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# Indanetricarbonylchromium: the effects of 1-*syn*- and 1-*anti* substituents on the regioselectivity of nucleophilic addition. Crystal structures of 1-*syn*- and 1-*anti*-methoxyindanetricarbonylchromium

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## Abstract

A series of diastereomeric *syn* and *anti* $Cr(CO)_3$ complexes of 1-substituted indanes have been prepared by thermolysis of $Cr(CO)_6$ or by arene exchange with naphthalene-$Cr(CO)_3$ (**3**). The regioselectivity of nucleophilic addition of α-nitrile carbon nucleophiles to *syn* and *anti* 1-R-indane $Cr(CO)_3$ complexes (R = OMe **4**, Me **10**) has been investigated and compared with that of analogous reactions with indane$Cr(CO)_3$ (**1**). The results of an X-ray study of *syn*- and *anti*-**4** are presented. Nucleophilic additions are shown to be sensitive to the steric and electronic effects of the benzylic substituent and the nucleophile. When the reaction mixtures are warmed to 0 °C, equilibration of the regioisomeric cyclohexadienyl intermediates takes place.

## Introduction

Aromatic substitution brought about by initial attachment of the arene to the electron-withdrawing group $Cr(CO)_3$, followed by the addition of a carbon nucleophile and oxidative decomplexation has recently found considerable application in synthesis [1,2]. When substituted arenes are involved the high regioselectivity of the nucleophilic addition step is a particularly useful feature of this addition-oxidation sequence. Charge and/or orbital considerations as well as steric factors are of importance in reactions under kinetic control [3–5]. With 1,1-dialkylindane$Cr(CO)_3$ complexes, a high selectivity for addition to C(5) has been demonstrated in two independent studies (Fig. 1) [6,7]. 1-Substituted indane $Cr(CO)_3$

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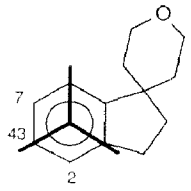
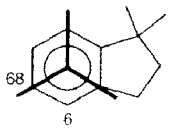



$LiCH(CH_3)CN$ [ref. 6] $LiC(CH_3)_2CN$ [ref. 7]

Fig. 1. Regioselectivity of nucleophilic addition reactions to 1,1-disubstituted indane $Cr(CO)_3$ complexes [6,7]. Numbers refer to product yields of the substituted arene obtained. The preferred conformation of the $Cr(CO)_3$ group is shown.

complexes are particularly good substrates with which to distinguish and evaluate steric and electronic factors in nucleophilic addition reactions. This is due to the stereochemical rigidity of these complexes and the availability of both the *syn*- and *anti*-diastereomers.

We report here the results of a study of the diastereoselective complexation of 1-substituted indanes and of the regioselectivity in nucleophilic additions to these complexes. We also consider the question of kinetic vs. thermodynamic control of the nucleophilic addition, this aspect having arisen as a result of recent reports of readily reversible carbanion additions at low temperatures [8,9]. Finally, we present the results of an X-ray diffraction study of 1-*syn* and 1-*anti*-methoxyindane$Cr(CO)_3$, and give $^1H$ NMR data for the series of diastereomeric 1-R-indane $Cr(CO)_3$ complexes (R = OH, OMe, Me, OAc), all first described by Gracey et al. [10].

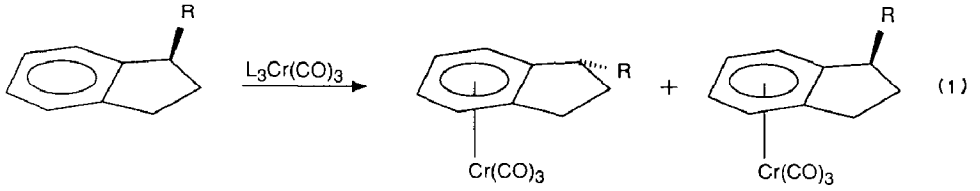
## Results and discussion

*Synthesis of 1-substituted indane $Cr(CO)_3$ complexes*

By the method described by Mahaffy and Pauson [11], indane$Cr(CO)_3$ [12] (**1**) was prepared from $Cr(CO)_6$ in 92% yield. Under similar conditions (dibutyl ether, THF (10/1), 140 °C, 3 d), the reaction with 1-indanol furnished a mixture containing the *syn* and *anti*-1-indanol$Cr(CO)_3$ [13] (**2**) complexes in a 4/1 ratio (85% yield). HPLC analysis of samples taken during the reaction indicated that the ratio of the *syn* and *anti* diastereomers remained constant throughout the reaction. After 45 h reaction only traces of $Cr(CO)_6$ remained, and there was no change in the proportion of *syn* and *anti*-**2** after prolonged reaction times. This is in accord with earlier reports that showed that conversion of the kinetically favoured *syn*- to the thermodynamically favoured *anti*-isomer occurs only under vigorous conditions [10,14]. Although *syn*-1-indanol$Cr(CO)_3$ (*syn*-**2**) has been reported to be the sole product when $Cr(CO)_3$pyridine$_3$ is used as $Cr(CO)_3$ precursor, only a very modest yield was obtained (18%) [10]. We therefore turned to naphthalene$Cr(CO)_3$ (**3**), which readily undergoes arene exchange reactions under mild conditions [15,16]. A solution of 1-indanol and **3** in diethyl ether was stirred in a closed system at 70 °C for 20 h to give *syn*-**2** as a single diastereomer in 83% yield. Methylation with NaH/MeI gave *syn*-1-methoxyindane $Cr(CO)_3$ (*syn*-**4**) in 83% yield based on **3**. Direct complexation of 1-methoxyindane was less selective [17*]. Thermolysis of $Cr(CO)_6$ in dibutylether and THF yielded the two diastereomers of **4** in a ratio of 65(*syn*)/35(*anti*), and the naphthalene exchange reaction gave the compounds in a

Table 1

*Syn/anti* selectivities in the direct complexation of 1-substituted indanes via thermolysis of $Cr(CO)_6$ or arene exchange in naphthalene$Cr(CO)_3$ (**3**)




| Complex | R | $L_3Cr(CO)_3$ | *syn* | *anti* [a] | Combined yield (%) [b] |
|---|---|---|---|---|---|
| **2** | OH | $Cr(CO)_6$ | 76–80 [c] | 24–20 [c] | 85 |
| **2** | OH | $C_{10}H_8Cr(CO)_3$ | > 98 | < 2 | 83 |
| **4** | OMe | $Cr(CO)_6$ | 65 | 35 | 92 |
| **4** | OMe | $C_{10}H_8Cr(CO)_3$ | 90 | 10 | 87 |
| **7** | OSi(t-Bu)$Me_2$ | $C_{10}H_8Cr(CO)_3$ | 67 | 33 | 74 |
| **8** | OSi(i-Pr)$_3$ | $Cr(CO)_6$ | 54 | 46 | 89 |
| **8** | OSi(i-Pr)$_3$ | $C_{10}H_8Cr(CO)_3$ | 67 | 33 | 96 |

[a] The *syn/anti* ratios were determined from the $^1H$ NMR spectra of the mixtures unless otherwise indicated. [b] Combined yields refer to isolated material. [c] The *syn/anti* ratio was determined by HPLC and $^1H$ NMR.

ratio of 90(*syn*)/10(*anti*). Fractional crystallization gave *syn* and *anti*-**4**, each containing less than 2% of the other diastereomer. The *syn* stereoselectivity of the complexation of arenes containing benzylic oxygen observed in reactions under kinetic control is well documented [10,16,18,19], and has been attributed to the coordination of the heteroatom to the metal, the chromium carbonyl fragment thus being directed towards the *syn* face of the arene. Table 1 illustrates the directing effect of the benzylic oxygen function to be surprisingly efficient, and to outweigh considerable adverse steric effects. Although the *syn/anti* ratio decreased in the series OH > OMe > $OSiR_3$ (as expected on steric grounds and decreasing coordinating capacity [20]) it did so less than we had expected, and even the bulky silyl-protected indanols **5** and **6** invariably gave mixtures in which the *syn*-isomer dominated. Even under more severe conditions of $Cr(CO)_6$ pyrolysis in butyl ether, the *anti*-isomer is not favoured, 54/46 mixture of *syn* and *anti*-**8** being isolated. Fractional crystallization provided samples of *syn* and *anti*-**7** and **8**, each containing less than 5% of the other diastereomer. Stereochemical assignment was made by comparison of the proton signals in the $^1H$ NMR spectra of *syn* and *anti*-**7** and **8** with those for *syn*- and *anti*-**4** and *syn*-**2**. This is discussed later.

Supporting evidence for the structural assignment came from the desilylation of the major isomer of **7**, which gave *syn*-1-indanol$Cr(CO)_3$ (*syn*-**2**) as single product, identified by spectral comparison. The solid state structure of *syn*- and *anti*-**4**, undertaken primarily to study the effect of 1-substituents on the conformation of the $Cr(CO)_3$ rotor, confirmed the structural assignments made from the $^1H$ NMR analysis.

*anti*-1-Methoxyindane $Cr(CO)_3$ (*anti*-**4**) was obtained from the reaction of **2** or of 1-acetoxyindane$Cr(CO)_3$ (**9**) [21] with sulfuric acid in methanol, as described by

* Reference number with asterisk indicates a note in the list of references.

Top, Meyer and Jaouen [22]. The two diastereomers of 1-methylindane$Cr(CO)_3$ were obtained separately by the route described by Uemura et al. [23,24*,25*], except that *syn*-**2** was directly synthesized by arene exchange rather than by reduction of indanone $Cr(CO)_3$. The $Cr(CO)_3$ group efficiently blocks the *syn*-face of the arene, and both nucleophiles and electrophiles react with very high *anti*-face stereoselectivity [26*,27,28].

The results reported here complement earlier observations on the complexing behaviour of 1-indanol derivatives (vide supra) and those recently described for the tetralol system [19].

*The crystal and molecular structures of syn- and anti-**4***

Crystals of *syn*- and *anti*-**4** suitable for X-ray study were obtained from diethyl ether/pentane. Both diastereomers crystallize in the monoclinic space group $P2_1/c$

Table 2

Bond lengths (Å) and bond angles (°) for the non-hydrogen atoms [a] in the complexes *syn*-**4** and *anti*-**4**

| | Bond lengths | | | Bond angles | |
|---|---|---|---|---|---|
| | *syn*-**4** | *anti*-**4** | | *syn*-**4** | *anti*-**4** |
| Cr–X | 1.716(4) | 1.724(2) | C(11)–Cr–C(12) | 88.8(2) | 88.3(1) |
| Cr–C(5) | 2.233(3) | 2.228(2) | C(11)–Cr–C(13) | 87.4(2) | 90.3(1) |
| Cr–C(6) | 2.228(4) | 2.226(3) | C(11)–Cr–X | 127.1(2) | 125.0(1) |
| Cr–C(7) | 2.211(4) | 2.220(3) | C(12)–Cr–C(13) | 90.6(2) | 89.3(1) |
| Cr–C(8) | 2.212(4) | 2.23(3) | C(12)–Cr–X | 124.9(2) | 125.5(1) |
| Cr–C(9) | 2.224(4) | 2.232(2) | C(13)–Cr–X | 126.0(2) | 126.7(1) |
| Cr–C(10) | 2.226(3) | 2.219(2) | Cr–X–C(5) | 90.9(2) | 90.2(2) |
| Cr–C(11) | 1.846(4) | 1.835(3) | Cr–X–C(6) | 89.8(2) | 89.8(2) |
| Cr–C(12) | 1.832(4) | 1.834(3) | Cr–X–C(7) | 89.7(2) | 90.0(2) |
| Cr–C(13) | 1.829(4) | 1.844(3) | Cr–X–C(8) | 89.7(2) | 90.0(2) |
| C(11)–O(2) | 1.163(4) | 1.157(3) | Cr–X–C(9) | 89.3(2) | 89.9(2) |
| C(12)–O(3) | 1.165(4) | 1.164(3) | Cr–X–C(10) | 90.6(2) | 90.0(2) |
| C(13)–O(4) | 1.162(5) | 1.145(3) | Cr–C(11)–O(2) | 177.7(3) | 178.5(2) |
| C(1)–O(1) | 1.427(5) | 1.422(4) | Cr–C(12)–O(3) | 178.7(3) | 178.8(2) |
| O(1)–C(2) | 1.410(4) | 1.433(3) | Cr–C(13)–O(4) | 178.8(3) | 179.6(3) |
| C(2)–C(3) | 1.540(5) | 1.543(4) | C(1)–O(1)–C(2) | 112.5(3) | 112.4(2) |
| C(3)–C(4) | 1.543(4) | 1.537(4) | O(1)–C(2)–C(3) | 114.1(3) | 112.0(3) |
| C(4)–C(5) | 1.510(5) | 1.516(3) | O(1)–C(2)–C(10) | 111.8(3) | 106.0(2) |
| C(5)–C(6) | 1.413(5) | 1.408(3) | C(3)–C(2)–C(10) | 103.6(3) | 103.0(2) |
| C(6)–C(7) | 1.402(5) | 1.400(4) | C(2)–C(3)–C(4) | 104.6(3) | 105.8(2) |
| C(7)–C(8) | 1.421(5) | 1.415(4) | C(3)–C(4)–C(5) | 103.1(3) | 102.6(2) |
| C(8)–C(9) | 1.410(5) | 1.397(4) | C(4)–C(5)–C(6) | 129.0(3) | 129.3(2) |
| C(9)–C(10) | 1.422(4) | 1.420(3) | C(4)–C(5)–C(10) | 110.3(3) | 110.6(2) |
| C(10)–C(5) | 1.406(4) | 1.399(3) | C(6)–C(5)–C(10) | 120.7(3) | 120.1(2) |
| C(10)–C(2) | 1.503(4) | 1.504(3) | C(2)–C(10)–C(5) | 109.8(3) | 110.4(2) |
| X–C(5) | 1.403(5) | 1.405(4) | C(2)–C(10)–C(9) | 129.1(3) | 128.7(2) |
| X–C(6) | 1.427(5) | 1.414(4) | C(5)–C(10)–C(9) | 121.1(3) | 121.0(2) |
| X–C(7) | 1.403(5) | 1.398(4) | C(5)–C(6)–C(7) | 118.7(3) | 119.3(2) |
| X–C(8) | 1.404(5) | 1.404(4) | C(6)–C(7)–C(8) | 120.7(3) | 120.6(2) |
| X–C(9) | 1.436(5) | 1.421(3) | C(7)–C(8)–C(9) | 120.9(3) | 120.4(2) |
| X–C(10) | 1.401(5) | 1.396(3) | C(8)–C(9)–C(10) | 117.8(3) | 118.6(2) |

