]chromium(0) (**24**) with t-butyl-lithium and methyl iodide gave a single diastereoisomer of tricarbonyl[η^6-(*S*)-2-α-dimethylbenzyldimethylamine]chromium(0) (**25**). This is consistent with a chelation-controlled metallation *via* transition states such as (**26**) in which the benzylic methyl group is positioned away from the bulky tricarbonylchromium(0) moiety (Scheme 9).[13]

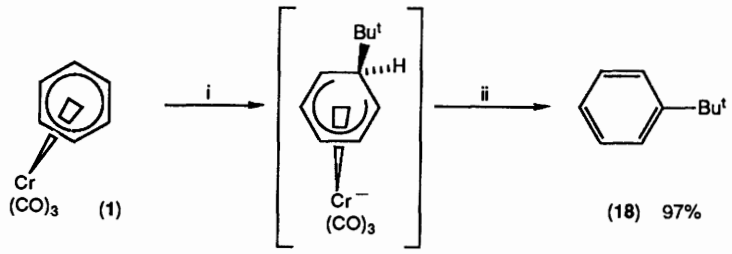
Jaouen has also demonstrated that chiral tricarbonyl(η^6-1-phenethanol)chromium(0) (**21**) undergoes the Ritter reaction with retention of configuration *via* the stabilised carbonium ion (**27**) (Scheme 10).[14]

It would, therefore, be expected that chelation controlled *ortho* attack by an alkyl-lithium onto complexes (**21**) or (**22**), *via* the least hindered transition states such as (**28**) (Scheme 11*) coupled with loss of the benzylic substituent from the *exo* face *via* neighbouring group participation from the chromium,

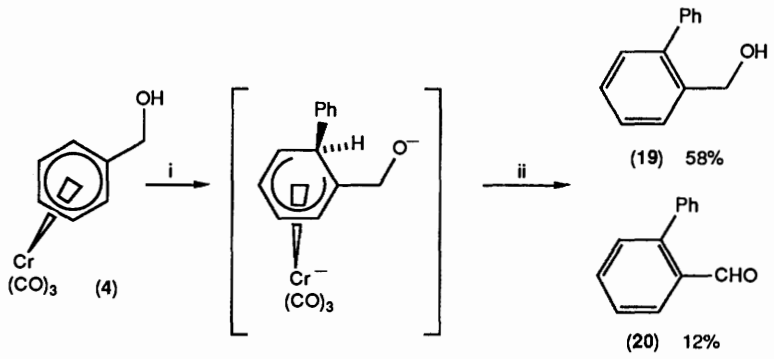
* Only one enantiomer is shown for clarity.



Scheme 5. *Reagents:* i, 2 RLi; ii, H^+; iii, *hν*, O_2.



Scheme 6. *Reagents:* i, Bu^tLi; ii, I_2.



Scheme 7. *Reagents:* i, 2 PhLi; ii, I_2.

would generate predominantly one isomer of the triene (**29**) with the *exo*-methylene substituent *trans* with respect to the C-6 substituent.

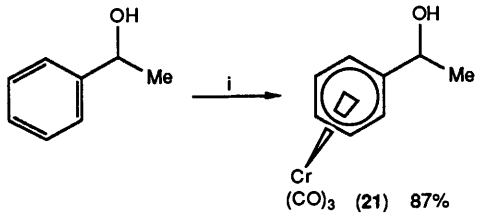
Treatment of complexes (**21**) or (**22**) with at least 2 equivalents of alkyl-lithium following the procedure outlined previously gave, in each case, a stable triene product as a mixture of isomers. The major isomer in each case was assumed to have the *exo*-methylene substituent in the sterically least demanding *trans* geometry (Scheme 12).

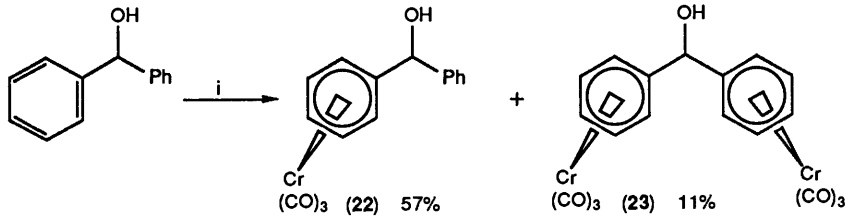
These results are consistent with both chelation-controlled regioselective nucleophilic addition *via* the least-hindered transition states such as (**28**) in which the bulky benzylic substituent is *exo* with respect to the tricarbonylchromium(0) moiety and subsequent loss of the benzylic substituent from the *exo* face *via* a neighbouring group participation from the chromium.

The major *trans* isomers (**32**) and (**34**) were purified by fractional crystallisation. Treatment of the mixture of trienes (**30**) and (**31**) with methanol gave tricarbonyl(η6-*o*-ethylbutylbenzene)chromium(0) (**36**).

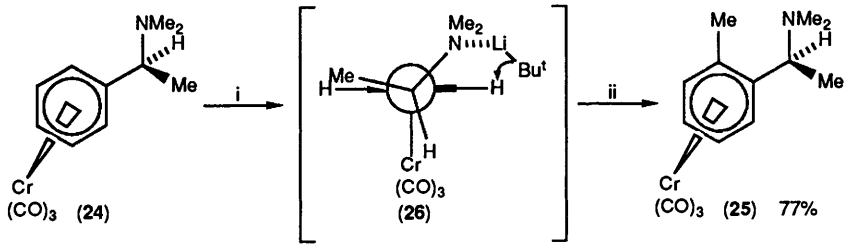
The triene (**5**) was also observed as a side-product in the t-butyl-lithium mediated metallation and subsequent alkylation of tricarbonyl(η^6-benzyldimethylamine)chromium(0) (**37**) in THF at −78 °C (Scheme 13).

A similar mechanism involving regioselective chelation-controlled addition of the carbanion to an *ortho* position to give the anion (**39**) followed by loss of the benzylic amino function, would account for the formation of (**5**) (Scheme 14).

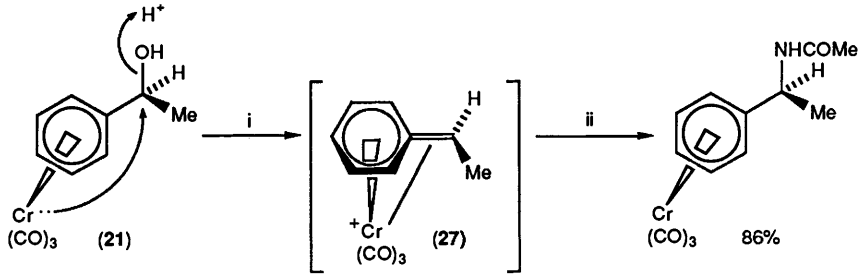




Scheme 8. *Reagents:* i, $Cr(CO)_6$.



Scheme 9. *Reagents:* i, Bu^tLi; ii, MeI.



