

Tricarbonylchromium complexes of centropolyindans. Part 4.†
Physicochemical and structural characterization of *anti*-Cr(CO)₃-
4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene, *syn*-Cr(CO)₃-4b,9,9a,10-
tetrahydroindeno[1,2-*a*]indene and *syn,anti*-[Cr(CO)₃]₂-4b,9,9a,10-
tetrahydroindeno[1,2-*a*]indene

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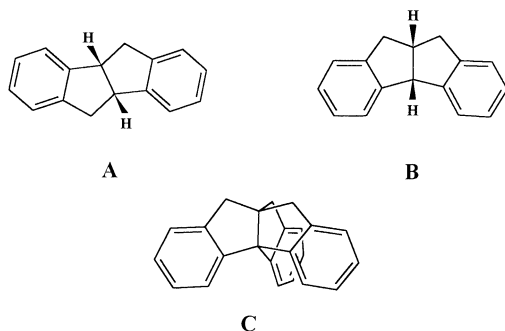
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The reaction of 4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene, **B**, with Cr(CO)₆ in boiling mixtures of Bu₂O and tetrahydrofuran (THF) (9: 1) affords two mono-complexes, one of which bears the Cr(CO)₃ group bonded to the convex side of the ligand (*anti* complex, **B1**) and the other inorganic unit to the concave side of **B** (*syn* complex, **B2**). After prolonged reaction times, two bis-complexes were isolated, the first having one Cr(CO)₃ group bonded to the convex side of **B** and the other to the concave side (*syn,anti* bis-complex, **B3**), and the second having both of the inorganic groups bonded to the convex side of **B** (*anti,anti* bis-complex, **B4**). The results of X-ray structural analysis support the hypothesis that the stereochemistry of the first and the second metallation reaction are related to the conformation of the ligand as induced by the steric interactions between aliphatic hydrogen atoms. The results confirm the existence of weak bonding interactions between oxygen atoms of the *syn*-Cr(CO)₃ carbonyl groups with vicinal benzene rings bearing an *anti*-Cr(CO)₃ group as well as methylene protons.

Introduction

Among the lower members of the centropolyindans,¹ 4b,5,9b,10-tetrahydroindeno[2,1-*a*]indene, **A**, and 4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene, **B**, represent the two possible



diindan isomers of different molecular symmetry arising from the linear and *cis* fusion of two indan units.

Recently, the chemistry of the C₂-*fuso*-diindan **A** with respect to the complexation with Cr(CO)₃ has been reported,² and its patterns of substitution have been found to be related to the C₂ molecular symmetry of the ligand. A particularly facile access to **B** has been published recently,³ and this isomer appears to

have the potential of possessing a perfect C_s symmetry. However, a twist about the central bond allows the molecule to relieve the strain associated with the nonbonded interactions, thus giving rise to a structure in which the two indan moieties are geometrically nonequivalent.⁴ Interestingly, the resulting asymmetric conformation of the C_s-*fuso*-diindan **B** resembles the propellane⁵ (the so-called triptindan, **C**), of which **B** can be thought to comprise two thirds of the whole molecule. We therefore anticipated close similarities in the complexation behaviour of **B** and **C**.

The complexation of **B** with Cr(CO)₃ under standard conditions leads to a series of isomers arising from the possibility of *syn* and *anti* orientation of the inorganic unit that can coordinate to the concave or convex side of this bent molecule. The relative yields and stability of these isomers are strongly controlled by steric effects.

We report here the synthesis and the crystal and molecular structure of the *anti*-mono-tricarbonylchromium, *syn*-mono-tricarbonylchromium and *syn,anti*-bis-tricarbonylchromium derivatives of C_s-diindan **B**. A correlation between chemical results and molecular geometries will be discussed.

Results

The Cr(CO)₃ complexes of **B** have been obtained following the procedure described previously.^{2,5,6} By working with an excess of the complexing agent, Cr(CO)₆, and prolonged reaction times

† For Part 3, see ref. 5.