[a] X is the centre of the benzene ring. Estimated standard deviations are given in parentheses. C–H distances range from 0.85(4)–1.03(4) Å for *syn*-**4** and from 0.89(4)–1.04(3) Å for *anti*-**4**.

Table 3

Selected torsion angles [a] in *syn*- and *anti*-**4**

| | *syn*-**4** | *anti*-**4** |
|---|---|---|
| C(11)–Cr–X–C(9) | 24.5(3) | 32.3(2) |
| C(11)–Cr–X–C(10) | −35.6(3) | −28.2(2) |
| C(12)–Cr–X–C(5) | 24.0(3) | 28.9(2) |
| C(12)–Cr–X–C(6) | −35.9(3) | −31.0(2) |
| C(13)–Cr–X–C(7) | 26.1(3) | 30.3(2) |
| C(13)–Cr–X–C(8) | −34.7(3) | −30.4(2) |
| C(1)–O(1)–C(2)–C(3) | −75.6(4) | 85.6(3) |
| C(1)–O(1)–C(2)–C(10) | 167.2(4) | −162.8(3) |
| O(1)–C(2)–C(3)–C(4) | −150.4(4) | 86.6(2) |
| C(2)–C(3)–C(4)–C(5) | 27.6(3) | 26.0(2) |
| C(3)–C(4)–C(5)–C(10) | −16.8(3) | −15.7(2) |
| C(4)–C(5)–C(10)–C(2) | −1.3(3) | −1.3(2) |
| C(5)–C(10)–C(2)–O(1) | 142.3(3) | −100.2(2) |

[a] For *syn*-**4** the angles refer to the molecule in $\bar{x}$, $\bar{y}$, $\bar{z}$. Estimated standard deviations are given in parentheses.

with four molecules in the unit cell, the non-standard setting $P2_1/n$ being chosen for *syn*-**4**. Connectivity relationships within the molecules are given in Tables 2 and 3. The crystallographic numbering is indicated in Fig. 2. Both diastereomers were found to have the $Cr(CO)_3$ unit in a staggered conformation relative to the aromatic ring carbons, cf. the stereoviews in Figs. 3 and 4. In *syn*-**4** the $Cr(CO)_3$ tripod is rotated away from the ideally staggered conformation by 6° (Table 3).

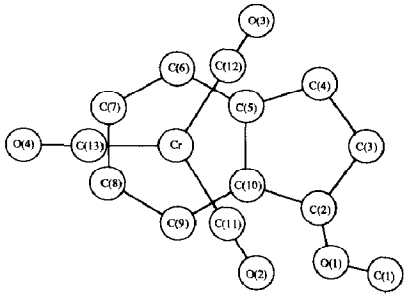



Fig. 2. Atom-labeling scheme used in the crystallographic data for *syn*- and *anti*-**4**.

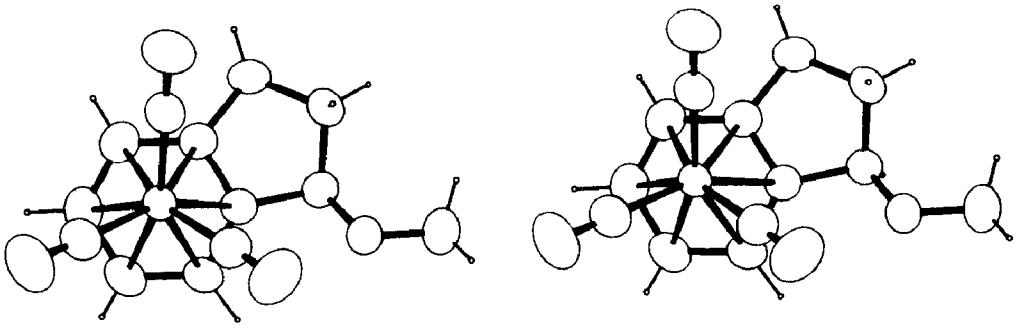


Fig. 3. Stereoview of 1-*syn*-methoxyindanetricarbonylchromium (*syn*-**4**).

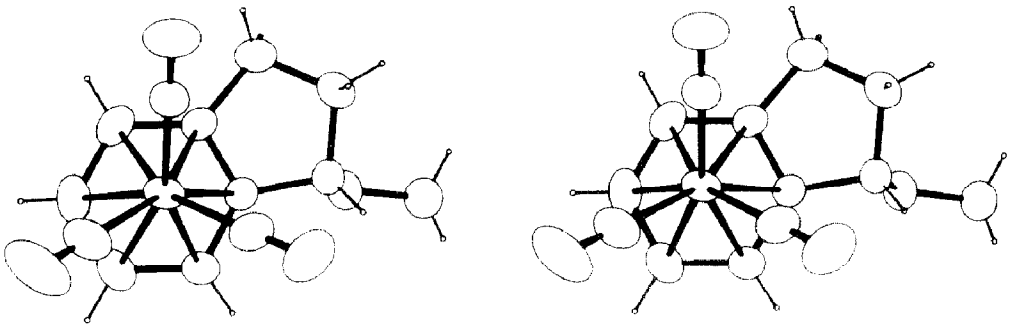


Fig. 4. Stereoview of 1-*anti*-methoxyindanetricarbonylchromium (*anti*-**4**).

The methoxy substituent in *anti*-**4** is in a pseudo-axial position, whereas it takes up a pseudo-equatorial position in *syn*-**4**, as illustrated in Fig. 5. In both isomers the aromatic ring is planar while the five-membered ring is slightly bent, with the carbon in the 2 position pointing towards the $Cr(CO)_3$ group.

*Solution structures of complexes* ***4****,* ***7****,* ***8*** *and* ***10***

Figure 6 shows the $^1H$ NMR spectra of 1-methoxyindane and its complexes *anti*-**4** and *syn*-**4**. The complexation of the $Cr(CO)_3$ group causes a large upfield shift of the aromatic ring proton resonances (ca. 2.5 ppm) and a smaller upfield shift of the alicyclic ring and methoxy proton resonances. In *syn*-**4** the pattern of proton–proton coupling in the five-membered ring of 1-methoxyindane is retained. The observed coupling for $H^1$ in the methoxyindane are 6.6 and 4.0 Hz and those in *syn*-**4** are 8.3 and 7.1 Hz. On the basis of the size of the coupling constants and previous analyses of the puckering of the alicyclic ring in 1-indanol [29] and 1-indanol $Cr(CO)_3$ derivatives [30], we assume that the preferred conformations of *syn*-**4** and 1-methoxyindane in solution have pseudo-equatorial methoxy groups. The conformation of the methoxyindane ligand in the solid *syn*-**4** is thus retained in solution in benzene. In contrast to *syn*-**4**, $H^1$ in *anti*-**4** is a doublet with a coupling constant $J = 5.4$ Hz. No coupling is observed to the other proton on $C^2$. This again would be in keeping with the preferred conformation in solution being analogous to that in the solid (pseudo-axial OMe group).

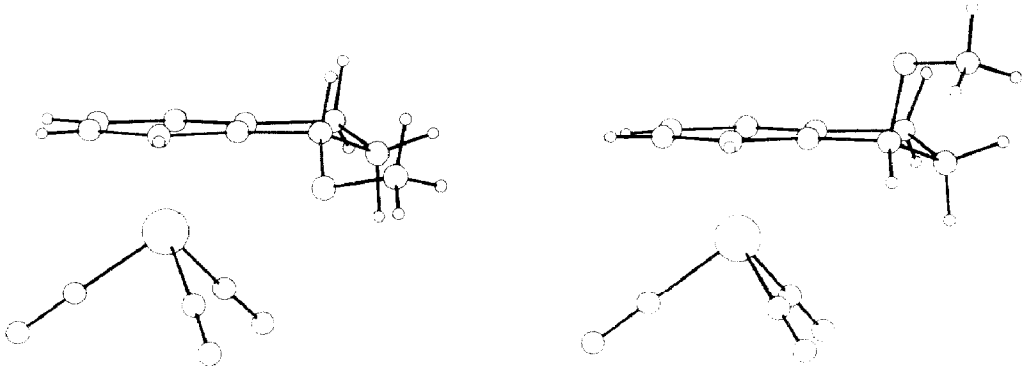


Fig. 5. Side view of *syn*-**4** and *anti*-**4**.

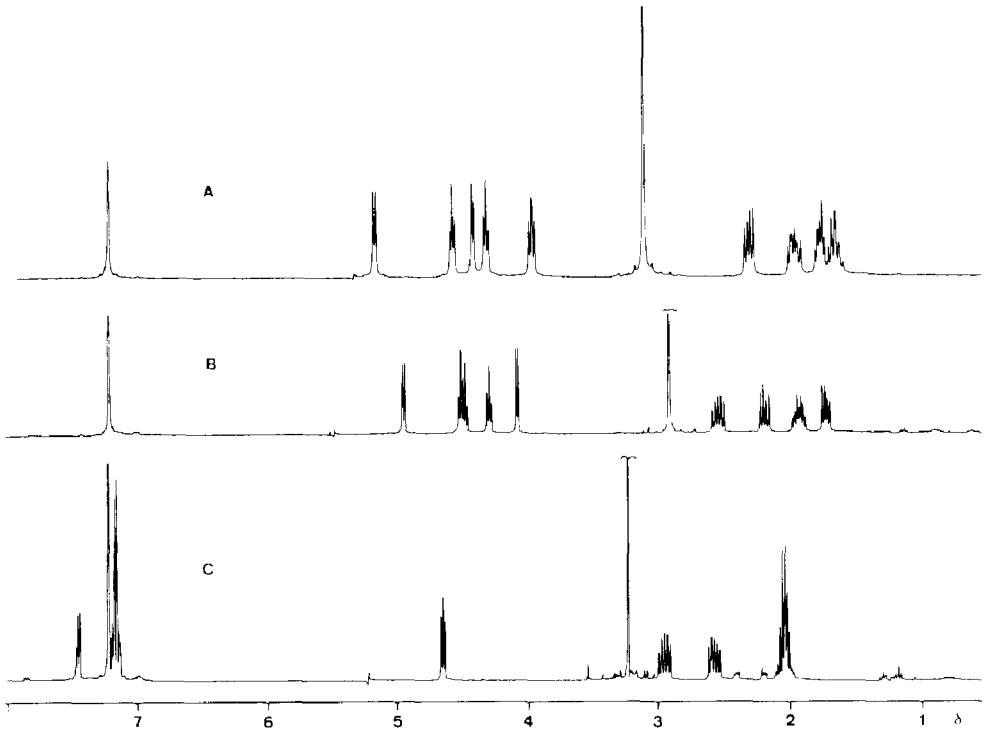



Fig. 6. $^1$H NMR spectra ($C_6D_6$, 360 MHz) of the two diastereomeric $Cr(CO)_3$ complexes *syn*-**4** (A) and *anti*-**4** (B) and of 1-methoxyindane (C).