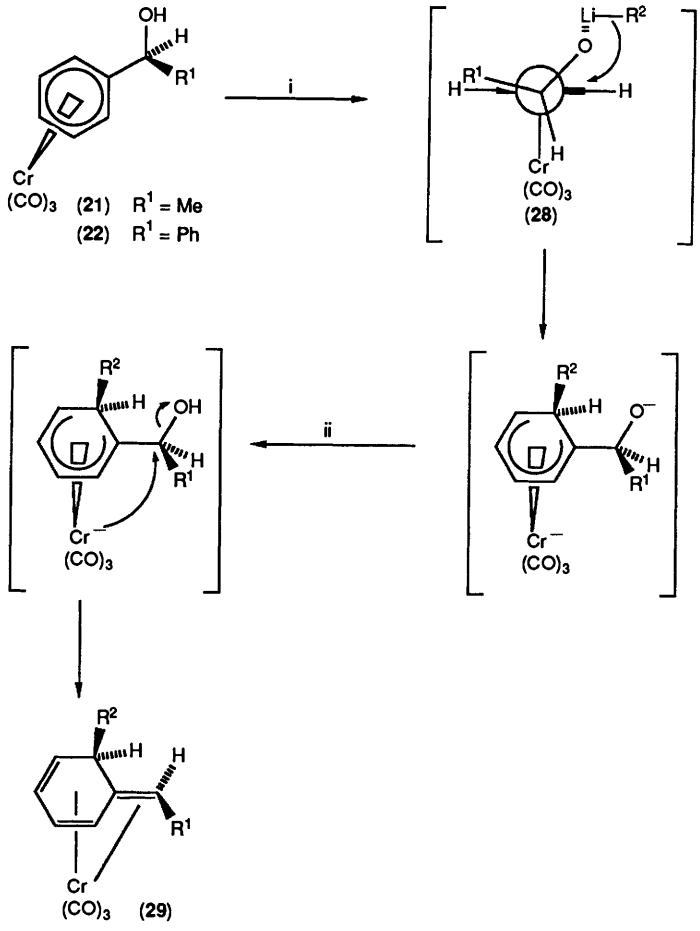
Scheme 10. *Reagents:* i, H^+; ii, MeCN, H_2O.

Formation of the *ortho* alkylated product (**38**) can be explained by chelation-controlled *ortho* deprotonation by t-butyl-lithium to give the stabilised organolithium (**40**) (Scheme 15).

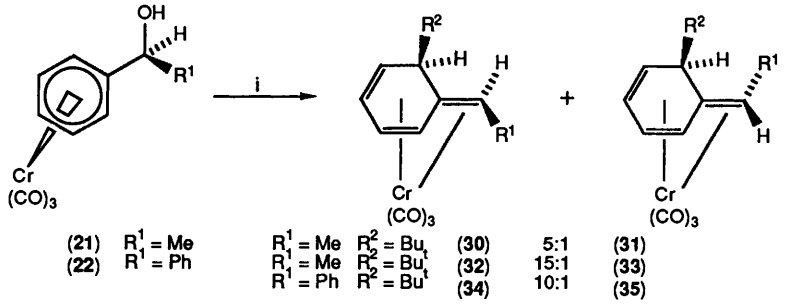
Nitrogen-directed lithiation of complex (**38**) with t-butyl-lithium in THF at −78 °C followed by addition of methyl iodide and quenching with methanol gave a red solution. Chromatography gave a yellow oil and a red solid (**41**). The oil was characterised as a mixture of tricarbonyl(η^6-*o*,*o*-dimethylbenzyldimethylamine)chromium(0) (**42**) and tricarbonyl(η^6-*o*-ethylbenzyldimethylamine)chromium(0) (**43**) in a ratio of 5:1. Fractional recrystallisation gave (**42**) as yellow crystals. The ^1H NMR spectrum of complex (**41**) was similiar to that of (**5**) but with the replacement of the doublet of doublets of δ 1.57 by a singlet at δ 1.74. Complex (**41**) was identified as tricarbonyl(η^6-4-methyl-5-methylene-6-*exo*-t-butylcyclohexa-1,3-diene) chromium(0) formed in 28% yield by a similar mechanism to the formation of (**5**) and (**37**) (Scheme 16).

Chelation control is not the only means of regioselective control in nucleophilic addition reactions. Treatment of a THF solution of (*SR*)-tricarbonyl(η^6-*o*-trimethylsilyl-α-methylbenzyldimethylamine)chromium(0) (**44**) {prepared from tricarbonyl[η^6-(*R*)-α-methylbenzyldimethylamine]chromium(0)}[13] with 2 equivalents of t-butyl-lithium at −40 °C, stirring for 2 h followed by stirring for 2 h at 0 °C before methanolic work-up gave the red triene complex (**45**). The ^1H NMR spectrum of (**45**) contained a lowfield AB quartet due to two adjacent olefinic ring protons, a single proton quartet δ 4.45 coupled to a methyl proton doublet δ 1.96 characteristic of an ethylidene group, and two nine proton singlets at δ 1.05 and 0.17 produced by a t-butyl and trimethylsilyl group. Three IR carbonyl stretching absorptions confirmed that the tricarbonylchromium(0) unit was intact and a high resolution mass spectrum confirmed the identity of (**45**) as tricarbonyl[η^6-(*E*)-1-t-butyl-4-trimethylsilyl-5-ethylidenecyclohexa-1,3-diene]chromium(0). *E* Stereochemistry was assumed at the exocyclic double bond. The formation of the triene (**45**) is consistent with exclusive *exo* attack of the alkyl-lithium *para* to the trimethylsilyl group to give the stabilised anion (**46**). Antiperiplanar elimination of the dimethylamide anion gives the cross-conjugated product (**47**), presumably with the indicated stereochemistry. On methanolic work-up (**47**) rearranges to the triene (**45**) (Scheme 17).

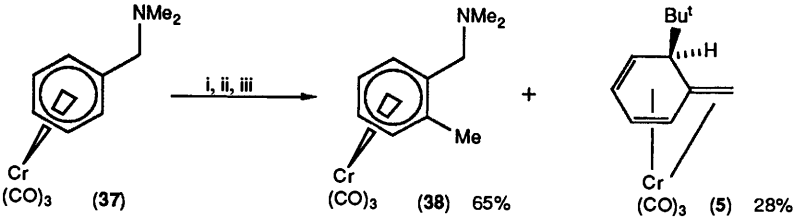
The first step of the triene formation involves nucleophilic addition of the alkyl-lithium to the tricarbonyl(η^6-arene)-



Scheme 11. *Reagents:* i, 2 R^2Li; ii, MeOH.



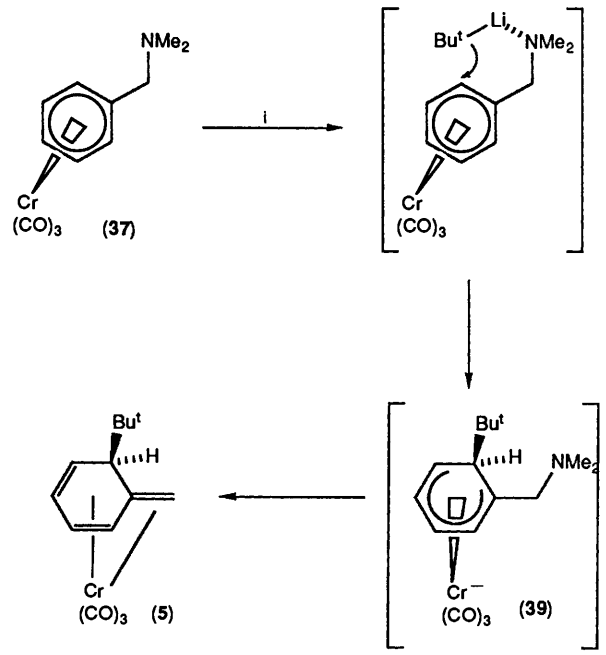
Scheme 12. *Reagents:* i, R^2Li.



Scheme 13. *Reagents:* i, Bu'Li; ii, MeI; iii, MeOH.

chromium(0) complex. In all the previous cases the organolithium reagent attacks at the *ortho* position presumably *via* co-ordination to the benzylic heteroatom substituent. However, in the formation of triene (**45**), t-butyl-lithium attacks at the position *meta* to the alkyl side-chain. This is because either the increased steric bulk around nitrogen disfavours co-ordination of the base or the trimethylsilyl group is exerting a strong *para*-directing effect. Where a single aryl substituent other than trimethylsilyl is present nucleophiles generally attack tricarbonyl(η^6-arene)chromium(0) complexes in the *meta* position.[7] The resultant anion may be oxidised or protonated to generate the corresponding uncomplexed substituted arenes or cyclohexa-

dienes respectively.[6] Two examples of nucleophilic attack on trimethylsilylarenes have been reported.[4,7] In both cases addition *para* to the trimethylsilyl group was observed, however the presence of other substituents meant that a *para* directing effect could not be unambiguously attributed to the trimethylsilyl group. In an attempt to provide conclusive evidence for activation of the *para* position the nucleophilic attack of t-butyl-lithium on tricarbonyl(η^6-phenyltrimethylsilane)chromium(0) (**48**) was investigated.