Table 1 Complexation products of 4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene, **B**^a

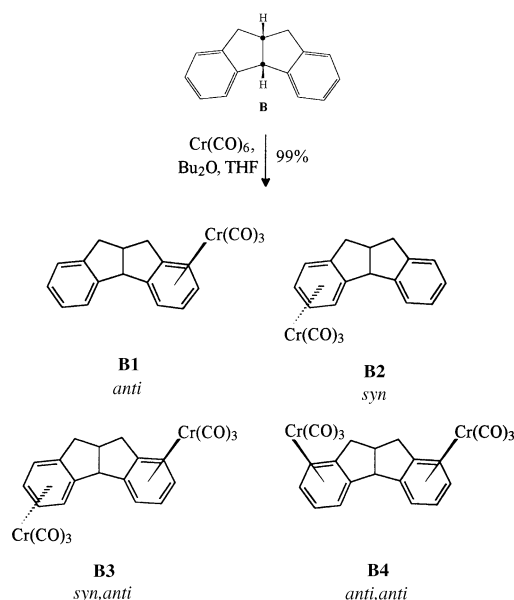
Run	Reagent	Cr(CO) ₆ /reagent (mol:mol)	Reaction time/ h	Conversion (%)	Yield (%) ^b				
					B	B1	B2	B3	B4
1 ^c	B	1:1	6	14	—	65	35	Traces	—
2 ^d	B	3:1	24	>99	<1	28	5	49	18
3 ^e	B1	3:1	7	0	—	—	—	—	—
			24	27	89	—	—	11	—
4 ^f	B2	3:1	7	15	—	30	—	70	—
			24	37	—	56	—	44	—

^a Solvent, Bu₂O–THF 90/10 v/v; *T*, 142 °C. Conversions and yields were determined by integration of the corresponding signals in the ¹H NMR spectra of the crude reaction mixtures. ^b Relative yields; each datum represents the mean of at least three experiments. ^c **B**, 0.1 g; Cr(CO)₆, 0.1 g; solvent, 15 ml. ^d **B**, 1 g; Cr(CO)₆, 3.3 g; solvent, 150 ml. ^e **B1**, 0.05 g; Cr(CO)₆, 0.15 g; solvent, 5 ml. ^f **B2**, 0.05 g; Cr(CO)₆, 0.15 g; solvent, 5 ml.

Table 2 ¹H NMR chemical shift values^a for the free and Cr(CO)₃-complexed 4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene, **B**

	H1	H21	H22	H4	H5	H6	H7	H1'	H2'1	H2'2	H4'	H5'	H6'	H7'
B	3.39	3.21	2.71	7.42	7.08–7.16		4.61	2.71	3.21	7.08–7.16		7.72		
B1	3.41	3.22	2.89	7.26	7.10–7.20	7.42	4.45	2.56	3.07	5.64	5.52	5.56	6.20	
B2	3.41	3.29	3.12	5.48	5.61	5.36	5.91	4.64	2.82	3.33	7.10–7.20		7.50	
B3	3.37	3.18	3.15	6.01	5.58	5.48	5.77	4.53	2.80	3.35	5.58	5.62	5.57	6.23
B4	3.47	3.23	2.97	5.82	5.58	5.56	6.24	4.47	2.87	3.23	5.82	5.58	5.56	6.24

^a δ from internal SiMe₄ taken as reference. Solvent, [2H₆]acetone; *T* 298 K. For proton labelling, see Figs. 4–6. For the assignment of the methylene protons, see Results.

**Scheme 1** Orientation of the Cr(CO)₃ units in mono- and bis-complexed **Bs**

(Table 1, run 2) we obtained almost quantitative conversion of the ligand into four different complexes that were isolated as yellow, crystalline and air-stable solids. On the basis of their mass and NMR spectra (see Experimental) and X-ray crystallographic measurements (see below), they have been identified as the complexes **B1–B4**.

Among the bis-complexes, the formation of **B3**, the unsymmetrical *syn,anti* isomer, is largely favoured with respect to **B4**, the symmetrical *anti,anti* complex. The yield of the *anti*-mono-complex **B1** bearing the Cr(CO)₃ unit at the convex side of the ligand, is much higher than that of the *syn* isomer, **B2**, even if the molar ratio Cr(CO)₆-ligand is lowered to 1:1 (*cf.* run 1). The preference for complexation of the *anti* face over the *syn* face of the C₂-diindenyl **B** may arise from steric considerations.