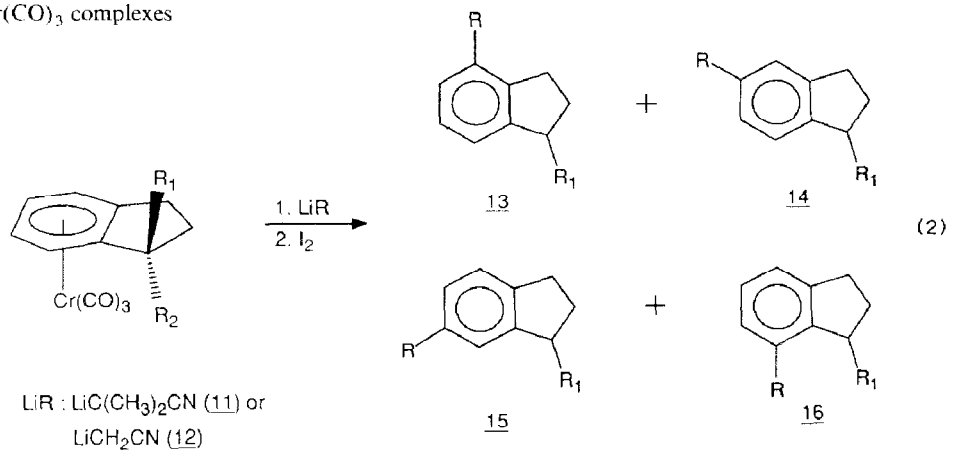
The main features of the $^1$H NMR spectra of *syn*-**4** and *anti*-**4** are also observed in the spectra of the *syn* and *anti* isomers of **7** and **8** and of *syn*-**10**. The $H^1$ protons of the *anti* isomers give doublets, with $J = 5.5$ and 6 Hz, respectively, while those in the *syn* isomers give doublets of doublets with $J_{12} = J_{12'} = 8$ Hz.

The major isomers of **2**, **4**, **7** and **8** obtained from the arene exchange reactions with complex **3**, all have the chemical shifts of the aromatic proton signals in the order $H^6 < H^4 < H^5 < H^7$, while the order of chemical shifts for the minor isomers is $H^6 < H^5 < H^4 < H^7$. The spread of $\delta$ values in the latter is slightly smaller than in the former. The preferred $Cr(CO)_3$ conformation is thought to be an important factor affecting chemical shifts of aromatic protons in arene $Cr(CO)_3$ complexes [4,12,31], and in 1-substituted indanes larger chemical shift differences of the aromatic protons are a characteristic feature of the *syn* diastereomers [12]. The $Cr(CO)_3$ fragment predominantly adopts a conformation in which adverse interactions with the *syn*-substituent are minimized. $H^5$ and $H^7$, being eclipsed by a Cr–CO vector in the preferred conformation, are deshielded relative to the other arene protons. This is particularly clear in 1-methylindane $Cr(CO)_3$ (**10**). The aromatic protons in the *anti*-isomer give rise to two multiplets in the range 4.41–4.69 ppm, assigned by analogy to the signals from indane $Cr(CO)_3$ to $H^{5,6}$ and $H^{4,7}$. A predominantly staggered conformation for the $Cr(CO)_3$ unit is inferred. In contrast, the signal in the *syn*-isomer show a triplet, doublet, triplet, doublet sequence for $H^6 < H^4 < H^5 < H^7$, and are spread over a much wider chemical shift range (4.28–4.74), typical of a preferred eclipsed conformation [32*]. Smaller differences are observed for **4**, **7** and **8**, and in view of the staggered conformation

adopted in the crystal structures of both *syn*- and *anti*-**4** the splitting may reflect anisotropic effects due to the substituent rather than conformational effects [12]. Full details of NMR structural assignments are included in the Experimental section.

Table 4

Regioisomer distributions from nucleophilic addition/oxidation reactions with 1-substituted indane $Cr(CO)_3$ complexes




LiR : $LiC(CH_3)_2CN$ (11) or $LiCH_2CN$ (12)

1 : $R_1 = R_2 = H$

*anti* - 4 : $R_1$ = OMe, $R_2$ = H

*syn* - 4 : $R_1$ = H, $R_2$ = OMe

*anti* - 10 : $R_1$ = Me, $R_2$ = H

*syn* - 10 : $R_1$ = H, $R_2$ = Me

13 - 16 **a** : $R_1$ = H, R = $C(CH_3)_2CN$

**b** : $R_1$ = OMe, R = $C(CH_3)_2CN$

**c** : $R_1$ = OMe, R = $CH_2CN$

**d** : $R_1$ = Me, R = $C(CH_3)_2CN$

| Compound | Nucleophile LiR | Reaction temp. (°C) [a] | Reaction time | Isomer distribution | | | | Comb. yield [b] (%) |
|---|---|---|---|---|---|---|---|---|
| | | | | **13** | **14** | **15** | **16** | |
| **1** | $LiCMe_2CN$ (**11**) | −90 | 5 min | 91 [c] | 9 [c] | | | 90 |
| | $LiCMe_2CN$ (**11**) | 0 | 2 h | 75 [c] | 25 [c] | | | 90 |
| *anti*-**4** | $LiCMe_2CN$ (**11**) | −78 | 1 h | 3 [d] | 48 [d] | 48 [d] | 1 [d] | 89 |
| | $LiCMe_2CN$ (**11**) | 0 | 2 h | 5 [d] | 57 [d] | 28 [d] | 10 [d] | 84 |
| *anti*-**4** | $LiCH_2CN$ (**12**) | −78 | 1 h | – | 59 [d] | 19 [d] | 22 [d] | 60 [e] |
| | $LiCH_2CN$ (**12**) | −10 | 1 h | – | 13 [d] | 9 [d] | 78 [d] | 86 [f] |
| *syn*-**4** | $LiCMe_2CN$ (**11**) | −78 | 1 h | 3 [d] | 32 [d] | 22 [d] | 43 [d] | 66 |
| | $LiCMe_2CN$ (**11**) | 0 | 2 h | 1 [d] | 29 [d,g] | | 70 [d] | 77 |
| *syn*-**4** | $LiCH_2CN$ (**12**) | −78 | 1 h | | | | > 98 | 77 [e] |
| *anti*-**10** | $LiCMe_2CN$ (**11**) | −78 | 30 min | 73 [c] | 13 [c] | 13 [c] | – | 89 |
| | $LiCMe_2CN$ (**11**) | 0 | 1.3 h | 55 [c] | 23 [c] | 22 [c] | – | 85 |
| *syn*-**10** | $LiCMe_2CN$ (**11**) | −90 | 5 min | 11 [c] | 25 [c] | – | 64 [c] | 95 |
| | $LiCMe_2CN$ (**11**) | 0 | 1 h | 12 [c] | 48 [c] | 5 [c] | 34 [c] | 73 |

[a] The reactants were mixed at low temperature (−90 or −78 °C), then the mixture was stirred at the temperature and for the time indicated then cooled to −78 °C and treated with the oxidant. Iodine was used as oxidant unless otherwise noted. [b] The percentage yield refers to isolated material. [c] Ratio determined by GLC. [d] Ratio determined by GLC/MS from the reduced ion current signal for each isomer. [e] $[Fe(DMF)_3Cl_2]FeCl_4$ was used as oxidant. [f] $[Fe(DMF)_3Cl_2]FeCl_4$ and iodine were used as oxidants. [g] Combined yield of **14** and **15** due to lack of base line separation on the GLC/MS chromatogram.

*Nucleophilic addition / oxidation reactions*

Nucleophilic addition reactions were carried out with the nucleophiles 2-lithio-2-methylpropionitrile **11**, and, in the case of complexes **4**, with 2-lithioacetonitrile **12**. The arene $Cr(CO)_3$ complexes (indane$Cr(CO)_3$ (**1**), *syn*- and *anti*-**4** and *syn*- and *anti*-**10**) were added to a THF solution of the nucleophile at low temperature (−90 to −78°C) and the mixture was stirred for the time and at the temperature indicated in Table 4. The substituted arenes were obtained by oxidative decomplexation involving use of either iodine, or the $Fe^{III}$ complex $[Fe(DMF)_3Cl_2][FeCl_4]$ [33], or a combination of both, as oxidant. In reactions involving complex **4** and nucleophile **12**, the $Fe^{III}$ complex was much superior to iodine. With the latter, only low yields of products were obtained after the usual work up with aqueous $NaHSO_3$. The presence of substituted indenes in some of the product mixtures arises from elimination of the methoxy group during oxidation and work up. The crude product mixtures were analyzed by capillary GLC or GLC/MS. In the GLC/MS analysis, the reduced ion current (RIC) was used to calculate the relative ratios of regioisomeric products. The results are summarized in Table 4.

*Structural assignment of the products from nucleophilic addition / oxidation reactions to complexes **4** and **10***

Three of the four regioisomeric products from the reactions between $LiCMe_2CN$ and complex **4** could be isolated by chromatography. The structural assignments are tentative, and based on the $^1H$ NMR spectra. The aromatic region of the compound first eluted consists of a triplet and two doublets, consistent with either 4- or 7-substitution on the indane (**13b** or **16b**). The two diastereotopic methyl groups in the 2-methylpropionitrile fragment give rise to two singlets at $\delta$ 1.78 and 1.84. This shift difference is the largest observed for the three compounds isolated, and accordingly the spectrum is assigned to 2-(1-methoxyindan-7-yl)-2-methylpropionitrile (**16b**).

The two remaining isomers proved difficult to separate and repeated preparative TLC was required. Structural attribution is based again on the aromatic proton resonances (one singlet and two doublets) and the 2-methylpropionitrile resonances (two singlets at $\delta$ 1.74 and 1.77 for 2-(1-methoxyindan-6-yl)-2-methylpropionitrile (**15b**) and one singlet for 2-(1-methoxyindan-5-yl)-2-methylpropionitrile (**14b**). The fourth isomer, which by elimination must be the 4-substituted indane (**13b**), was present only in low yield, and could not be separated from the mixture of the 5- and 6-isomers. It was detected only in the GLC/MS spectrum.

The three regioisomers from the reaction with complex **4** and $LiCH_2CN$ were isolated by chromatography (column and TLC) and structures were assigned on the same criteria as those for the products with the $CMe_2CN$ group. The diastereotopic $CH_2CN$ hydrogens gave only two doublets for the 7-substituted product (**16c**), and singlets for the 5- and 6-substituted products (**14c** and **15c**, identified from the $^1H$ NMR signals from their aromatic hydrogens); this made their assignment ambiguous.

Of the four regioisomers from the reactions of $LiCMe_2CN$ (**11**) with complexes *syn*- and *anti*-**10**, only the 7-substituted product (**16d**) could be isolated by preparative GLC from the mixture. Its structure assignment is based on the pattern of aromatic resonances, the weak shielding of the 1-methyl group, and, in particular, on the splitting of the $CMe_2CN$ methyl signals. The products containing 4-, 5- and

6-substitution (**13d–15d**) were assigned from NMR spectra of mixtures containing two or all three of the above compounds (partial separation by preparative GLC). Assignment of 5- and 6-substitution is ambiguous.

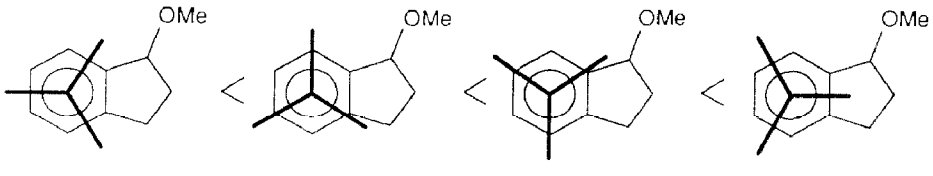
*Theoretical considerations of regioselectivity*

Previous discussions of observed regioselectivity of nucleophilic addition/oxidation reactions with arene $Cr(CO)_3$ complexes have focused on the correlation of regioselectivity with calculated properties of the arene $Cr(CO)_3$ compounds [3–5]. Kinetic control was assumed in the nucleophilic addition step and oxidation was shown not to affect the product distribution [2,9]. The size of the coefficients of the lowest arene-centered unoccupied molecular orbital of the complex is thought to indicate the addition-site (frontier orbital controlled reaction) [3]. Extended Hückel (EHT) calculations also have indicated that the conformation of the $Cr(CO)_3$ group affects the charge distribution in the aromatic ring of arene $Cr(CO)_3$ complexes. Charge induced on arene centers eclipsed by a Cr–CO bond offers a second explanation of the site of attack (charge controlled addition) [4,5]. Experimental evidence for the validity of these considerations has been presented for the 1,1-disubstituted indane complexes (Fig. 1), [6,7] in which the $Cr(CO)_3$ group adopts a highly preferred conformation for steric reasons. Nucleophilic addition occurs preferentially at C(5) which is eclipsed by a chromium carbonyl vector and which is sterically more accessible than C(7). Finally, on the basis of a detailed investigation of a series of reactions of substituted phenyldithiane nucleophiles with alkylarene complexes, Semmelhack et al. have argued for a balance of charge and orbital control [3b].