Scheme 14. *Reagents:* i, Bu^{t}Li.

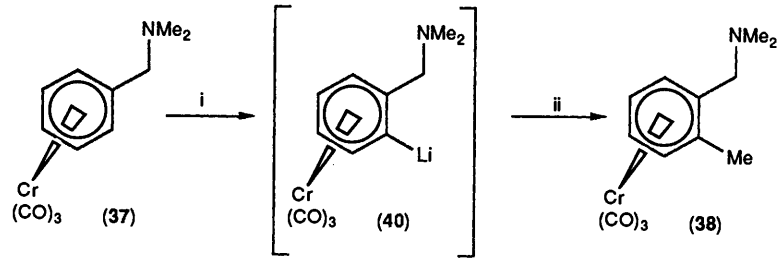
t-Butyl-lithium in THF at −78 °C was treated dropwise with a THF solution of half an equivalent of complex (**48**) and the mixture stirred for 1.5 h. Warming to 0 °C for 1 h followed by addition of an excess of iodine in THF and stirring at room temperature for 3 h gave, after work-up and sublimation, white crystals of 4-t-butylphenyltrimethylsilane (**49**). Formation of (**49**) presumably occurs *via* the intermediate anion (**50**) (Scheme 18).

Conclusion

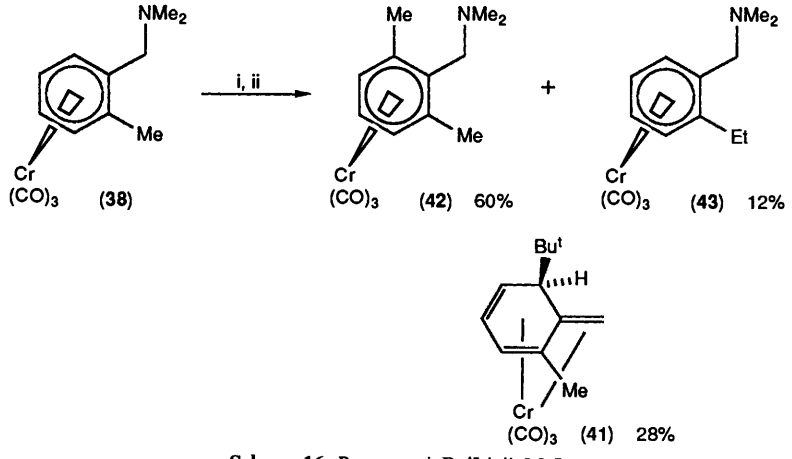
The work presented here provides a new example of the enhanced susceptibility of tricarbonyl(η^6-arene)chromium(0) complexes towards nucleophilic attack. Tricarbonyl(η^6-arene)-chromium(0) complexes with benzylic hydroxy or dimethylamino substituents undergo novel chelation-controlled regio- and stereo-selective nucleophilic attack by alkyl-lithiums to give, after loss of the heteroatom substituent, trienes such as (**5**), (**10**)–(**12**), and (**41**). These complexes rearrange in methanol to give the corresponding *ortho* alkylated toluene complexes (**8**) and (**13**)–(**15**). The remarkable stability of the trienes (**5**), (**12**), (**30**)–(**35**), (**41**), and (**45**) towards aromatisation can be attributed to the unfavourable steric interaction which would result from bringing two bulky *ortho* substituents into the plane of the newly formed aromatic ring. This interaction is particularly unfavourable in the case of 6-t-butyl substituted trienes or those bearing a substituent on the 5-*exo*-methylene group.

Experimental

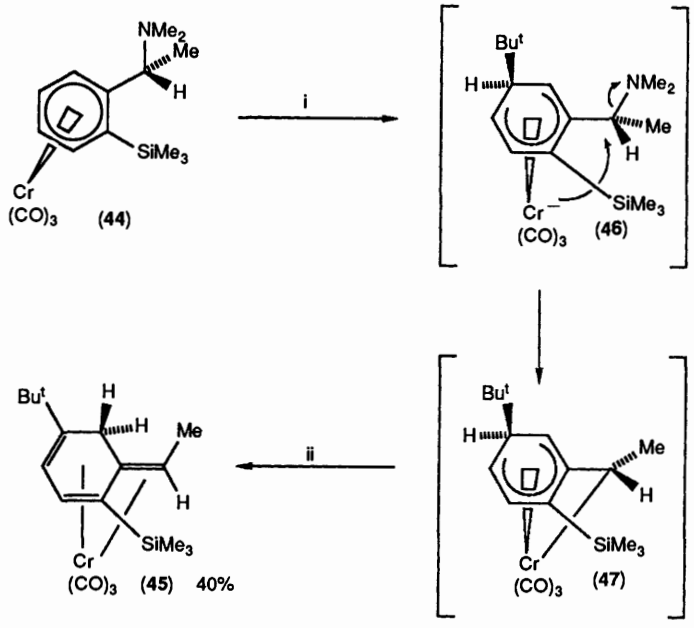
All reactions involving the preparation or utilisation of tricarbonyl(η^6-arene)chromium(0) complexes were performed under an atmosphere of nitrogen. All commercial reagents were purified according to standard techniques.[15] THF was distilled from sodium benzophenone ketyl under an atmosphere of



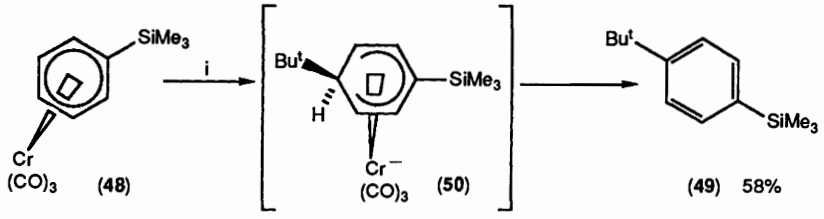
Scheme 15. *Reagents:* i, Bu^{t}Li; ii, MeI.



Scheme 16. *Reagents:* i, Bu^{t}Li; ii, MeI.



Scheme 17. *Reagents:* i, Bu^{t}Li; ii, MeOH.



Scheme 18. *Reagents:* i, Bu^{t}Li.

nitrogen. Diethyl ether was peroxide free and dibutyl ether was dried over sodium and distilled under an atmosphere of nitrogen prior to use. Hexacarbonylchromium(0) was steam distilled prior to use. Butyl-lithium was used as a 1.6M solution in hexanes, t-butyl-lithium as a 2.36M solution in pentane and methyl-lithium as a 1.5M solution in diethyl ether. M.p.s were obtained on a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained in chloroform solution and ^{1}H NMR spectra were obtained at 300 MHz unless otherwise stated. Mass spectra were obtained using In Beam Electron Impact techniques.

Tricarbonyl(η^6-*benzyl alcohol*)*chromium*(0) (**4**).—A deoxygenated mixture of dibutyl ether (90 ml), THF (9 ml), benzyl alcohol (3.00 g, 27.8 mmol) and hexacarbonylchromium(0) (7.00 g, 31.8 mmol) was heated at reflux (24 h). The cooled solution was filtered and the solvents removed. Column chromatography (Al_2O_3 Grade V; CH_2Cl_2) gave the title compound (**4**) as yellow flakes (5.50 g, 81%), m.p. 94–95 °C (lit.,[16] m.p. 95–96 °C); ν_{max} 3 280 and 3 180br (OH), and 1 980, 1 950, and 1 910 cm^{-1} (CO); δ($CDCl_3$ 60 MHz), 5.35 (s, 5 H, Ar H), 4.45 (s, 2 H, ArCH_2OH), and 2.35 (s, br, 1 H, ArCH_2O*H*); *m*/*z* 244 (M^+).