In order to induce the possible mobility of the Cr(CO)₃ group in the various complexes, we heated the substrates **B1–B4** in decalin at 150 °C in the presence of a large excess (50 equiv., or more) of hexamethylbenzene as a Cr(CO)₃ scavenger. All com-

Table 3 ¹³C NMR chemical shift values^a for the free and Cr(CO)₃-complexed 4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene, **B**

	B	B1	B2	B3	B4
Cr1–C≡O	—	—	233.98	234.07	234.54
C1	43.64	42.92	41.56	40.75	42.39
C2	39.49	37.84	40.64	36.65	38.76
C3	145.36	143.41	120.55	115.48	115.69
C4	125.45	126.29	88.49	91.73	92.19
C5	127.47	127.78	95.87	96.39	94.78
C6	127.35	128.48	92.78	91.90	93.66
C7	125.09	125.22	91.16	92.43	92.45
C8	143.67	142.90	118.65	116.97	115.19
Cr2–C≡O	—	234.99	—	234.88	234.54
C1'	57.47	56.57	56.10	55.58	55.96
C2'	39.49	39.02	37.69	39.77	38.76
C3'	145.36	115.81	139.58	116.15	115.69
C4'	125.45	91.82	125.58	89.26	92.19
C5'	127.47	94.58	127.92	95.72	94.78
C6'	127.35	93.77	128.52	93.48	93.66
C7'	125.09	92.43	124.75	92.62	92.45
C8'	143.67	117.04	143.70	115.02	115.19

^a δ from internal SiMe₄ taken as reference. Solvent, [2H₆]acetone; *T* 298 K. For carbon labelling, see Figs. 4–6.

plexes turned out to be remarkably stable. Even after prolonged heating, the exchange product, Cr(CO)₃-C₆Me₆, was never observed and the different complexes do not display any tendency to lose the organic unit under such conditions. This behaviour clearly parallels that shown by the complexes of isomer **A**² and is in contrast with the different reactivity exhibited by the Cr(CO)₃ complexes of **C** and with another related centrotriindenyl, 10-methyltribenzotriquinacene.⁶

In contrast with the stability of **B1–B4** in decalin-hexamethylbenzene solutions, attempts to examine the relative reactivity of **B1** and **B2** under Cr(CO)₃ complexation conditions led to more complex results. As shown in Table 1, reaction of the *anti* complex **B1** with Cr(CO)₆ for 7 h gave no conversion; prolonged heating, however, gave rise to formation of the *syn,anti* complex **B3** along with prevailing decomposition. In contrast, reaction of the *syn* isomer **B2** under similar conditions led to slow conversion to **B3** and, in even smaller amounts, to the *anti* complex **B1**. Prolonged heating disfavoured the twofold complexation, generating increased amounts of **B1**. Moreover,

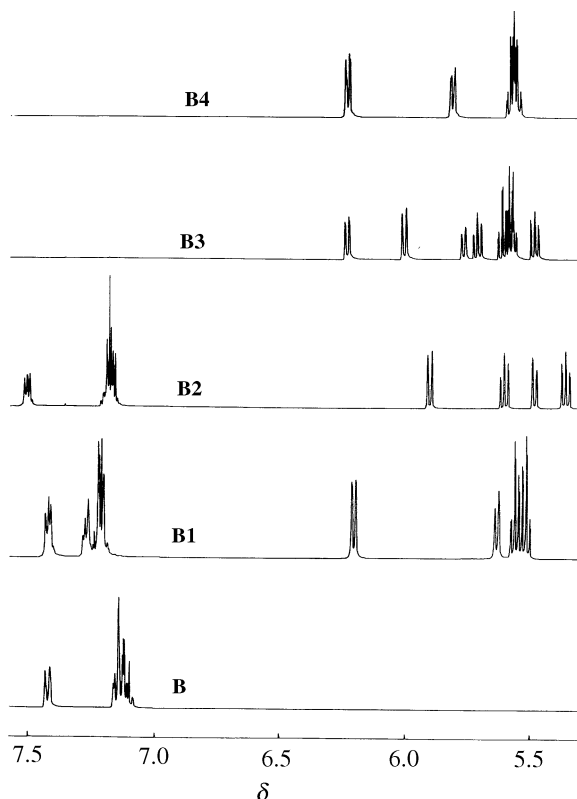


Fig. 1 Low-field portion of the ^1H NMR spectra of the free and $\text{Cr}(\text{CO})_3$ -complexed **B**. Solvent, $[\text{d}_6]\text{acetone}$; T 298 K; ν_0 400.13 MHz; δ in ppm from internal SiMe_4

it is remarkable that the *anti,anti* bis-complex **B4** was not obtained upon reaction of **B1** and **B2** with additional $\text{Cr}(\text{CO})_6$. Clearly, **B3** is the only direct metallation product possible from **B2**, but it is not evident whether the observed mono-complex **B1** results from decomplexation of **B2** and recomplexation to give **B1**, or from demetallation of **B3**.