More recently, nucleophilic addition reactions with nitrile stabilized carbanions have been shown to be under kinetic control only at very low temperatures [8,9]. In our work, therefore, the timespan and temperature of the addition reactions were varied to give product distributions both under kinetic control and under equilibrium conditions. EHT calculations on four conformations of each of *syn*-**4** and *anti*-**4** were carried out for comparison of observed regioselectivities with those theoretically predicted.

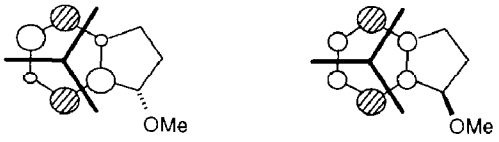
*Calculations*

The structural parameters determined by X-ray diffraction were used as the basis for the calculations on *syn*-**4** and *anti*-**4**. The total energies and the coefficients for the lowest unoccupied arene-centered orbitals were calculated. The calculations were then repeated for three hypothetical structures for each compound with the $Cr(CO)_3$ group rotated to staggered and eclipsed conformations.




For both compounds the observed staggered conformation was found to have the lowest energy, followed by the eclipsed conformations, and finally the second staggered conformation. The calculated energy difference between the extremes is only ca. 8 kJ/mol for both compounds; the barrier to rotation of the $Cr(CO)_3$ unit

is thus very small, in keeping with earlier findings [34]. As previously noted, the coefficients of the lowest unoccupied arene-centered orbitals show only very small variation with change of conformation of the $Cr(CO)_3$ group [3b]. The coefficients for the observed staggered conformations are shown in Fig. 7.




*anti* - 4 *syn* - 4

Fig. 7. Coefficients of the lowest unoccupied arene centered molecular orbital of *syn*- and *anti*-**4**.

The nodal properties of the lowest unoccupied arene-centered MO of *syn*- and *anti*-**4** differ. Orbital-controlled nucleophilic addition to *anti*-**4** is predicted to occur with almost equal probability at C(4), C(5) and C(7), whereas for *syn*-**4**, addition to C(4) and C(7) should be favoured over that to C(5) or C(6). We have not carried out calculations on the methyl complexes *syn*- and *anti*-**10**, but predictions of regioselectivity for *syn*-**10** can be made on the basis of previous data for nucleophilic additions to $Cr(CO)_3$ complexes of 1,1-disubstituted indanes (Fig. 1) [6,7], taking into account the absence of the *anti* substituent which shields C(7). *Anti*-**10** has a preferred staggered conformation and so, as for **1**, addition to C(4) should be favoured.

By use of Allinger's MMP [35] program, molecular mechanics calculations on 1-methoxyindane were carried out. Minima were found for two conformations of the parent hydrocarbon which were very close to the conformations observed for the solid state structures of *anti*-**4** and *syn*-**4**. In the lowest energy conformation of 1-methoxyindane, carbon 2 is slightly bent out of the plane defined by the aromatic ring and carbons 1 and 3. The methoxy substituent occupies a pseudo-equatorial position as found for *syn*-**4**. The second energy minimum is for a conformation that also has a bent five-membered ring but with the 1-methoxy substituent in a pseudo-axial position, as found in the structure of *anti*-**4**.

*Regioselectivity of the nucleophilic addition*

Addition of $LiCMe_2CN$ to indane $Cr(CO)_3$ (**1**) under conditions favoring kinetic control gave predominantly the 4-substituted product (**13a**); this is in good agreement with the proposal of a frontier orbital controlled addition. *Anti*-**4** reacted with the nucleophile $LiCMe_2CN$ to give, after oxidation, almost exclusively the 5- and 6-substituted products (**14b** and **15b**). The near absence of the 7-substituted product (**16b**) can be rationalized in terms of adverse steric interactions between the *anti*-1-substituent and the incoming nucleophile; this is widely observed with all *anti*-1-substituted indane$Cr(CO)_3$ complexes. This effect cannot, however, account for the virtual absence of the 4-isomer (**13b**), particularly as this was the major product from the reaction with the methyl-analogue *anti*-**10**. We suspect that the origin for the predominant 5- and 6-substitution is associated with the coordination of the lithium atom of the incoming nucleophile to the methoxy group of *anti*-**4** as well as to the nitrile nitrogen of the nucleophile [36]. The nucleophilic carbon is thus rather far from C(4) but well located for addition to the other ring positions. We

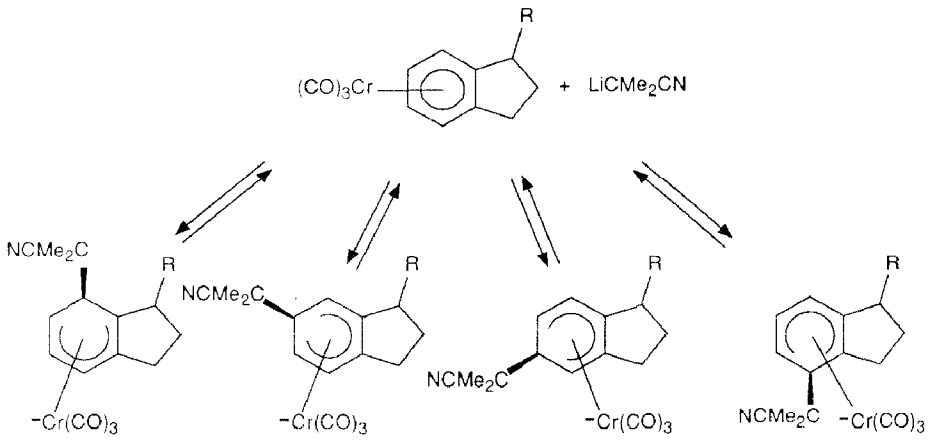



Fig. 8. Equilibration of cyclohexadienyl intermediates via nucleophile dissociation at 0 °C.

note, however, that addition to C(6), which represents close to 50% of the outcome, is predicted neither by orbital nor charge considerations. With *syn*-**10** the addition at low temperature took place preferentially at C(7), and to a minor extent at C(5) and C(4). Thus, addition occurred preferentially to carbons eclipsed by a Cr–CO vector in the dominant eclipsed conformation [38*]. In contrast to the otherwise very similar examples shown in Fig. 1, addition to C(7) in *syn*-**10** is not hindered, and C(7) is manifestly the most reactive center. The product distribution in the reaction of nucleophile **11** with complex *syn*-**4** may be ascribed to a analogous but much less pronounced influence of conformational preference in solution. The small nucleophile $LiCH_2CN$ added exclusively to C(7) in this complex.

The above discussion, centred on the properties of the reactants, is limited to kinetic control of the reaction. The data in Table 4 plainly show that such control operates only at very low reaction temperatures. When the temperature is increased, equilibration of the intermediate cyclohexadienyl complexes takes place and the relative thermodynamic stabilities of the addition products control the product composition (Fig. 8) [38*]. The extent of re-isomerization is particularly striking in the reactions of $LiCH_2CN$ with *anti*-**4** where the proportion of the 7-isomer (**16c**) is increased at the expense of the 5-isomer (**14c**). The same feature is found in the reaction of $LiCMe_2CN$ with *syn*-**4**, whereas in the reactions of indane $Cr(CO)_3$ (**1**), *syn*- and *anti*-**10** the isomerization is less marked and in the opposite direction. Clearly, at equilibrium only very small energy differences are involved, and this makes prediction difficult in these cases.

## Experimental

All manipulations of organometallic reagents were performed under an atmosphere of dry argon or nitrogen by standard Schlenk techniques [39]. Ether solvents were distilled from sodium benzophenone ketyl immediately before use. Volatile reagents were distilled under nitrogen from suitable drying agents. Commercially available butyllithium, 1.6 *M* (Aldrich or Fluka) was titrated immediately before use [40]. $^1H$ and $^{13}C$ NMR spectra were recorded on Bruker WH-360 and WH-500 or Varian XL-200 and XL-400 instruments. Chemical shifts are reported in ppm

relative to tetramethylsilane, TMS. IR spectra were recorded on a Perkin–Elmer 681 or a Mattson Polaris FT-IR spectrophotometer. Melting points were determined with a Mettler FP5-Olympus BH apparatus. Were indicated, crude reaction mixtures were analyzed on a Finnigan 1020 GLC-MS instrument fitted with a capillary column. Relative ratios of regioisomeric products were determined from the RIC (reduced ion current) signal for each regioisomer. Alternatively, relative ratios were determined by capillary GC and $^1$H NMR analysis.

*1-(t-Butyldimethylsiloxy)indane* (**5**) and *1-(tris-iso-propylsiloxy)indane* (**6**) were prepared in 95 and 96% yields from 1-indanol by the methods described by Corey [41] and Cunico [42].

*1-(t-Butyldimethylsiloxy)indane* (**5**). $^1$H NMR (360 MHz, $CDCl_3$) $\delta$: 0.18 (s, 3H), 0.20 (s, 3H), 0.98 (s, 9H), 1.87–2.00 (m, 1H, $H^2$), 2.39–2.50 (m, 1H, $H^{2'}$), 2.73–2.85 (m, 1H, $H^3$), 2.95–3.06 (m, 1H, $H^{3'}$), 5.29 (t, 1H, $J$ 7.0 Hz, $H^1$), 7.21–7.27 (m, 3H, aryl-H), 7.32–7.37 (m, 1H, aryl-H).

*1-(tris-iso-Propylsiloxy)indane* (**6**). $^1$H NMR (360 MHz, $CDCl_3$) $\delta$: 1.10–1.28 (m, 21H), 1.93–2.04 (m, 1H, $H^2$), 2.43–2.54 (m, 1H, $H^{2'}$), 2.73–2.84 (m, 1H, $H^3$), 2.95–3.05 (m, 1H, $H^{3'}$), 5.40 (t, 1H, $J$ 7.5 Hz, $H^1$), 7.21–7.28 (m, 3H, aryl-H), 7.41–7.47 (m, 1H, aryl-H).

*1-Methoxyindane* was prepared in 90% yield by treating 1-indanol with a suspension of sodium hydride in THF followed by addition of iodomethane [43]. Its structure was confirmed by $^1$H NMR spectroscopy [44,45*]. $^1$H NMR (360 MHz, $CDCl_3$) $\delta$: 2.07–2.17 (m, 1H, $H^2$), 2.33–2.43 (m, 1H, $H^{2'}$), 2.79–1.89 (m, 1H, $H^3$), 3.07–3.17 (m, 1H, $H^{3'}$), 3.43 (s, 3H, OMe), 4.84 (dd, 1H, $J_{12}$ 4.0, $J_{12'}$ 6.6 Hz, $H^1$), 7.21–7.31 (m, 3H, aryl-H), 7.39 (d, 1H, $J$ 6.8 Hz, aryl-H).

*Synthesis of tricarbonylchromium complexes*

*Indanetricarbonylchromium (1) [12,32b].* Indane (8.0 g, 18.2 mmol) was refluxed with $Cr(CO)_6$ (8.0 g, 67.8 mmol) in dibutyl ether (60 ml) and THF (4 ml) for 42 h. After evaporation of the solvents the crude solid was taken up in hot hexane (100 ml) and the extract filtered through Celite. Cooling overnight to $-30\,^\circ$C yielded 4.25 g (92%) of crystalline **1**. m.p. 81–82° C (lit. 12, 81–82° C). IR (hexane): 1977vs, 1907vs cm$^{-1}$. $^1$H NMR (360 MHz, $CDCl_3$): $\delta$ 2.02–2.15 (m, 2H, $H^2$), 2.65—.90 (m, 4H, $H^{1,3}$), 5.20–5.30 (m, 2H, $H^{5,6}$), 5.42–5.52 (m, 2H, $H^{4,7}$), $^{13}$C NMR (90.56 MHz, $C_6D_6$): $\delta$ 23.5, 31.6 ($CH_2$), 90.2, 91.5 (aryl-CH), 114.2 (aryl-C), 234.0 (CO).

*Naphthalenetricarbonylchromium (3)* was prepared according to a published procedure [46].

*Preparation of syn-1-indanol $Cr(CO)_3$ (syn-2) [10]*

*(a) Thermolysis of $Cr(CO)_6$ with 1-indanol.* A mixture of 1-indanol (1.0 g, 7.45 mmol) and $Cr(CO)_6$ (1.48 g, 6.72 mmol) in dibutyl ether (45 ml) and THF (5 ml) was heated under reflux (bath temperature: 150° C) for 72 h. Samples were taken after 0.5, 15, 30, 45 and 72 h and analyzed by HPLC (250 mm Silica-Spheri 5 column, eluent: diisopropyl ether/hexane (3/1), flow rate 5 ml/min). The retention times for compounds observed at 254 nm were as follows: $Cr(CO)_6$ 0.6 min, 1-indanol 1.6 min, *syn*-1-indanol $Cr(CO)_3$ 4.8 min and *anti*-1-indanol $Cr(CO)_3$ 12 min. After 45 h only traces of $Cr(CO)_6$ remained. The ratio of *syn*- and *anti*-isomer (80/20) was constant throughout the 72 h reaction time. The mixture was taken to dryness and the excess of 1-indanol was removed by sublimation. The residue was

taken up in toluene/hexane, the solution filtered, and the mixture of *syn*- and *anti*-1-indanol $Cr(CO)_3$ precipitated by adding hexane and keeping the mixture at −78°C (1.54 g, 85%). $^1H$ NMR indicated a 74/26 ratio of *syn*- to *anti*-1-indanol $Cr(CO)_3$ (**2**) [10,13,14].