Tricarbonyl(η^6-5-*methylene*-6-exo-*t-butylcyclohexa*-1,3-*diene*)*chromium*(0) (**5**): *Formation at* −78 °C.—t-Butyl-lithium (2.0 ml, 4.72 mmol) was added to a stirred solution of tricarbonyl(η^6-benzyl alcohol)chromium(0) (**4**) (400 mg, 1.64 mmol) in THF (20 ml) at −78 °C. The initial yellow solution rapidly turned red. The mixture was stirred (2 h, −78 °C) and then methyl iodide (0.5 ml, 8.03 mmol) was added and stirring continued (2 h, −78 °C). Methanol was added to the mixture which was then warmed to 20 °C and evaporated to give a red gum. Column chromatography (Al_2O_3, Grade V) of this gave two fractions. Fraction one (1:10, Et_2O–light petroleum) gave the title compound (**5**) as a red gum which upon crystallisation (pentane) gave crimson needles (25.0 mg), 5.4%), m.p. 108–111 °C (Found: C, 59.4; H, 5.8; $C_{14}H_{16}CrO_3$ requires C, 59.2; H, 5.7%); ν_{max} 1 980, 1 900, and 1 880 cm^{-1} (CO); δ($CDCl_3$) 5.61–5.59 (m, 1 H, 3-H), 5.28–5.25 (m, 1 H, 2-H), 4.49 (d, *J* 5.4 Hz, 1 H, 4-H), 4.13 (s, 1 H, $RR^1C{=}CH_2$), 3.73 (s, 1 H, $RR^1C{=}CH_2$), 2.94 (dt, *J* 6.5, 1.2, 1H, 1-H), 1.57 (dd, *J* 6.5, 1.4 Hz, 1 H, 6-H), and 0.74 [s, 9 H, $RC(CH_3)_3$]; *m*/*z* 284 (M^+). Fraction two (CH_2Cl_2) gave starting material (**4**) as a yellow solid (250 mg, 63%), Fraction two (CH_2Cl_2) gave tricarbonyl(η^6-benzyl alcohol)chromium(0) (**4**) as a yellow solid (250 mg, 63%) identified by comparison with an authentic sample.

Tricarbonyl(η^6-5-*methylene*-6-exo-*t-butylcyclohexa*-1,3-*diene*)*chromium*(0) (**5**): *Formation at* 20 °C.—t-Butyl-lithium (2.1 ml, 4.96 mmol) was added to a stirred solution of tricarbonyl(η^6-benzyl alcohol)chromium(0) (**4**) (450 mg, 1.84 mmol) in THF (25 ml) at −78 °C. The initial yellow solution rapidly turned red and was allowed to warm to 20 °C. After being stirred (2 h, 20 °C), the solution was cooled (−78 °C) and treated with methanol (2 ml). The mixture was warmed (20 °C) and evaporated to give a red gum. Column chromatography (Al_2O_3 Grade V; 1:10, Et_2O–light petroleum) gave the title compound (**5**) as a red gum. Crystallisation (pentane) gave crimson needles (250 mg, 50%), identified by comparison with an authentic sample.

X-*Ray Crystal Structure Analysis of Tricarbonyl*(η^6-5-*methylene*-6-exo-*t-butylcyclohexa*-1,3-*diene*)*chromium*(0) (**5**).—

Cell parameters and reflection intensities were measured using graphite monochromated Cu-K_α radiation on an Enraf-Nonius CAD-4-diffractometer operating in the $\omega/2\theta$ scan mode. The scan range (ω) was calculated from $[1.00 + 0.14 \tan\theta]°$, and the scan speed varied from 1.0 to 6.7°/min depending upon the intensity. Reflections were measured in the range $0 < \theta < 60°$. Three standard reflections measured every hour were used to scale the data and correct for crystal decomposition. The data were corrected for Lorentz-polarisation and absorption effects[17] (relative transmission factors 1.00–2.06) and equivalent reflections were merged to give 2 054 unique reflections of which 1 356 were considered to be observed [$I > 3\sigma(I)$] and used in the structure analysis. Scattering factors were taken from International Tables.[18]

Crystal data. $C_{14}H_{16}O_3Cr$, $M = 284.28$. Orthorhombic, space group *Pbca* (established from systematic absences), $a = 17.038(3)$, $b = 12.988(2)$, $c = 12.572(2)$ Å, $U = 2\,782$ Å^3, $Z = 8$, D_{calc} 1.36 Mgm^{-3}, μ(Cu-K_α) 68.1 cm^{-1}.

The structure was solved by direct methods and electron density Fourier synthesis and refined by full-matrix least-squares methods. Parameters in the final cycles of refinement included those for positional co-ordinates, anisotropic temperature factors (non-hydrogen atoms), an overall scale factor, and an extinction parameter.[19] Hydrogen atoms were included in calculated positions and were allowed to ride on their respective carbon atoms. The refinement was terminated when all shifts were less than 0.001 σ with $R = 0.052$ ($R_w = 0.066$). The weight for each reflection was calculated from the Chebyshev series $w = [418.6t_0(X) + 572.8t_1(X) + 187.6t_2(X)]$ where $X = F_0/F_{max}$.[20] Final difference electron-density Fourier synthesis revealed no significant features and a detailed analysis failed to reveal any systematic errors. All calculations were performed using the CRYSTALS package[21] on the Chemical Crystallography Laboratory VAX 11/750 computer.

Tricarbonyl(η^6-o-*t-butyltoluene*)*chromium*(0) (**8**).—Methanol (5 ml) was added to tricarbonyl(η^6-5-methylene-6-*exo*-t-butylcyclohexa-1,3-diene)chromium(0) (**5**) (100 mg, 0.35 mmol) and the red solution heated at gentle reflux (5 h). The resulting yellow solution was cooled and the solvent removed to give a green gum. Column chromatography (Al_2O_3 Grade V; 1:1, Et_2O–light petroleum) gave the title compound (**8**) as a yellow powder (30 mg, 30%); ν_{max} 1 965 and 1 870br cm^{-1} (CO); $\delta(CDCl_3)$ 5.72 (d, 1 H, ArH), 5.49 (t, 1 H, ArH), 5.03 (t, 1 H, ArH), 4.96 (d, 1 H, ArH), 2.43 (s, 3 H, ArCH_3), and 1.41 [s, 9 H, ArC(CH_3)$_3$] [Found: *m/z* 284.0504 (M^+). $C_{14}H_{16}CrO_3$ requires *m/z* 284.0504].

Tricarbonyl(η^6-o-*t-butyl-α-monodeuteriotoluene*)*chromium*(0) (**9**).—Deuteriomethanol (4 ml) was added to tricarbonyl(η^6-5-methylene-6-*exo*-t-butylcyclohexa-1,3-diene)-chromium(0) (**5**) (300 mg, 1.06 mmol) and the red solution heated at gentle reflux (4 h). The resulting orange solution was cooled and the solvent removed to leave an orange gum. Column chromatography (Al_2O_3 Grade V) gave two fractions. Fraction one (1:10, Et_2O–light petroleum) gave a red gum (50 mg, 17%) identical in all respects with an authentic sample of the triene (**5**). Fraction two (1:1, Et_2O–light petroleum) gave the title compound (**9**) as a yellow powder (100 mg, 33%), ν_{max} 1 965 and 1 870 cm^{-1} (CO); $\delta(CDCl_3)$ 5.82 (d, 1 H, ArH), 5.49 (t, 1 H, ArH), 5.03 (t, 1 H, ArH), 4.96 (d, 1 H, ArH), 2.43–2.41 (m, 2 H, ArCH_2D), and 1.41 [s, 9 H, ArC(CH_3)$_3$]; *m/z* 285 (M^+).