NMR spectroscopic measurements

The ^1H and ^{13}C NMR spectra of **B1**–**B4** have been used for identification. The proton assignments given in Table 2 were determined by selective decoupling and $\{^1\text{H}\}$ – ^1H NOE measurements. The spectra of the aromatic and alicyclic parts of the molecules are shown in Figs. 1 and 2, respectively. The ^{13}C resonances collected in Table 3 were assigned to the corresponding nuclei by partially relaxed spectra (in the case of the quaternary carbon atoms) and by 2D heterocorrelated inverse detection measurements (see Experimental and Fig. 3 for an example).

The ligand

The formal C_s molecular symmetry of the molecule **B** is maintained in its ^1H NMR spectrum which exhibits an ABCD pattern due to the eight aromatic protons in the range δ 7.42–7.08. The apparent doublet centred at δ 4.61 (1 proton) is attributed to the benzhydryl nucleus $\text{H1}'$ by its relatively low field δ value, while the multiplet at δ 3.39 (1 proton) is assigned to the methine proton H1 . The signals due to the methylene protons appear as two multiplets (2 protons each) at δ 3.21 and δ 2.71; the multiplet at lower field is attributed to the hydrogen atoms located at the convex side of the molecule since they exhibit strong NOE with the methine H1 proton. The same NOE measurement allows assignment of the lowest field aromatic resonance to H4 , *i.e.* to the protons at the *ortho* positions relative to $\text{H1}'$. Finally, in the ^{13}C spectrum, the resonance C3 (*i.e.* of the quaternary carbon bonded to the methylene subunit) appears at higher field than that of C8 . All these findings represent common features for the ^1H NMR

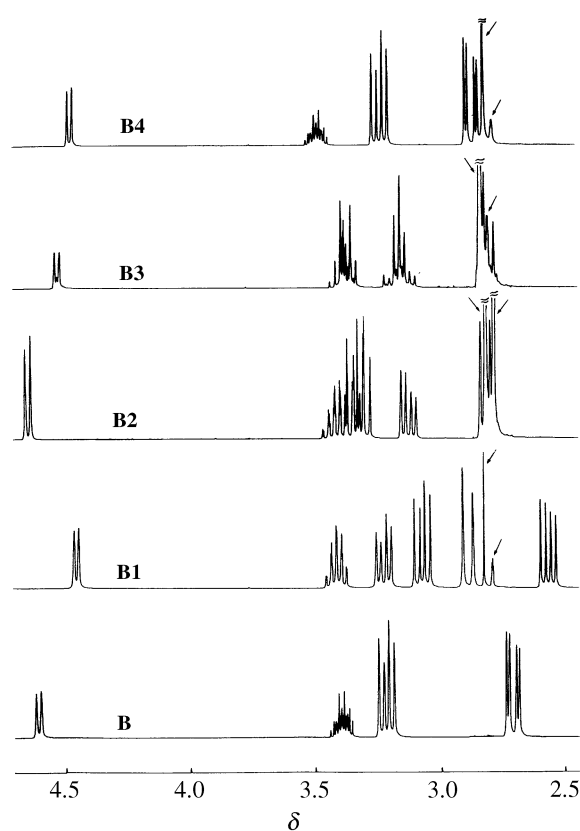


Fig. 2 High-field portion of the ^1H NMR spectra of the free and $\text{Cr}(\text{CO})_3$ -complexed **B**. Arrows indicate HDO and H_2O impurities.

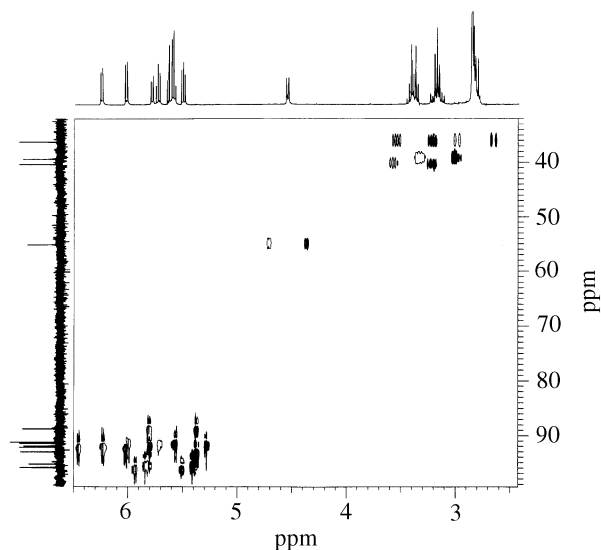


Fig. 3 2D ^1H – ^{13}C reverse detection NMR spectrum of **B3**. For the experimental conditions, see the Experimental section.

spectra of the centropolyindans of this series and those reported previously.^{2,5,6}