*(b) Via arene exchange reaction in naphthalene $Cr(CO)_3$ [15].* A mixture of naphthalene$Cr(CO)_3$ (**3**) (0.53 g, 2 mmol), 1-indanol (0.4 g, 3 mmol), and diethyl ether (7 ml) was sealed in a Carius tube under nitrogen. The mixture was kept at 70°C for 20 h. The mixture was then cooled and filtered and volatiles were taken off on a vacuum line. The residue was recrystallized from ether/hexane at −78°C, and the solid washed with cold pentane and dried to give 0.45 g (83%) of pure *syn*-**2** as yellow needles.

*Syn-1-indanoltricarbonylchromium (syn-2) [10,13].* m.p. 104–105°C (lit 13: 104–106°C). IR (hexane): 1963vs, 1915vs, 1900vs $cm^{-1}$. $^1H$ NMR (360 MHz, $C_6D_6$) δ 1.30–1.54 (m, 3H, $H^{2,2'}$, -OH) (decreases in intensity on addition of $D_2O$), 1.78–1.94 (m, 1H, $H^3$), 2.12–2.22 (m, 1H, $H^{3'}$), 4.28 (t, 1H, $J_{56} = J_{67} = 6$ Hz, $H^6$), 4.37 (d, 1H, $J_{45}$ 6 Hz, $H^4$), 4.37–4.49 (m, 1H, $H^1$) (Dcpl. at 1.40 gives a large singlet), 4.59 (t, 1H, $J_{45} = J_{56} = 6$ Hz, $H^5$), 5.15 (d, 1H, $J_{67}$ 6 Hz, $H^7$). MS ($C_{12}H_{10}CrO_4$: 270), 270 (19), 214 (6), 184 (84), 168 (25), 133 (84), 116 (88), 115 (100), 77 (22), 52 (97). HRMS: ($C_{12}H_{10}CrO_4$) Calcd, 269.9984; found, 269.9969.

*Preparation of syn- and anti-(1-methoxyindane)tricarbonylchromium (4)*

*(a) Via thermolysis of $Cr(CO)_6$*

A solution of 1-methoxyindane (3.70 g, 25 mmol) and $Cr(CO)_6$ (4.00 g, 18.0 mmol) in a mixture of dibutyl ether (100 ml) and THF (10 ml) was refluxed for 72 h. Volatiles were removed in vacuo, the residue was taken up in ether, and the solution filtered through Celite and then taken to dryness. 5.82 g of crude product were isolated, and was shown by $^1H$ NMR spectroscopy to contain *syn*- and *anti*-**4** in a 65/35 ratio. After removal of the excess of 1-methoxyindane by washing with cold ether/pentane 4.0 g (92%) of *syn*- and *anti*-**4** was obtained. The regioisomers were separated by fractional crystallization; the crude product was dissolved in a mixture of diethyl ether and pentane (2/1) and the solution kept at −78°C. Yellow crystals separated and were isolated after 24 h and identified (cf. X-ray data) as *syn*-**4**, the major isomer. $^1H$ NMR spectroscopy indicated the presence < 2% of the *anti*-isomer as an impurity.

*Syn-(1-methoxyindane)tricarbonylchromium (syn-4) [10].* IR (hexane): 1980, 1915, 1900 $cm^{-1}$. $^1H$ NMR (500 MHz, $C_6D_6$): δ 1.58–1.66 (m, 1H, $H^2$), 1.70–1.76 (m, 1H, $H^{2'}$), 1.89–1.96 (m, 1H, $J_{2',3}$ 7.6 Hz, $H^3$), 2.27 (dd, 1H, $J_{33'}$ 15.5 Hz, $J_{23'}$ 8.6 Hz, $H^{3'}$), 3.07 (s, 3H, $-OCH_3$), 3.93 (dd, 1H, $J_{12}$ 8.3, $J_{12'}$ 7.1 Hz, $H^1$), 4.27 (t, 1H, $H^6$), 4.38 (d, 1H, $J_{45}$ 6.3 Hz, $H^4$), 4.54 (t, 1H, $J_{56}$ 6.0 Hz, $H^5$), 5.15 (d, 1H, $J_{67}$ 6.3 Hz, $H^7$). $^{13}C$ NMR (125.75 MHz, $C_6D_6$): δ 28.0, 30.7 ($CH_2$), 57.1 ($CH_3$), 81.6 ($C^1$), 86.9, 88.5, 90.2, 93.5 (aryl-CH), 113.4, 113.5 (aryl-C), 233.5 (CO).

The filtrate was taken to dryness and the residue recrystallized from ether/pentane (1/4). After three recrystallization *anti*-**4** containing less than 2% of the *syn*-isomer was obtained.

*Anti-(1-methoxyindane)tricarbonylchromium (anti-4) [21].* IR (hexane): 1980, 1905 $cm^{-1}$. $^1H$ NMR (500 MHz, $C_6D_6$): δ 1.75 (dd, 1H, $J_{23'}$, ~ 8 Hz, $J_{23}$ ~ 0 Hz, $H^2$), 1.91–1.99 (m, 1H, $J_{22'}$ 15.4 Hz, $H^{2'}$), 2.21 (dd, 1H, $J_{33'}$ 15.5, $J_{2',3}$ ~ 6 Hz, $H^3$),

2.48–2.64 (m, 1H, $J_{2'3'} \sim 9$ Hz, $H^{3'}$), 2.93 (s, 3H, $OCH_3$), 4.09 (d, 1H, $J_{12'}$ 5.4 Hz, $J_{12} \sim 0$ Hz, $H^1$) (dcpl. at 1.95 gives a large singlet), 4.32 (t, 1H, $J_{56}$ 5.7 Hz, $H^6$), 4.51 (t, 1H, $H^5$), 4.54 (d, 1H, $J_{45}$ 6.0 Hz, $H^4$), 4.96 (d, 1H, $J_{67}$ 6.1 Hz, $H^7$). $^{13}C$ NMR (125.75 MHz, $C_6D_6$): δ 29.7 ($CH_2$), 30.5 ($CH_2$), 56.2 ($CH_3$), 83.6 ($C^1$), 89.1, 90.1, 91.9, 93.7 (aryl-CH), 109.7, 115.6 (aryl-C), 233.3 (CO).

*(b) Via arene exchange in naphthalene $Cr(CO)_3$*

A mixture of naphthaleneCr(CO)$_3$ (**3**) (0.26 g, 1.0 mmol), 1-methoxyindane (0.29 g, 2.0 mmol), THF (0.24 ml, 3.0 mmol) and diethyl ether (1.0 ml) was sealed in a 5 ml Carius tube and kept for 24 h at 70 °C. The solution was cooled, and filtered through Celite, and the volatiles were removed in vacuo to leave a mixture of *syn*- and *anti*-**4**; the *syn/anti* ratio was shown to be 9/1 by integration of the $CH_3O$ signals in the $^1H$ NMR spectrum. Pure *syn*-**4** (by NMR) (0.24 g, 86%) was isolated by slow crystallization from diethyl ether and pentane (1/10).

*(c) Via methylation of syn-1-indanolCr(CO)$_3$ (syn-2)*

syn-IndanolCr(CO)$_3$ was prepared as described above by keeping a solution of naphthaleneCr(CO)$_3$ (1.5 g, 5.68 mmol) and 1-indanol (1.22 g, 9.1 mmol) in ether (15 ml) at 70 °C for 18 h. The crude product (*syn*-**2**) (1.95 g) was dissolved in THF (15 ml) and the solution added to a suspension of NaH (500 mg, 11.4 mmol) in THF (10 ml) at −20 °C. After 0.5 h stirring at this temperature methyl iodide (1.62 g, 11.4 mmol) was added dropwise, and after 15 min the temperature was raised to −10 °C. TLC indicated that *syn*-**2** had completely disappeared after 2 h. The excess NaH was destroyed by dropwise addition of MeOH at −30 °C. Volatiles were removed on a vacuum line, the residue taken up in ether, the solution filtered, and the solvent removed in vacuo. Recrystallization from hexane at −40 °C yielded pure *syn*-**4** (1.34 g, 83%) of m.p. 83–84 °C (Lit. 10: 84–85 °C).

*(d) Via solvolysis of 1-acetoxyindaneCr(CO)$_3$ (9).*

A mixture (1 g; 3.2 mmol) of *syn*- and *anti*-1-acetoxyindaneCr(CO)$_3$ (**9**) obtained by acetylation of a *syn-/anti* mixture of **2** [13] was dissolved in a mixture of methanol (25 ml) and THF (10 ml). The mixture was cooled to −30 °C and 10 ml of concentrated $H_2SO_4$ were added dropwise [21]. The temperature was raised to 20 °C and the reaction monitored by TLC. After 3.5 h the reaction was quenched by addition of water and the product was extracted with toluene (100 ml). Filtration through Florisil followed by two crystallizations from toluene/pentane yielded 0.62 g (68%) *anti*-**4** (containing 1.5% of *syn*-**4** (NMR)).

*Preparation of syn- and anti-1-(t-butyldimethylsiloxy)indanetricarbonylchromium (7)*

*(a) Via arene exchange in naphthaleneCr(CO)$_3$*

By the procedure described above for 1-methoxyindane, a mixture of naphthalenetricarbonylchromium (**3**) (2.38 g, 9 mmol) and 1-(t-butyldimethylsiloxy)indane (**5**) (4.50 g, 18 mmol), THF (2.2 ml), and diethyl ether (9 ml) was kept at 70 °C for 26 h, after which the color of the solution had changed from red to yellow and complex **3** could no longer be detected by TLC. Ether was added, the solution filtered, and volatiles were removed. Crystallization of the solid residue from hexane afforded 3.32 g (96%) of a 2/1 mixture (by $^1H$ NMR) of the *syn/anti* isomers of **7**.

Three fractional recrystallizations from ether/hexane at −78 °C gave a sample of the major isomer *syn*-**7** as yellow crystals with less than 2% of the *anti* isomer.

*Syn-1-(t-butyldimethylsiloxy)indanetricarbonylchromium (syn-7).* IR (hexane): 1985, 1921, 1910 $cm^{-1}$. $^1H$ NMR (360 MHz, $C_6D_6$): δ 0.06 (s, 3H, $-CH_3$), 0.08 (s, 3H, $-CH_3$), 1.05 (s, 9H, $-C(CH_3)_3$), 1.71–1.76 (m, 2H, $H^{2,2'}$), 1.91–2.02 (m, 1H, $H^3$), 2.23–2.31 (m, 1H, $H^{3'}$), 4.37 (dt, 1H, $J_{56} = J_{67} = 6.3$ Hz, $J_{46}$ 1 Hz, $H^6$), 4.47 (br.d, 1H, $J_{45}$ 6.3 Hz, $H^4$), 4.50 (t, 1H, $J$ 8 Hz, $H^1$), 4.58 (dt, 1H, $J_{45} = J_{56} = 6.3$ Hz, $J_{57}$ 1 Hz, $H^5$), 5.13 (br.d, 1H, $J_{67}$ 6.3 Hz, $H^7$).

The minor isomer was obtained by crystallization of the residue from toluene/hexane, and identified as the *anti*-isomer **7**. The $^1H$ NMR spectrum indicated the presence of 3% of the *syn* isomer.

*Anti-1-(t-butyldimethylsiloxy)indanetricarbonylchromium (anti-7).* IR (hexane): 1982, 1917, 1910 $cm^{-1}$. $^1H$ NMR (360 MHz, $C_6D_6$): δ 0.04 (s, 6H, $-CH_3$), 0.92 (s, 9H, $-C(CH_3)_3$), 1.60–1.68 (m, 1H, $H^2$), 2.05–2.16 (m, 1H, $H^{2'}$), 2.22–2.32 (m, 1H, $H^3$), 2.57–2.69 (m, 1H, $H^{3'}$), 4.37 (t, 1H, $J_{56} = J_{67} = 6$ Hz, $H^6$), 4.48 (t, 1H, $J_{45} = J_{56} = 6$ Hz, $H^5$), 4.56 (d, 1H, $J_{45}$ 6 Hz, $H^4$), 4.84 (dd, 1H, $J_{12'}$ 5.5, $J_{12}$ 1 Hz, $H^1$) (dcpl. at 1.20 gives a large singlet), 5.08 (d, 1H, $J_{67}$ 6 Hz, $H^7$).