Tricarbonyl(η^6-o-*xylene*)*chromium*(0) (**13**).—A deoxygenated mixture of dibutyl ether (40 ml), THF (4 ml), *o*-xylene (1.00 g, 9.43 mmol), and hexacarbonylchromium(0) (2.50 g, 11.36 mmol) was heated at reflux (27 h). The cooled solution was filtered and the solvents removed to give a yellow oil. Column chromatography (Al_2O_3 Grade V, 1:1, Et_2O–light petroleum) of this gave the title compound (**13**) as a yellow powder (1.51 g, 66%), m.p. 89–91 °C (lit.,[16] 90–91.5 °C); ν_{max} 1 970, 1 940, and 1 900br cm^{-1} (CO); $\delta(CDCl_3)$ 5.31–5.22 (m, 4 H, ArH) and 2.17 (s, 6 H, ArCH_3); *m/z* 242 (M^+).

Tricarbonyl(η^6-o-*xylene*)*chromium*(0) (**13**) *from Tricarbonyl*(η^6-*benzyl alcohol*)*chromium*(0) (**4**).—A solution of tricarbonyl(η^6-benzyl alcohol)chromium(0) (**4**) (400 mg, 1.64 mmol) in THF (10 ml) at −78 °C was added dropwise to a mixture of methyl-lithium (2.73 ml, 4.10 mmol) and TMEDA (0.60 ml, 4.00 mmol) in THF (10 ml) at −78 °C. The mixture was allowed to warm to 20 °C and was stirred (3 h). Methanol (2 ml) was added and the mixture evaporated to give a red gum. Column chromatography (Al_2O_3 Grade V; 1:1, Et_2O–light petroleum) gave the title compound (**13**) as a yellow powder (159 mg, 40%) which was identical in all respects with an authentic sample.

Tricarbonyl(η^6-o-*butyltoluene*)*chromium*(0) (**14**).—Butyl-lithium (1.7 ml, 2.72 mmol) was added to a stirred solution of tricarbonyl(η^6-benzyl alcohol)chromium(0) (**4**) (300 mg, 1.23 mmol) in THF (25 ml) at −78 °C. The mixture was allowed to warm to 20 °C and was stirred (4 h). Methanol (2 ml) was added and the solution evaporated to a red gum. Column chromatography (Al_2O_3 Grade V; 1:1, Et_2O–light petroleum) gave the title compound (**14**) as an orange oil (150 mg, 43%), ν_{max} 1 970 and 1 870br cm^{-1} (CO); $\delta(CDCl_3)$ 5.32–5.22 (m, 4 H, ArH), 2.62–2.49 (m, 1 H, ArCH_2R), 2.30–2.17 (m, 1 H, ArCH_2R), 2.17 (s, 3 H, ArCH_3), 1.58–1.35 (m, 4 H, RCH_2CH_2CH$_3$), and 0.97 (t, *J* 6.7 Hz, 3 H, RCH$_2$CH_3) [Found: *m/z* 284.0502 (M^+). $C_{14}H_{16}CrO_3$ requires *m/z* 284.0504].

Tricarbonyl(η^6-5-*methylene*-6-exo-*phenylcyclohexa*-1,3-*diene*)*chromium*(0) (**12**).—Phenyl-lithium[22] (6.0 ml, 5.70 mmol) was added to a solution of tricarbonyl(η^6-benzyl alcohol)-chromium(0) (**4**) (500 mg, 2.05 mmol) in THF (20 ml) at −78 °C. The red solution was allowed to warm to 20 °C and was stirred (3 h). Methanol (3 ml) was added and the solvents evaporated to give a red gum. Column chromatography (Al_2O_3 Grade V; 1:1, Et_2O–light petroleum) gave a yellow oil which was crystallised to give the title compound (**12**) as orange needles (pentane) (449 mg, 72%) (Found: C, 63.1; H, 3.9. $C_{16}H_{12}CrO_3$ requires C, 63.2; H, 4.0%); ν_{max} 1 980, 1 910, and 1 880br cm^{-1} (CO); $\delta(CDCl_3)$ 7.28–7.16 (m, 5 H, ArH), 6.07 (d, *J* 5.1 Hz, 1-H), 5.28 (t, *J* 6.0 Hz, 1 H), 4.36, 3.79 (2s, 2 H, RR^{1}C=CH_2), 2.70 (t, *J* 6.7 Hz, 1 H), 2.47 (d, *J* 13.1 Hz, 1 H), and 2.19–2.13 (m, 1 H).

Tricarbonyl(η^6-o-*methylbiphenyl*)*chromium*(0) (**15**).—Methanol (40 ml) and water (10 ml) were added to tricarbonyl(η^6-5-methylene-6-*exo*-phenylcyclohexa-1,3-diene)chromium(0) (**12**) (375 mg, 1.23 mmol) and the red solution was heated under gentle reflux (8 h). The resulting yellow solution was cooled and the solvent removed to give a yellow gum. Column chromatography (Al_2O_3 Grade V; 1:1, Et_2O–light petroleum) gave the title compound (**15**) as an orange powder (172 mg, 46%) (Found: C, 63.1; H, 3.9 $C_{16}H_{12}CrO_3$ requires C, 63.2; H, 4.0%); ν_{max} 1 965 and 1 879br cm^{-1} (CO); $\delta(CDCl_3)$ 7.62–7.40 (m, 5 H, ArH), 5.57–5.51 (m, 2 H, complexed ArH), 5.22–5.18 (m, 2 H, complexed ArH), and 2.14 (s, 3 H, ArCH_3); *m/z* 304 (M^+).

General Procedure for Decomplexation of Complexes (**13**) *and* (**15**).—A solution of complex (**13**) or (**15**) in Et_2O (20 mg, ml^{-1}) was exposed to air and sunlight until colourless. Filtration (Celite) followed by evaporation gave a clear oil in essentially quantitative yield.

o-*Xylene* (**16**). This product was identical in all respects with an authentic sample.[23]

o-*Methylbiphenyl* (**17**). B.p. 65–66 °C (0.1 mmHg) (lit.,[24] 76–78 °C, 0.5 mmHg); ν_{max} 1 600 and 1 480 cm^{-1} (aromatic ring); δ($CDCl_3$) (sample contained *o*-methylbiphenyl prepared as above and an authentic sample[23] in a ratio of 1:1) 7.49–7.22 (m, 9 H, ArH), 2.37 (s, 3 H, ArCH_3); ^{13}C-{^1H}-NMR δ_C($CDCl_3$) (sample contained *o*-methylbiphenyl prepared as above and an authentic sample[23] in a ratio of 1:1) 142.0, 135.5, 130.3, 129.8, 129.2, 128.0, 127.2, 126.7, 125.7, and 20.4; *m/z* 168 (M^+).

Biphenyl-2-ylmethanol (**19**) *and* o-*Biphenylformaldehyde* (**20**).—Phenyl-lithium (3.4 ml, 4.93 mmol) was added to a stirred solution of tricarbonyl(η^6-benzyl alcohol)chromium(0) (**4**) (330 mg, 1.35 mmol) in THF (30 ml) at −78 °C. The resulting red solution was allowed to warm to 20 °C and was stirred (3 h). The solution was cooled to −78 °C and treated with a solution of iodine (800 mg, 6.30 mmol) in THF (10 ml). The red mixture was allowed to warm to 20 °C and was stirred (12 h). The solvent was removed and Et_2O (50 ml) added. The organic layer was washed with saturated aqueous $Na_2S_2O_5$ (50 ml), 1M HCl (2 × 25 ml), and saturated brine (25 ml). Drying ($MgSO_4$) followed by evaporation gave a pale yellow gum. Flash chromatography (SiO_2; 1:3, Et_2O–light petroleum) gave two major fractions. Fraction one gave the title compound (**20**) as a colourless oil (30 mg, 12%); ν_{max} 1 710 cm^{-1} (C=O); δ($CDCl_3$) 10.00 (s, 1 H, ArC*H*O) and 8.05–7.29 (m, 9 H, ArH). Fraction two gave the title compound (**19**) as a colourless oil (145 mg, 58%); ν_{max} 3 400br cm^{-1} (OH); δ($CDCl_3$) (sample contained biphenyl-2-ylmethanol prepared as above and an authentic sample[23] in a ratio of 1:1) 7.58–7.26 (m, 9 H, ArH), 4.63 (s, 2 H, ArCH_2OH), 1.75 (s, br, 1 H, ArCH_2O*H*); ^{13}C-{^1H}-NMR δ_C($CDCl_3$) (sample contained biphenyl-2-ylmethanol prepared as above and an authentic sample[23] in a ratio of 1:1) 141.25, 140.6, 138.0, 130.0, 129.1, 128.3, 128.2, 127.65, 127.60, 127.2, and 63.0; *m/z* 184 (M^+).

Tricarbonyl(η^6-1-*phenethanol*)*chromium*(0) (**21**).—1-Phenethanol (3.00 g, 24.6 mmol) and hexacarbonylchromium(0) (5.9 g, 26.8 mmol) were added to dibutyl ether (90 ml) containing THF (9 ml) and the solution was heated under reflux (48 h). The cooled mixture was filtered and concentrated to a yellow oil. Column chromatography (Al_2O_3 Grade V; Et_2O) gave, after evaporation, the title compound (**21**) as a yellow oil (5.50 g, 87%); ν_{max}(liquid film) 3 590 (OH, non-H-bonded), 3 420br (OH, H-bonded), 1 959, and 1 869br cm^{-1} (CO); δ($CDCl_3$) 5.56–5.27 (m, 5 H, ArH), 4.53 [q, *J* 6.1 Hz, 1 H, ArC*H*(OH)CH_3], 2.78 (s, br, 1 H, ROH), and 1.44 [d, *J* 6.3 Hz, 3 H, ArCH(OH)CH_3]; *m/z* 258 (M^+).

Tricarbonyl(η^6-*diplenylmethanol*)*chromium*(0) (**22**).—A deoxygenated mixture of dibutyl ether (60 ml), THF (6 ml), diphenylmethanol (2.00 g, 10.87 mmol) and hexacarbonylchromium(0) (2.20 g, 10.00 mmol) was heated at reflux (20 h). The cooled solution was filtered and the solvents evaporated to give a yellow oil. Flash chromatography (SiO_2, 1:2 Et_2O–light petroleum) gave two fractions. Fraction one gave the title compound (**22**) as a yellow solid which was recrystallised (CH_2Cl_2–hexane) to give yellow blocks (1.83 g, 57%) (Found: C, 60.1; H, 3.7. $C_{16}H_{12}CrO_4$ requires C, 60.0; H, 3.8%); ν_{max} 3 590 (OH) and 1 975 and 1 890br cm^{-1} (CO); δ($CDCl_3$) 7.47–7.35 (m, 5 H, uncomplexed ArH), 5.73 (d, *J* 6.5 Hz, 1 H, complexed ArH), 5.49 [d, *J* 3.3 Hz, 1 H, ArC*H*(OH)Ar], 5.42–5.25 (m, 4 H, complexed ArH), 2.41 [d, *J* 3.3 Hz, ArCH(O*H*)Ar, D_2O suppressed]; *m/z* 320 (M^+). Fraction two gave bistricarbonyl(η^{12}-diphenylmethanol)bischromium(0) (**23**) as a yellow solid which was recrystallised (CH_2Cl_2–hexane) to give yellow blocks (0.50 g, 11%) (Found: C, 49.8; H, 2.6. $C_{19}H_{12}Cr_2O_7$ requires C, 50.0; H, 2.65%); ν_{max} 3 600 (OH), 1 890br cm^{-1} (CO); δ($CDCl_3$) 5.63 (d, *J* 6.5 Hz, 2 H, ArH), 5.43–5.28 (m, 8 H, ArH), 5.12 [d, *J* 3.3 Hz, 1 H, ArC*H*(OH)Ar], and 2.28 [d, *J* 3.3 Hz, 1 H, ArCH(O*H*)Ar, D_2O suppressed]; *m/z* 456 (M^+).

Treatment of Tricarbonyl(η^6-1-*phenethanol*)*chromium*(0) (**21**) *with Butyl-lithium*.—Butyl-lithium (2.20 ml, 3.52 mmol) was added to a stirred solution of tricarbonyl(η^6-1-phenethanol)-chromium(0) (**21**) (350 mg, 1.36 mmol) in THF (25 ml) at −78 °C. The solution was allowed to warm to 20 °C and was stirred (4 h). Methanol (3 ml) was added and the solvent evaporated to give a red gum. Column chromatography (Al_2O_3 Grade V; 1:1 Et_2O–light petroleum) gave a red oil (250 mg, 62%); ν_{max} 1 980, 1 900, and 1 890 cm^{-1} (CO); δ($CDCl_3$) [*trans*-triene (**30**) selected features] 5.67–5.63 (m, 1 H, 3-H), 5.20–5.15 (m, 1 H, 2-H), 4.58 [q, *J* 6.8 Hz, 1 H, RR^1C=C*H*(CH_3)], 4.28 (d, *J* 5 Hz, 1 H, 4-H), 3.05–2.99 (m, 1 H, 1-H), 1.98 [d, *J* 6.8 Hz, 3 H, RR^1C=CH(CH_3)], and 0.85 (t, *J* 6.7 Hz, 3 H, RCH_2CH_3); *cis*- triene (**31**) (selected features) δ 4.65 (q, *J* 6.8 Hz, 1 H, RR^1C=C*H*(CH_3)] and 2.04 [d, *J* 6.8 Hz, 3 H, RR^1C=CH(CH_3)]. Ratio of complexes (**30**) and (**31**) 5:1.

Treatment of Tricarbonyl(η^6-1-*phenethanol*)*chromium*(0) (**21**) *with t-Butyl-lithium*.—t-Butyl-lithium (2.5 ml, 5.90 mmol) was added to a stirred solution of tricarbonyl(η^6-1-phenethanol)-chromium(0) (**21**) (500 mg, 1.94 mmol) in THF (30 ml) at −78 °C. The mixture was allowed to warm to 20 °C and was stirred (2 h). The resulting red solution was re-cooled to −78 °C and treated with methanol (5 ml). The mixture was warmed to 20 °C and evaporated to afford a red gum. Column chromatography (Al_2O_3 Grade V; light petroleum) gave a red oil (275 mg, 48%); ν_{max} 1 980br cm^{-1} (CO); δ($CDCl_3$) [*trans*-triene (**32**)] 5.61–5.57 (m, 1 H, 3-H), 5.32–5.28 (m, 1 H, 2-H), 4.62 [q, *J* 6.8 Hz, 1 H, RR^1C=C*H*(CH_3)], 4.31 (d, *J* 5.8 Hz, 1 H, 4-H), 3.04–2.99 (m, 1 H, 1-H), 2.16 (dd, *J* 6.7, 1.5 Hz, 1 H, 6-H), 2.02 [d, *J* 6.8 Hz, 3 H, RR^1C=CH(CH_3)], and 0.74 [s, 9H, RC(CH_3)$_3$]; *cis*-triene (**33**) (selected features) 1.83 [d, *J* 6.8 Hz, 3 H, RR^1C=CH(CH_3)] and 0.68 [s, 9 H, RC(CH_3)$_3$]; ratio of complexes (**32**) and (**33**) 15:1. The major isomer (**32**) was obtained pure by crystallisation (pentane) (Found: C, 60.3; H, 6.1. $C_{15}H_{18}CrO_3$ requires C, 60.5; H, 6.1%); *m/z* 298 (M^+).