*Syn- and anti-1-(tris-iso-propylsiloxy)indanetricarbonylchromium (8)* were obtained analogously in 73% as a 2/1 mixture of syn- and anti-isomer. Fractional crystallization from ether/pentane (1/8) at −78 °C afforded the major product as orange/yellow crystals, and this was identified as *syn*-**8** by spectral comparison with *syn*-**4** and by desilylation to give *syn*-**2**.

*Syn-1-(tris-iso-propylsiloxy)indanetricarbonylchromium (syn-8).* IR (hexane): 1983, 1920, 1910 $cm^{-1}$. $^1H$ NMR (360 MHz, $C_6D_6$): δ 1.05–1.2 (m, 3H, Si–C*H*), 1.16 (d, 12 H, $J$ 5.5 Hz, Si–CH($CH_3$)$_2$), 1.18 (d, 6H, $J$ 5.5 Hz, Si–CH($CH_3$)$_2$), 1.84–1.97(m, 2H, $H^{2,2'}$), 1.97–2.05 (m, 1H, $H^3$), 2.26–2.35 (m, 1H, $H^{3'}$), 4.38 (dt, 1H, $J_{56} = J_{67} = 6.2$ Hz, $J_{46}$ 1 Hz, $H^6$), 4.47 (d, 1H, $J_{45}$ 6.2 Hz, $H^4$), 4.57 (dt, 1H, $J_{45} = J_{56} = 6.2$ Hz, $J_{57}$ 1 Hz, $H^5$), 4.74 (t, 1H, $J_{12} \sim J_{12'} = 8$ Hz, $H^1$), 5.32 (d, 1H, $J_{67}$ 6.2 Hz, $H^7$).

Evaporation of the mother liquor and crystallization of the residue from toluene/hexane yielded *anti*-**8** containing only traces of *syn*-**8** (< 3%).

*Anti-1-(tris-iso-propylsiloxy)indanetricarbonylchromium (anti-8).* IR (hexane): 1982, 1917, 1910 $cm^{-1}$. $^1H$ NMR (360 MHz, $C_6D_6$): δ 0.90–1.20 (m, 3H, Si–C*H*), 1.05 (m, 18H, Si–CH($CH_3$)$_2$), 1.68–1.77 (m, 1H, $H^2$), 2.07–2.18 (m, 1H, $H^{2'}$), 2.23–2.33 (m, 1H, $H^3$), 2.66 (m, 1H, $H^{3'}$), 4.38 (t, 1H, $J_{56} = J_{67} = 6$ Hz, $H^6$), 4.50 (t, 1H, $J_{45} = J_{56} = 6$ Hz, $H^5$), 4.59 (d, 1H, $J_{45}$ 6 Hz, $H^4$), 5.03 (d, 1H, $J$ 6 Hz, $H^1$), 5.26 (d, 1H, $J_{67}$ 6 Hz, $H^7$).

*(b) Via thermolysis of $Cr(CO)_6$*

Thermolysis (bath temperature 150 °C, 71 h) of $Cr(CO)_6$ (0.88 g, 4 mmol) in dibutyl ether (30 ml) and THF (3 ml) in the presence of the indanol derivative **6** (1.45 g, 5 mmol) yielded a 54/46 mixture (by $^1H$ NMR) of *syn*- and *anti*-**8** in 89% yield.

*Desilylation of syn-8 to give syn-2*

*Syn*-**8** (0.384 g, 1 mmol) and tetrabutylammonium fluoride trishydrate (0.38 g, 1.2 mmol) were mixed. THF (5 ml) was added, and the mixture stirred at 20 °C for 2 h, after which *syn*-**8** could no longer be detected by TLC. Aqueous work up and extraction with ether yielded 270 mg (95%) of *syn*-**2**.

*Preparation of anti-1-methylindanetricarbonylchromium (anti-**10**)*

*Anti*-**10** was prepared according to the procedure described by Uemura et al. [23] except that 1-indanol was complexed via arene exchange with naphthaleneCr(CO)$_3$ (**3**) to give *syn*-1-indanol Cr(CO)$_3$ (*syn*-**2**) directly rather than via reduction of 1-indanone Cr(CO)$_3$. The crude *syn*-**2** was reacted with acetic anhydride in the presence of pyridine to give *syn*-1-acetoxyindaneCr(CO)$_3$ (*syn*-**9**) in 75% yield from **3**. Reaction of *syn*-**9** with $Me_3Al$ afforded *anti*-**10** diastereomerically pure in 62% yield in accord with the earlier report [23].

*Syn-1-acetoxytricarbonylchromium (syn-**9**) [13].* m.p. 102–103°C (lit. 13: 104–106°C). IR (hexane): 1978vs, 1908vs, 1746w, 1465s, 1381w, 1229m, 677w, 623w cm$^{-1}$. $^1$H NMR (360 MHz, $C_6D_6$) $\delta$ 1.69–1.82 (m, 1H, H$^2$), 1.84–1.98 (m, 2H, H, H$^{2',3}$), 1.88 (s, 3H, -CH$_3$), 2.10–2.32 (m, 1H, H$^{3'}$), 4.24 (t, 1H, $J_{67} = J_{56} = 6.5$ Hz, H$^6$), 4.32 (d, 1H, $J_{45}$ 6.5 Hz, H$^4$), 4.57 (t, 1H, $J_{45} = J_{56} = 6.5$ Hz, H$^5$), 5.13 (d, 1H, $J_{67}$ 6.5 Hz, H$^7$), 5.64 (t, 1H, $J$ 8 Hz, H$^1$) (dcpl. at 1.80 gives a singlet). MS ($C_{14}H_{12}CrO_5$: 312), 312 (13), 226 (100), 182 (15), 167 (21), 111 (27), 67 (8), 52 (78); an accurate mass determination for the molecular ion gave a value of 312.0075 (calcd. for $C_{14}H_{12}CrO_5$, 312.0090).

*Anti-1-methylindanetricarbonylchromium (anti-**10**) [23,24b].* m.p. 50°C (lit. 24b: 51°C). IR (hexane): 1974vs, 1905vs, 660m, 631m, cm$^{-1}$. $^1$H NMR (360 MHz, $C_6D_6$): $\delta$ 0.67 (d, 3H, $^3J$ 7.5 Hz, CH$_3$) (Dcpl. at 2.64 gives a singlet), 1.08–1.17 (m, 1H, H$^2$) (decoupling at 2.24 gives a doublet of doublets at 1.12 with $J_{22'}$ 11.5 and $J_{23}$ 1.5 Hz), 1.97–2.10 (m, 1H, H$^{2'}$), 2.17–2.33 (m, 2H, H$^{3,3'}$), 2.58–2.70 (m, 1H, $J$ 7.5 Hz, H$^1$), 4.41–4.48 (m, 2H, H$^{5,6}$), 4.61–4.69 (m, 2H, H$^{5,7}$). MS ($C_{13}H_{12}CrO_3$: 268), 268 (20), 212 (6), 184 (88), 117 (16), 52 (100); accurate mass 268.0208. Calcd. for $C_{13}H_{12}CrO_3$; 268.0191.

*Preparation of syn-1-methylindanetricarbonylchromium (syn-**10**)*

Syn-**10** was synthesized by the procedure described by Uemura et al. for the tetralin analog [23]. 1-Indanone Cr(CO)$_3$ [47] was prepared by arene exchange from naphthaleneCr(CO)$_3$ and purified by flash chromatography (62% yield) [15]. Addition of MeLi to 1-indanone Cr(CO)$_3$ afforded *anti*-1-methyl-*syn*-1-indanol Cr(CO)$_3$ in 82% yield. Ionic hydrogenolysis with $Et_3SiH/CF_3COOH$ [23,48] gave *syn*-**10** in 95% yield.

*1-Indanonetricarbonylchromium [49,50].* IR (hexane): 3010m, 2975w, 2940w, 1985s, 1918s, 1716m, 1610w, 1525w, 1430w, 1270w, 660m, 620m cm$^{-1}$. $^1$H NMR (360 MHz, $C_6D_6$): $\delta$ 1.78–2.02 (m, 2H, H$^2$), 2.08–2.29 (m, 2H, H$^3$), 4.09 (t, 1H, $J_{56} = J_{67} = 6$ Hz, H$^6$), 4.27 (d, 1H, $J_{45}$ 6 Hz, H$^4$), 4.61 (t, 1H, $J_{45} = J_{56} = 6$ Hz, H$^5$), 5.53 (d, 1H, $J_{67}$ 6 Hz, H$^7$).

*Anti-1-methyl-syn-1-indanoltricarbonylchromium [51].* m.p. 88–90°C (lit. 51: 81°C). IR (hexane): 1977vs, 1911vs, 1900vs cm$^{-1}$. $^1$H NMR (360 MHz, $C_6D_6$) $\delta$ 1.04 (s, 3H, -CH$_3$), 1.57–1.67 (m, 1H, H$^2$), 1.59 (s, 1H, -OH), 1.70–1.82 (m, 1H, H$^{2'}$), 1.91–2.03 (m, 1H, H$^3$), 2.13–2.23 (m, 1H, H$^{3'}$), 4.24 (t, 1H, $J_{56} = J_{67} = 6.5$ Hz, H$^6$), 4.32 (d, 1H, $J_{45}$ 6.5 Hz, H$^4$), 4.53 (t, 1H, $J_{45} = J_{56} = 6.5$ Hz, H$^5$), 5.09 (d, 1H, $J_{67} = 6.5$ Hz, H$^7$). MS ($C_{13}H_{12}CrO_4$: 284), 284 (15), 223 (10), 207 (20), 198 (41), 182 (40), 167 (11), 149 (100), 131 (33), 115 (21), 91 (32), 69 (33), 57 (73), 52 (74); accurate mass 284.0153. Calc. for $C_{13}H_{12}CrO_4$; 284.0140.

*Syn-1-methylindanetricarbonylchromium (syn-**10**).* m.p. 100–102°C. IR (hexane): 1973vs, 1904vs, 665m, 627m cm$^{-1}$. $^1$H NMR (360 MHz, $C_6D_6$): $\delta$ 1.1 (d, 3H, $J$ 7

Table 5

Crystal and experimental data for *syn*-**4** ($\eta^6$-methoxyindane)tricarbonylchromium(0) and *anti*-**4** ($\eta^6$-methoxyindane)tricarbonylchromium(0)

| | *syn*-**4** | *anti*-**4** |
|---|---|---|
| $M_r$ | 284.2 | 284.2 |
| m.p. | 83–84 °C | 95–96 °C |
| Unit-cell dimensions | *a* 9.557(6), *b* 17.479(10) | *a* 8.282(3), *b* 10.398(4) |
| | *c* 7.600(3) Å, $\beta$ 98.83(4)° | *c* 14.353(5) Å, $\beta$ 93.16(3)° |
| Space group | $P2_1/n$ (No. 14) [56] non-standard setting | $P2_1/c$ (No. 14) |
| $Z$ | 4 | 4 |
| $D_c$ | 1.50 g cm$^{-3}$ | 1.53 g cm$^{-3}$ |
| $\mu$ (Mo-$K_\alpha$) | 0.943 mm$^{-1}$ | 0.970 mm$^{-1}$ |
| Habit | Yellow plates | Yellow prisms |
| Crystal size | 0.19×0.19×0.22 mm | 0.35×0.35×0.30 mm |
| Temperature (data collection) | 290 K | 290 K |
| $2\theta_{max}$ | 50° | 50° |
| Scan mode | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| $2\theta$ scan rate | 2.5–15.0° min$^{-1}$ | 2.5–15.0° min$^{-1}$ |
| No. of independent reflections measured | 2224 | 2186 |
| No. of observed independent reflections [$I > 3.0\sigma(I)$] | 1683 | 1854 |
| Method used to solve structure | Direct methods (MITHRIL) [54] | Patterson, successive electron-density maps |
| No. of parameters refined | 199 | 199 |
| Reflections weighted according to | $w = [\sigma(F_o)^2 + 0.0001(F_o)^2]^{-1}$ | $w = [\sigma(F_o)^2 + 0.0004(F_o)^2]^{-1}$ |
| $R$ | 0.039 | 0.037 |
| $R_w$ | 0.041 | 0.043 |
| Maximum residual electron density | 0.26 e Å$^{-3}$ | 0.34 e Å$^{-3}$ |

Hz, -$CH_3$), 1.37–1.51 (m, 1H, $H^2$), 1.56–1.65 (m, 1H, $H^{2'}$), 2.00–2.12 (m, 1H, $H^3$), 2.18–2.27 (m, 1H, $H^{3'}$), 2.30–2.40(m, 1H,$H^1$), 4.28 (dt, 1H, $J_{56} = J_{67} = 6.5$ Hz, $J_{46}$ 1 Hz, $H^6$), 4.43 (br.d, 1H, $J_{45}$ 6.5 Hz, $H^4$), 4.63 (dt, 1H, $J_{45} = J_{56} = 6.5$ Hz, $J_{57}$ 1 Hz, $H^5$), 4.74 (br.d, 1H, $J_{67}$ 6.5 Hz, $H^7$). MS ($C_{13}H_{12}CrO_3$: 268), 268 (14), 212 (5), 187 (72), 117 (6), 52 (100): accurate mass 268.0181. Calcd. for $C_{13}H_{12}CrO_3$, 268.0191.