Treatment of Tricarbonyl(η^6-*diphenylmethanol*)*chromium*(0) (**22**) *with t-Butyl-lithium*.—t-Butyl-lithium (1.3 ml, 3.07 mmol) was added to a stirred solution of tricarbonyl(η^6-diphenyl-methanol)chromium(0) (**22**) (400 mg, 1.25 mmol) in THF (30 ml) at −78 °C. The solution was allowed to warm to 20 °C and was stirred (2 h). The resulting red solution was cooled to −78 °C and treated with methanol (5 ml). The mixture was warmed to room temperature and then evaporated to give a red gum. Column chromatography (Al_2O_3 Grade V; 1:1, Et_2O–light petroleum) of this gave a red oil (245 mg, 54%); ν_{max} 1 980 and 1 890br cm^{-1} (CO); δ($CDCl_3$) [*trans*-triene (**34**)] 7.60–7.32 (m, 5 H, ArH), 5.67–5.65 (m, 1 H, 3-H) 5.45 (s, 1 H, RR′C=C*H*Ar), 5.33–5.29 (m, 1H, 2-H), 4.36 (d, *J* 5.8 Hz, 1 H, 4-H), 3.14–3.09 (m, 1 H, 1-H), 2.73 (dd, *J* 6.8 Hz, *J* 1.4 Hz, 1 H, 6-H), 0.79 [s, 9 H, RC(CH_3)$_3$]; [*cis*-triene (**35**) selected features] 4.80 (d, *J* 5.8 Hz, 1 H, 4-H), 3.36–3.30 (m, 1 H, 1-H), 0.97 [s, 9 H, RC(CH_3)$_3$]; ratio of complexes (**34**) and (**35**) 10:1. Crystallisation of the mixture of isomer (**34**) and (**35**) gave the pure triene (**34**). (Found: C, 66.5; H, 5.6. $C_{20}H_{20}CrO_3$ requires C, 66.65; H, 5.6%); *m/z* 360 (M^+).

Tricarbonyl(η^6-o-*butylethylbenzene*)*chromium*(0) (**36**).—Methanol (5 ml) was added to the mixture of trienes (**30**) and (**31**) (240 mg, 0.84 mmol) and the resulting red solution heated at gentle reflux (5 h). Removal of the solvent followed by column chromatography (Al_2O_3 Grade V; 1:1, Et_2O–light petroleum)

gave the title compound (**36**) as a yellow oil (120 mg, 48%); ν_{max} 1 970 and 1 865br cm^{-1} (CO); δ($CDCl_3$) 5.30–5.23 (m, 4 H, ArH), 2.67–2.22 (m, 4 H, $ArCH_2R$), 1.58–1.38 (m, 4 H, $RCH_2CH_2CH_3$), 1.23 (t, *J* 6.7 Hz, 3 H, RCH_2CH_3), and 0.97 (t, *J* 6.7 Hz, 3 H, RCH_2H_3) [Found: *m/z* 298.0663 (M^+). $C_{15}H_{18}CrO_3$ requires *m/z* 298.0661].

Tricarbonyl(η⁶-*benzyldimethylamine*)*chromium*(0) (**37**).—A deoxygenated mixture of dibutyl ether (140 ml), THF (14 ml), and benzyldimethylamine (4.00 g, 29.6 mmol) was heated at reflux (40 h). The cooled solution was filtered and the solvents removed. Column chromatography (Al_2O_3 Grade V; Et_2O) gave the title compound (**37**) as a yellow solid (5.52 g, 69%), m.p. 48–50 °C; ν_{max} 2 790 [$N(CH_3)_2$] and 1 970 and 1 900br cm^{-1} (CO); δ($CDCl_3$) 5.41–5.25 (m, 5 H, ArH), 3.16 (s, 2 H, $ArCH_2NR_2$), and 2.30 [s, 6 H, $RN(CH_3)_2$]; *m/z* 271 (M^+).

Tricarbonyl(η⁶-o-*methylbenzyldimethylamine*)*chromium*(0) (**38**) *and Tricarbonyl*(η⁶-5-*methylene*-6-exo-*t-butylcyclohexa*-1,3-*diene*)*chromium*(0) (**5**).—t-Butyl-lithium (0.7 ml, 1.65 mmol) was added to a stirred solution of tricarbonyl(η⁶-benzyldimethylamine)chromium(0) (**37**) (400 mg, 1.48 mmol) in THF (20 ml) at −78 °C. The initial yellow solution rapidly turned red. The mixture was stirred (2 h, −78 °C) and then methyl iodide (0.3 ml, 4.82 mmol) was added and stirring continued (2 h, −78 °C). Methanol (1 ml) was added, the solution warmed (20 °C), and then evaporated. Column chromatography (Al_2O_3 Grade V) gave two fractions. Fraction one (1:10, Et_2O–light petroleum) gave the title compound (**5**) as a red gum (105 mg, 25%) identified by comparison with an authentic sample. Fraction two (5:1, Et_2O–light petroleum) gave the title compound (**38**) as a yellow solid (285 mg, 68%), m.p. 52–54 °C (Found: C, 54.85; H, 5.3; N, 4.85. $C_{13}H_{15}CrNO_3$ requires C, 54.7; H, 5.3; N, 4.9%); ν_{max} 2 770 [$N(CH_3)_2$] and 1 970 and 1 890 cm^{-1} (CO); δ($CDCl_3$) 5.47–5.21 (m, 4 H ArH), 3.47, 2.88 (AB system, J_{AB} 13.0 Hz, 2 H, $ArCH_2NR_2$), 2.29 [s, 6 H, $RN(CH_3)_2$], and 2.24 (s, 3 H, $ArCH_3$); *m/z* 285 (M^+).

Methylation of Tricarbonyl(η⁶-o-*methylbenzyldimethylamine*)*chromium*(0) (**38**).—t-Butyl-lithium (2.36M solution in pentane; 0.97 ml) was added to a stirred solution of tricarbonyl(η⁶-2-methylbenzyldimethylamine)chromium(0) (**38**) (653 mg, 2.29 mmol) in THF (15 ml) at −78 °C. The orange solution was stirred (−78 °C, 2 h) and methyl iodide added (0.36 ml, 5.73 mmol). After 2 h methanol (2 ml) was added and the mixture evaporated to afford a red oil. Column chromatography (Al_2O_3 Grade V) gave two fractions. Fraction one (1:10, Et_2O–light petroleum) was evaporated to give, after recrystallisation (pentane), tricarbonyl(η⁶-4-ethyl-5-methylene-6-*exo*-t-butylcyclohexa-1,3-diene)chromium(0) (**41**) as red granular crystals (191 mg, 28%), m.p. 109–111 °C (Found: C, 60.3; H, 6.1. $C_{15}H_{18}CrO_3$ requires C, 60.4; H, 6.1%); ν_{max} 1 982, 1 908, and 1 882 cm^{-1} (CO); δ($CDCl_3$) 5.40 (d, *J* 4.8 Hz, 1 H, 3-H), 5.21–5.17 (m, 1 H, 2-H), 4.13, 3.98 (2 s, 2H, $RR^1C{=}CH_2$), 2.89–2.84 (m, 1 H, 1-H), 1.74 (s, 3 H, RCH_3), 1.55 (d, *J* 6.4 Hz, 1 H, 6-H), 0.71 [s, 9H, $RC(CH_3)_3$]; *m/z* 298 (M^+). Fraction two (Et_2O) was evaporated to give a mixture of tricarbonyl(η⁶-*o,o*-dimethylbenzyldimethylamine)chromium(0) (**42**) (413 mg, 60%) and tricarbonyl(η⁶-*o*-ethylbenzyldimethylamine)chromium(0) (**43**) (82 mg, 12%) as a yellow solid; δ($CDCl_3$) 5.43–5.38 [m, 1 H, *p*-ArH, (**42**)], 5.10–5.08 [m, 2 H, *m*-ArH, (**42**)], 3.23 [s, 2 H, $ArCH_2NR_2$, (**42**)], 2.30, 2.26 [2s, 12 H, $RN(CH_3)_2$, $ArCH_3$, (**42**)], 5.54–5.38 [m, 4 H, ArH, (**43**)], 3.55, 2.28 [AB system, J_{AB} 15.0 Hz, 2 H, $ArCHNR_2$, (**43**)], 2.28 [s, 6 H, $RN(CH_3)_2$, (**43**)], 2.19–2.16 [m, 2 H, $ArCH_2CH_3$, (**43**)], 1.25 (t, *J* 6.0 Hz, $ArCH_2CH_3$, (**43**)]. Recrystallisation from CH_2Cl_2–light petroleum solution gave complex (**42**) as yellow needles, m.p. 111–113 °C (Found: C, 56.1; H, 5.8; N, 4.5; $C_{14}H_{17}NO_3Cr$ requires C, 56.1; H, 5.7; N, 4.7%); ν_{max} 1 967 and 1 888br cm^{-1} (CO); δ($CDCl_3$) only peaks assigned to complex (**42**) above; *m/z* 299 (M^+).

Tricarbonyl[η⁶-(*E*)-1-*t-butyl*-4-*trimethylsilyl*-5-*ethylidene*-*cyclohexa*-1,3-*diene*)*chromium*(0) (**45**).—t-Butyl-lithium (0.46 ml, 0.93 mmol) was added to a stirred solution of tricarbonyl[η⁶-(*R*)-2-trimethylsilyl-α-methylbenzyldimethylamine]chromium(0) (**44**)[13] (166 mg, 0.46 mmol) in THF (10 ml) at −40 °C. The red solution was stirred at −40 °C (2 h) and then at 0 °C (2 h). Column chromatography (Al_2O_3 Grade V; 1:20, Et_2O–light petroleum) gave, after removal of the solvent, the title compound (**45**) as a red solid (68 mg, 40%); ν_{max} 1 964, 1 890, and 1 865 cm^{-1} (CO); δ($CDCl_3$) 5.42, 5.23 (AB system, J_{AB} 5.2 Hz, 2 H, 2-H, 3-H), 4.45 [q, *J* 6.7 Hz, 1 H, $RR^1C{=}CH(CH_3)$], 2.57, 1.86 (AB system, J_{AB} 13.3 Hz, 2 H, 6-H), 1.96 [d, *J* 6.7 Hz, 3 H, $RR^1C{=}CH(CH_3)$], 1.05 [s, 9 H, $RC(CH_3)_3$], and 0.17 [s, 9H, $RSi(CH_3)_3$]; [Found: *m/z* 370.1056 (M^+). $C_{18}H_{26}CrO_3Si$ requires *m/z* 370.1056].

p-*t-Butylphenyltrimethylsilane* (**49**).—t-Butyl-lithium (2.1 ml, 4.2 mmol) in THF (5 ml) was cooled to −78 °C and tricarbonyl(η⁶-phenyltrimethylsilane)chromium(0) (**48**) (581 mg, 2.03 mmol) in THF (5 ml) added dropwise over 5 min. The solution was stirred (−78 °C, 1.5 h) and warmed to 0 °C (1 h), and then cooled to −78 °C again. Iodine (2.00 g, 7.90 mmol) in THF (5 ml) was rapidly added and the solution warmed to room temperature and stirred for 3 h. The mixture was diluted with Et_2O and washed sequentially with aqueous $NaHSO_4$ and brine. Drying ($MgSO_4$) followed by evaporation, gave after sublimation, the title compound (**49**) as white crystals (243 mg, 58%), sublimes 80 °C (0.1 mmHg); ν_{max} 1 598 cm^{-1} (arene ring); δ ($CDCl_3$) 7.48, 7.40 (AB system, J_{AB} 8.2 Hz, 4 H, ArH), 1.34 [s, 9 H, $ArC(CH_3)_3$], 0.27 [s, 9 H, $ArSi(CH_3)_3$] {lit.,[25] δ($CDCl_3$ 60 MHz) 0.25 [s, $ArSi(CH_3)_3$}; *m/z* 206 (M^+).

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References

1 H. W. Gschwend and H. R. Rodriguez, *Org. React.* (*N.Y.*), 1979, **26**, 1.
2 J-F. Biellmann and J-B. Ducep, *Org. React.* (*N.Y.*), 1982, **27**, 1.
3 A. N. Nesmeyanov, N. E. Kolobova, K. N. Anisimov, and Y. U. Makarov, *Izv. Akad. Nauk. SSSR. Ser Khim.*, 1968, 2665; M. D. Rausch and R. E. Gloth, *J. Organomet. Chem.*, 1978, **153**, 59.
4 M. F. Semmelhack, J. Bisaha, and M. Czarny, *J. Am Chem. Soc.*, 1979, **101**, 768.
5 S. G. Davies, 'Organotransition Metal Chemistry: Applications to Organic Synthesis,' Pergamon Press, Oxford, 1982; G. Jaouen, 'Transition Metal Organometallics in Organic Synthesis,' (H. Alper ed.), II, 65, Academic Press, London, 1978; A. J. Pearson, 'Metallo-Organic Chemistry,' John Wiley and sons, New York, 1985; M. F. Semmelhack, *Ann. N.Y. Acad. Sci.*, 1977, **295**, 36; M. Ghavshou and D. A. Widdowson, *J. Chem. Soc., Perkin Trans. 1*, 1983, 3065; A. Alemagna, C. Baldoli, P. Del Buttero, E. Licandro, and S. Maiorana, *J. Chem. Soc., Chem. Commun.*, 1985, 417; C. Baldoli, P. Del Buttero, S. Maiorana, and A. Papagni, *ibid.*, p. 1181; J-C. Boutonnet, F. Rose-Munch, and E. Rose, *Tetrahedron Lett.*, 1985, 3989.
6 M. F. Semmelhack, H. T. Hall, R. Farina, M. Yoshifuji, G. Clarke, T. Bargar, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 3535.
7 M. F. Semmelhack, G. R. Clarke, J. L. Garcia, J. J. Harrison, Y. Thebtaranonth, W. Wulff, and A. Yamashita, *Tetrahedron*, 1981, **37**, 3957.
8 M. F. Semmelhack, H. T. Hall, M. Yoshifuji, and G. Clarke, *J. Am. Chem. Soc.*, 1975, **97**, 1247.

9 J. Blagg, S. G. Davies, C. L. Goodfellow, and K. H. Sutton, *J. Chem. Soc., Chem. Commun.*, 1986, 1283.
10 M. F. Semmelhack and G. Clark, *J. Am. Chem. Soc.*, 1977, **99**, 1675.
11 M. F. Semmelhack, G. R. Clark, R. Farina, and M. Saeman, *J. Am. Chem. Soc.*, 1979, **101**, 217.
12 N. Meyer and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 521.
13 J. Blagg, S. G. Davies, C. L. Goodfellow, and K. H. Sutton, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1805.
14 G. Jaouen and S. Top, *J. Org. Chem.*, 1981, **46**, 78.
15 D. D. Perrin and W. L. F. Armarego, 'Purification of Laboratory Chemicals,' Pergamon Press, Oxford 1988.
16 B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 551.
17 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
18 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. IV, p. 99–101 and 149–150.
19 A. C. Larson, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksguard, 1970, p. 170.
20 J. R. Carruthers and D. J. Watkin, *Acta Crystallogr., Sect. A*, 1979, **35**, 698.
21 J. R. Carruthers and D. J. Watkin, 'CRYSTALS User Guide,' Chemical Crystallography Laboratory, University of Oxford, 1984, Issue 8.
22 H. Gilman and R. G. Jones, *Org. React. (N.Y.)*, 1951, **6**, 353.
23 An authentic sample was purchased from Aldrich Chemical Co. Ltd.
24 R. A. Benkeser, D. F. Ehler, and G. S. Li, *Org. Synth.*, 1977, **56**, 83.
25 R. E. Hess, C. K. Haas, B. A. Kaduk, C. D. Schaeffer Jr., and C. H. Yoder, *Inorg. Chim. Acta*, 1971, **5**, 161.

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