*Determination of the crystal and molecular structures of syn- and anti-(1-methoxyindane)tricarbonylchromium (4)*

*Crystal and intensity data.* Intensities of reflections were measured with a Syntex $P2_1$ diffractometer using graphite-monochromated Mo-$K_\alpha$ radiation. A 96-step profile was recorded for each reflection and the Lehmann and Larsen profile-analysis method [52] was used to calculate the intensities [53]. Data were corrected for Lorentz and polarization effects; empirical corrections were made for the effects of absorption [54] after solution of the structure. Unit-cell parameters were determined from setting angles for 15 reflections. Crystal data and further details of the collection of intensity data are given in Table 5 [55].

*Structure determination and refinement.* The structures were solved by the methods indicated in Table 5. Hydrogen atoms were located from the difference maps and their coordinates included in the full matrix least-squares refinement, the isotropic thermal parameters of these atoms being set equal to $B_{eq}$ of the carrying

Table 6

Fractional coordinates and equivalent isotropic thermal parameters (Å$^2$) for the non-hydrogen atoms in *syn*-**4** [a]

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Cr | 0.21416(5) | 0.15612(3) | −0.10117(7) | 2.94(1) |
| C(1) | 0.0599(5) | −0.1196(3) | −0.3012(7) | 6.2(1) |
| O(1) | 0.0976(2) | −0.0475(1) | −0.2196(3) | 4.1(1) |
| C(2) | 0.2434(3) | −0.0316(2) | −0.2075(4) | 3.5(1) |
| C(3) | 0.2894(4) | −0.0075(2) | −0.3849(5) | 4.7(1) |
| C(4) | 0.4172(4) | 0.0459(2) | −0.3305(5) | 4.2(1) |
| C(5) | 0.3888(3) | 0.0791(2) | −0.1560(4) | 3.5(1) |
| C(6) | 0.4490(4) | 0.1445(2) | −0.0645(5) | 4.2(1) |
| C(7) | 0.4076(4) | 0.1636(2) | 0.0992(5) | 4.5(1) |
| C(8) | 0.3054(4) | 0.1188(2) | 0.1704(5) | 4.4(1) |
| C(9) | 0.2421(4) | 0.0547(2) | 0.0775(4) | 3.8(1) |
| C(10) | 0.2871(3) | 0.0350(2) | −0.0865(4) | 3.2(1) |
| C(11) | 0.0266(4) | 0.1299(2) | −0.1689(5) | 4.1(1) |
| O(2) | −0.0929(3) | 0.1159(2) | −0.2102(4) | 6.2(1) |
| C(12) | 0.2133(3) | 0.1990(2) | −0.3213(5) | 3.8(1) |
| O(3) | 0.2149(3) | 0.2255(2) | 0.4616(3) | 5.6(1) |
| C(13) | 0.1517(4) | 0.2460(2) | −0.0176(5) | 4.2(1) |
| O(4) | 0.1096(3) | 0.3028(2) | 0.0343(4) | 6.7(1) |

[a] $B_{eq}$ is defined as $8\pi^2/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. Estimated standard deviations are given in parentheses.

carbon atoms. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [56]. Further details concerning the refinement of the structures are given in Table 5. The computer programs used are described in ref. 57. The stereoviews were drawn with ORTEP [58].

Table 7

Fractional coordinates and equivalent isotropic thermal parameters (Å$^2$) for the non-hydrogen atoms in *anti*-**4** [a]

| Atom | $x$ | $y$ | $z$ | $B_{eq}$ |
|---|---|---|---|---|
| Cr | 0.23503(4) | 0.24641(3) | −0.09793(2) | 2.37(1) |
| C(1) | 0.3459(5) | −0.2860(3) | −0.1613(2) | 4.7(1) |
| O(1) | 0.2369(2) | −0.1834(2) | −0.1463(1) | 3.6(1) |
| C(2) | 0.3086(3) | −0.0598(2) | −0.1597(2) | 2.9(1) |
| C(3) | 0.2958(3) | −0.0179(3) | −0.2630(2) | 3.5(1) |
| C(4) | 0.1306(3) | 0.0486(3) | −0.2776(2) | 3.7(1) |
| C(5) | 0.0991(3) | 0.0963(2) | −0.1805(2) | 2.9(1) |
| C(6) | −0.0115(3) | 0.1900(2) | −0.1529(2) | 3.6(1) |
| C(7) | −0.0182(3) | 0.2202(3) | −0.0582(2) | 3.7(1) |
| C(8) | 0.0585(3) | 0.1585(2) | 0.0093(2) | 3.5(1) |
| C(9) | 0.1967(3) | 0.0663(2) | −0.0175(2) | 3.0(1) |
| C(10) | 0.2021(3) | 0.0356(2) | −0.1137(2) | 2.5(1) |
| C(11) | 0.4546(3) | 0.2224(2) | −0.0850(2) | 3.5(1) |
| O(2) | 0.5926(2) | 0.2044(3) | −0.0776(2) | 5.6(1) |
| C(12) | 0.2663(3) | 0.3365(2) | −0.2053(2) | 3.3(1) |
| O(3) | 0.2833(3) | 0.3930(2) | −0.2740(1) | 5.4(1) |
| C(13) | 0.2546(4) | 0.3977(3) | −0.0312(2) | 4.1(1) |
| O(4) | 0.2662(4) | 0.4920(2) | 0.0098(2) | 7.3(1) |

[a] $B_{eq}$ is defined as $8\pi^2/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. Estimated standard deviations are given in parentheses.

Atomic coordinates and equivalent isotropic thermal parameters are listed in Tables 6 and 7. Lists of structure factors, hydrogen-atom coordinates, and anisotropic thermal parameters may be obtained from the authors (S.J.).

*Nucleophilic addition / oxidation reactions*

*Preparation of nucleophiles*

*2-Lithio-2-methylpropionitrile (**11**).* Butyllithium (1.06 ml, 1.70 mmol) was added via syringe to a −78 °C solution of diisopropylamine (0.26 ml, 1.8 mmol) in THF (10 ml). After 20 min, 2-methylpropionitrile (0.15 ml, 1.7 mmol) was added and the solution stirred for 20 min at −78 °C before addition of the areneCr(CO)$_3$ complex.

*2-Lithioacetonitrile (**12**)* was prepared analogously that the mixture was warmed to −20 °C for a few minutes to give a homogeneous solution.

*The reaction between anti-(1-methoxyindane)tricarbonylchromium (anti-**4**) and 2-lithio-2-methylpropionitrile (**11**)*

A solution of anti-**4** (0.40 g, 1.4 mmol) in 10 ml THF was added at −78 °C through a canula to a solution of **11** (1.7 mmol) in 10 ml THF. After 60 min stirring at −78 °C iodine was added (1.80 g, 7.1 mmol, in 10 ml of THF). The mixture was allowed to reach room temperature and was stirred for 2 h before addition of aqueous $NaHSO_3$ to remove the excess of $I_2$. The mixture was extracted three times with ether. The combined ether fractions were washed with aqueous $NaHCO_3$ and brine, then dried and filtered through Celite. GC-MS analysis of the crude product showed 4 regioisomeric products in the ratio 1/3/48/48 in order of elution from the capillary column. No 1-methoxyindane was detected.

The crude product was flash chromatographed on silica with pentane/ether (95/5) as eluent. The first fractions yielded traces of a minor component corresponding to the first compound in the GLC. The two major isomers were obtained as a mixture, 0.268 g, in 89% combined yield.

Under identical conditions except that reaction was carried on for 2 h at 0 °C, a 10/5/28/57 mixture of the same products as above was obtained in 84% yield. The mixture of regioisomeric products was separated by flash chromatography. The first two isomers were separated fairly easily, while the other two were difficult to obtain pure. The products in the order of elution from the capillary GLC column were identified as:

*2-(1-Methoxyindan-7-yl)-2-methylpropionitrile (**16b**).* $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 1.78 (s, 3H, -$CH_3$), 1.85 (s, 3H, -$CH_3$), 2.18–2.21 (m, 2H, $H^2$), 2.80 (ddd, 1H, $J_{3,3'}$ 15.9, $J_{23}$ 6.5 Hz, $H^3$), 3.08 (ddd, 1H, $J_{23'}$ 7.9 Hz, $H^{3'}$), 3.43 (s, 3H, -$OCH_3$), 5.43 (dd, 1H, $J_{12} = J_{12'} = 4.6$ Hz, $H^1$), 7.18 (d, 2H, $J_{45} = J_{56} = 7.5$ Hz, $H^{4,6}$), 7.24 (1H, dd, $J_{45} = J_{56} = 7.5$ Hz, $H^5$). $^{13}$C NMR (125.75 MHz, $CDCl_3$): $\delta$ 28.7, 29.7, 29.9, 30.1 ($CH_3$, $CH'_3$, $C^2$, $C^3$), 36.0, (*C*CN), 55.5 ($OCH_3$), 83.1 ($C^1$), 123.0 (aryl-CH), 124.5 (aryl-CH), 124.9 (*C*N), 129.1 (aryl-CH), 138.5 (aryl-C), 139.9 (aryl-C), 146.1 (aryl-C). MS ($C_{14}H_{17}NO$: 215), 215 (20), 188 (70) 184 (50), 157 (100), 115 (75).

*2-(1-Methoxyindan-4-yl)-2-methylpropionitrile (**13b**).* MS ($C_{14}H_{17}NO$: 215), 215 (20), 214 (30), 184 (100), 117 (70), 115 (60); tentatively identified as the 4-substituted product.

*2-(1-Methoxyindan-6-yl)-2-methylpropionitrile (**15b**).* $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.74 (s, 3H, -$CH_3$), 1.77 (s, 3H, -$CH_3$), 2.08–2.16 (m, 1H, $H^2$), 2.33–2.42 (m, 1H, $H^{2'}$), 3.07–3.16 (m, 1H, $H^3$), 3.29–3.37 (m, 1H, $H^{3'}$), 3.43 (s, 3H, -$OCH_3$), 4.79 (dd, 1H, $J_{12}$ 4.2, $J_{12'}$ 6.5 Hz, $H^1$), 7.26 (d, 1H, $H^{Ar}$), 7.28 (s, 1H, $H^{Ar}$), 7.40 (d, 1H, $H^{Ar}$). MS ($C_{14}H_{17}NO$: 215), 215 (25), 214 (40), 157 (80), 117 (55), 115 (75).

*2-(1-Methoxyindan-5-yl)-2-methylpropionitrile (**14b**).* $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 1.72 (s, 6H, -$CH_3$), 2.07–2.16 (m, 1H, $H^2$), 2.31–2.40 (m, 1H, $H^{2'}$), 2.80–2.87 (m, 1H, $H^3$), 3.05–3.13 (m, 1H, $H^{3'}$), 3.42 (s, 3H, -$OCH_3$), 4.81 (dd, 1H, $J_{12}$ 4.0, $J_{12'}$ 6.4 Hz, $H^1$), 7.32 (dd, 1H, $J_{67}$ 7.9, $J_{64}$ 1.2 Hz, $H^6$), 7.39 (s, 1H, $H^4$), 7.41 (d, 1H, $J_{67}$ 7.9 Hz, $H^7$). $^{13}$C NMR (100.60 MHz, $CDCl_3$) $\delta$: 29.3, 30.2, 32.0 ($CCH_3$, $C^2$, $C^3$), 37.2 ($CCN$), 56.2 ($OCH_3$), 84.0 ($C^1$), 121.7 (aryl-CH), 123.2 (aryl-CH), 125.0 ($CN$), 125.4 (aryl-CH), 141.8 (aryl-C), 142.4 (aryl-C), 145.0 (aryl-C). MS ($C_{14}H_{17}NO$: 215), 215 (20), 214 (30), 184 (100), 147 (30), 117 (60), 115 (50).

The assignment of the 5- and 6-substituted products is tentative.

*The reaction between syn-(1-methoxyindane)tricarbonylchromium (syn-**4**) and 2-lithio-2-methylpropionitrile (**11**)*

Analogous reactions to those described above for *anti*-**4** were carried out to yield mixtures of the same products in the ratios and yields given in Table 4.

*The reaction between syn-(1-methoxyindane)tricarbonylchromium (syn-**4**) and lithioacetonitrile (**12**)*

A reaction between *syn*-**4** and **12** was carried out analogously and on the same scale as that described above except that the oxidation was with $[Fe(DMF)_3Cl_2][FeCl_4]$ [33] (2.72 g, 5 mmol in 15 ml of cold THF). After the addition of the oxidant at $-78°C$ the mixture was stirred for 2 h at ambient temperature then water was added. After extraction with ether, the combined extracts were washed with 1 *M* aqueous HCl, aqueous $NaHCO_3$, and brine, then dried over $MgSO_4$ and filtered through Celite. GLC-MS analysis of the crude product revealed a single regioisomer, which was isolated by flash chromatography (pentane/ether 95/5) and identified as (1-methoxyindan-7-yl)acetonitrile (0.20 g, 77%) on the basis of its NMR spectra.

*(1-Methoxyindan-7-yl)acetonitrile (**16c**).* $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 2.06–2.13 (m, 1H, $H^2$), 2.38–2.45 (m, 1H, $H^{2'}$), 2.82–2.88 (m, 1H, $H^3$), 3.04–5.10 (m, 1H, $H^{3'}$), 3.42 (s, 3H, -$OCH_3$), 3.79 (d, 1H, $J$ 18.3 Hz, -$CH_2CN$), 3.94 (d, 1H, $J$ 18.3 Hz, -$CH_2CN$), 5.06 (dd, 1H, $J_{12}$ 4.9, $J_{12'}$ 6.7 Hz, $H^1$), 7.21 (d, 2H, $J_{45} = J_{56} = 7.6$ Hz, $H^{4,6}$), 7.27 (dd, 1H, $H^5$). $^{13}$C NMR (125.75 MHz, $CDCl_3$) $\delta$: 20.6 ($CH_2CN$), 30.16, 30.31 ($C^2$, $C^3$), 56.0 ($OCH_3$), 83.6 ($C^1$), 117.7 ($CN$), 124.7 (CH), 26.7 (CH), 127.7 ($C^7$), 129.4 (CH), 140.3 ($C^{7a}$), 144.5 ($C^{3a}$). MS ($C_{12}H_{13}NO$: 187), 187 (20), 160 (50), 156 (45), 129 (100), 116 (90).

*The reaction between anti-(1-methoxyindane)tricarbonylchromium (anti-**4**) and lithioacetonitrile (**12**)*

An analogous procedure to that described above for *syn*-**4** and **12** was carried out with *anti*-**4** ($-78°C$, 3 h) to yield ca. 50% of unchanged 1-methoxyindane together with a mixture of 3 regioisomeric addition products in the ratio 24/59/17 (GLC/MS). Flash chromatography yielded the three regioisomers in 43% combined yield. An improved yield (60%) was obtained when $[Fe(DMF)_3Cl_2]FeCl_4$ was used as oxidizing agent.

In a separate experiment, on the standard 1.4 mmol scale, the reaction mixture was kept at −10 °C for 1 h prior to oxidation. The reaction was quenched by the addition of a cold solution of $[Fe(DMF)_3Cl_2](FeCl_4)$ (3.06 g, 5.63 mmol) in THF. The mixture was stirred for 30 min at room temperature, then treated with iodine (1.80 g, 7.1 mmol), and stirred for another 60 min. After the usual work-up the crude product was analyzed by capillary GLC-MS, which indicated the presence in 29/59/17 ratio of the same three products as in the previous experiment (86% yield after flash chromatography). Pure samples were obtained by preparative TLC with pentane/ether as eluent. The first product was identified as (1-methoxyindan-7-yl)acetonitrile from its NMR spectra. The other two products were the 5- and 6-substituted isomers, and are tentatively assigned as follows:

*(1-Methoxyindan-5-yl)acetonitrile* ***(14c)***. $^1$H NMR (500 MHz, $CDCl_3$): δ 2.09–2.15 (m, 1H, $H^2$), 2.33–2.40 (m, 1H, $H^{2'}$), 2.76–2.82 (m, 1H, $H^3$), 2.99–3.05 (m, 1H, $H^{3'}$), 3.40 (s, 3H, $-OCH_3$), 3.63 (s, 2H, $CH_2CN$), 4.82 (dd, 1H, $J_{12}$ 4.2, $J_{12'}$ 6.4 Hz, $H^1$), 7.25 (d, 1H, $J_{67}$ 7.1 Hz, $H^6$), 7.27 (s, 1H, $H^4$), 7.38 (d, 1H, $J_{67}$ 7.1 Hz, $H^7$). $^{13}$C NMR (125.75 MHz, $CDCl_3$): δ 21.3 ($CH_2CN$), 28.4 ($C^2$), 31.4 ($C^3$), 56.1 ($OCH_3$), 84.3 ($C^1$), 117.2 (*C*N), 125.0 (aryl-CH), 126.2 (aryl-C), 127.4 (aryl-CH), 127.9 (aryl-CH), 142.3 (aryl-C), 143.6 (aryl-C). MS ($C_{12}H_{13}NO$: 187), 187 (30), 186 (35), 156 (85), 147 (30), 129 (60), 116 (100).

*(1-Methoxyindan-6-yl)acetonitrile* ***(15c)***. $^1$H NMR (500 MHz, $CDCl_3$): δ 2.07–2.13 (m, 1H, $H^2$), 2.35 (m, 1H, $H^{2'}$), 2.79–2.85 (m, 1H, $H^3$), 3.04–3.10 (m, 1H, $H^{3'}$), 3.40 (s, 3H, $-OCH_3$), 3.73 (s, 2H, $-CH_2CN$), 4.80 (d, 1H, $J_{12} = J_{12'} = 6.7$ Hz, $H^1$), 7.16 (d, 1H, $J_{45}$ 7.7 Hz, $H^5$ or $H^4$), 7.24 (s, 1H, $H^7$), 7.39 (d, 1H, $J_{45}$ 7.7 Hz, $H^4$ or $H^5$). $^{13}$C NMR (125.75 MHz, $CDCl_3$) δ: 23.5 ($CH_2CN$), 30.0 ($C^2$), 32.0 ($C^3$), 56.2 ($OCH_3$), 84.0 ($C^1$), 117.9 (*C*N), 124.5 (aryl-CH), 125.7 (aryl-CH), 126.1 (aryl-CH), 130.0 (aryl-C), 142.8 (aryl-C), 145.3 (aryl-C). MS ($C_{12}H_{13}NO$: 187), 187 (35), 186 (40), 156 (75), 147 (30), 129 (100), 116 (40), 115 (70).

*The reaction between anti-1-methylindane $Cr(CO)_3$ (anti-**10**) and 2-lithio-2-methylpropionitrile (**11**)*

The solid complex *anti*-**10** (0.43 g, 1.5 mmol) was added to a solution of **11** (1.51 mmol) in 10 ml of THF at −78 °C. The mixture was stirred at −78 °C for 30 min followed by the addition of a cold solution of $I_2$ (2.2 g, 8.7 mmol) in10 ml of THF. After the usual work-up the crude product was analyzed by capillary GLC, which revealed the presence of three regioisomers products in the ratio 73/13/13, which were identified as the 4-, 5-, and 6-substituted products respectively (see text). The mixture of the three products was isolated in 89% yield.

*2-(1-Methylindan-4-yl)-2-methylpropionitrile* ***(13d)***. $^1$H NMR (360 MHz, $CDCl_3$) δ: 1.26 (d, 3H, *J* 7 Hz, $C^1$-$CH_3$), 1.55–1.68 (m, 1H, $H^2$), 1.72 (s, 6H, $C(CH_3)_2CN$), 2.25–2.40 (m, 1H, $H^{2'}$), 2.95–3.02 (m, 1H, $H^3$), 3.02–3.12 (m, 1H, $H^1$), 3.12–3.23 (m, 1H, $H^{3'}$), 7.15–7.25 (m, 3H, aryl-H).

*2-(1-Methylindan-5-yl)-2-methylpropionitrile* ***(14d)*** *(tentative)*. $^1$H NMR (360 MHz, $CDCl_3$) δ: 1.26 (d, 3H, *J* 7 Hz, $C^1$-$CH_3$), 1.55–1.68 (m 1H, $H^2$), 1.68 (s, 6H, $C(CH_3)_2CN$), 2.25–2.40 (m, 1H, $H^{2'}$), 2.70–2.90 (m, 2H, $H^{3,3'}$), 3.02–3.12 (m, 1H, $H^1$), 7.15–7.25 (m, 2H, $H^{6,7}$), 7.33 (s, 1H, $H^4$).

*2-(1-Methylindan-6-yl)-2-methylpropionitrile* ***(15d)*** *(tentative)*. $^1$H NMR (360 MHz, $CDCl_3$) δ: 1.24 (d, 3H, *J* 7 Hz, $C^1$-$CH_3$), 1.55–1.68 (m, 1H, $H^2$), 1.69 (s, 6H, $C(CH_3)_2CN$), 2.25–2.40 (m, 1H, $H^{2'}$), 2.75–2.95 (m, 2H, $H^3$), 3.02–3.12 (m, 1H, $H^1$), 7.15–7.25 (m, 2H, $H^{4,5}$), 7.29 (s, 1H, $H^7$).

Under identical conditions, except that the reaction temperature was 0 °C and the reaction time was 1.3 h the same three regioisomers were isolated in 85% yield in the ratio 55/23/22 (the 4-, 5-, and 6-substituted products, respectively).

*The reaction between syn-1-methylindaneCr(CO)$_3$ (syn-**10**) and 2-lithio-2-methylpropionitrile (**11**)*

Analogous reactions to those with *anti*-**10** were carried out with *syn*-**10**. Quenching after 5 min at −90 °C gave the 4-, 5- and 7-substitution products as an 11/25/64 mixture in 95% yield, whereas quenching after 1 h at 0 °C gave the 4-, 5-, 6-, and 7-substitution products as a 12/48/5/34 mixture in 73% yield. 2-(1-Methylindan-7-yl)-2-methylpropionitrile was isolated by preparative GLC.

*2-(1-Methylindan-7-yl)-2-methylpropionitrile (**16d**).* IR ($CHCl_3$): 3019m, 2987m, 2956m, 2875w, 2238w, 1579w, 1475m, 1459m, 1375m, 1233m, 1218m, 1125m, 672m $cm^{-1}$. $^1H$ NMR (360 MHz, $CDCl_3$) $\delta$ 1.25 (d, 3H, $J$ 7 Hz, $C^1$-$CH_3$), 1.78 (s, 3H, $C(CH_3)_2CN$), 1.79 (s, 3H, $C(CH_3)_2CN$), 1.78–1.87 (m, 1H, $H^2$), 2.12–2.26 (m, 1H, $H^{2'}$), 2.71–2.80 (m, 1H, $H^3$), 3.02–3.15 (m, 1H, $H^{3'}$), 3.92 (m, 1H, $H^1$), 7.15–7.26 (m, 3H, aryl-H). MS ($C_{14}H_{17}N$: 199), 199 (31), 184 (78), 172 (44), 157 (100), 141 (14), 129 (23), 117 (42), 116 (30), 115 (35), 91 (11), 84 (11), 77 (8), 63 (6), 51 (7); accurate mass, 199.1360, calcd. for $C_{14}H_{17}N$, 199.1361.

*The reaction between indaneCr(CO)$_3$ (**1**) and 2-lithio-2-methylpropionitrile (**11**)*

The solid complex **1** (0.381 g, 1.5 mmol) was added to a cold (−78 °C) solution of **11** (1.51 mmol) in 10 ml THF. The solution was stirred for the time and at the temperature indicated in Table 4 and the reaction quenched by addition of iodine at −78 °C. After the usual work-up the product mixture was analyzed by capillary GLC and $^1H$ NMR. The ratios of 4- and 5-substituted indanes were 91/9 for the reaction at low temperature (−90 °C/5 min) and 75/25 after equilibration (0 °C/2 h) [59*].

*2-(Indan-4-yl)-2-methylpropionitrile (**13a**).* $^1H$ NMR (360 MHz, $CDCl_3$): $\delta$ 1.74 (s, 6H, $-(CH_3)_2CN$), 2.09 (quint, 2H, $J_{12} = J_{23} = 7.5$ Hz, $H^2$), 2.91 (t, 2H, $J_{12}$ 7.5 Hz, $H^1$), 3.19 (t, 2H, $J_{23}$ 7.5 Hz, $H^3$), 7.15–7.27 (m, 3H, $H^{5,6,7}$). MS ($C_{13}H_{15}N$: 185), 185 (31), 170 (55), 158 (100), 143 (24), 128 (15), 117 (30), 115 (32), 91 (16), 77 (5).

*2-(Indan-5-yl)-2-methylpropionitrile (**14a**).* $^1H$ NMR (360 MHz, $CDCl_3$): $\delta$ 1.69 (s, 6H, $-C(CH_3)_2CN$), 2.07 (quint, 2H, $J_{12} = J_{23} = 7.5$ Hz, $H^2$), 2.86–2.95 (m, 4H, $H^{1,3}$), 7.15–7.27 (m, 2H, $H^{6,7}$), 7.36 (s, 1H, $H^4$).

*Calculations*

Molecular mechanics calculations on 1-methoxyindane were performed by use of Allinger's MMPI [35] program and a standard set of parameters. Extended Hückel calculations on *syn*-**4** and *anti*-**4** were performed using Hoffmann's standard parameters with geometries obtained from the X-ray structure analysis [60].

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