Mono-complexes **B1** and **B2**

The complexation of one of the benzene rings with $\text{Cr}(\text{CO})_3$ at either the concave or the convex face of **B** removes the molecular symmetry of the ligand and makes the resonances of the aromatic and alicyclic moieties distinguishable enough to allow a first-order analysis of the chemical shift values (see Fig. 2). In particular, the ^1H NMR spectra of **B1** and **B2** exhibit two sets of ABCD spin systems, one between δ 7.5 and 7.1 and a second one between δ 6.2 and 5.5 for **B1** and between δ 5.9 and 5.3 for **B2**. In both cases, the lower-field ABCD pattern

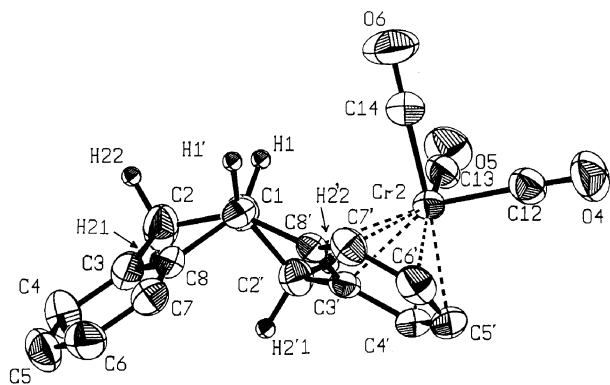


Fig. 4 Projection of the molecule of **B1** as viewed along the C(1)–C(1') bond

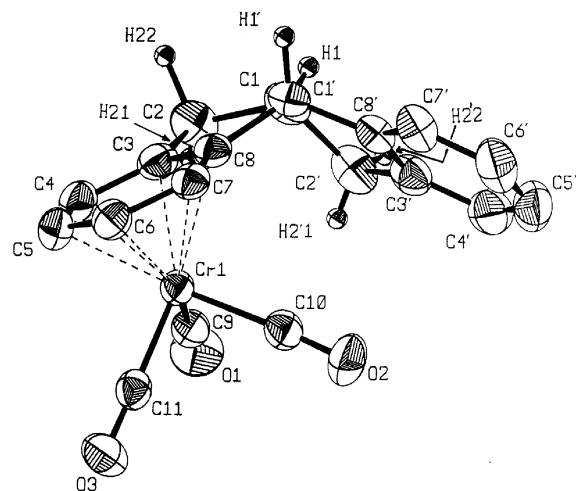


Fig. 5 Projection of the molecule of **B2** as viewed along the C(1)–C(1') bond

belongs to the protons on the uncomplexed ring, while the higher-field set belongs to the protons on the complexed ring. The resonances due to the methylene protons also appear as two well-defined sets and the assignments were accomplished by NOE measurements. The number of resonances in the $\{^1\text{H}\}-^{13}\text{C}$ NMR spectra is consistent with the absence of molecular symmetry due to coordination with the metal carbonyl unit. The metal carbonyl resonance in the *anti* complex **B1** (δ 234.99) appears downfield with respect to that of the *syn* complex **B2** (δ 233.98), as already found for the stereoisomeric $\text{Cr}(\text{CO})_3$ complexes of related centropolyindans.^{2,5,6} It appears that the uncomplexed ring is positioned in such a way that it exerts a slight shielding anisotropy to the *syn* metal carbonyls.

Bis-complexes **B3** and **B4**

The NMR spectrum of the *syn-anti* complex **B3** also reflects the absence of molecular symmetry. In fact, two different ABCD systems were observed in the range δ 6.25–5.45 for the aromatic protons and two AB patterns in the range δ 2.8–3.4 for the methylene protons. Moreover, in the ^{13}C NMR spectrum, all 16 of the ligand carbon atoms have distinct resonances in addition to the two signals for the metal carbonyl resonances that are observed at δ 234.88 and 234.07. Symmetry and steric considerations require that one of the $\text{Cr}(\text{CO})_3$ units is coordinated to the concave side of the ligand and the second to the convex side. This geometry is confirmed by the X-ray structure of **B3** (see below). Conversely, the ^1H NMR spectrum of the *anti,anti* complex **B4** consists of a single ABCD pattern between δ 6.3 and 5.5, and a single AB system the components of which are centred at δ 2.87 and 3.23. The carbon spectrum indicates a symmetrically complexed ligand and resonance for the metal carbonyls at δ 234.54. Steric considerations require that both $\text{Cr}(\text{CO})_3$ units are bound in the *anti* orientation.

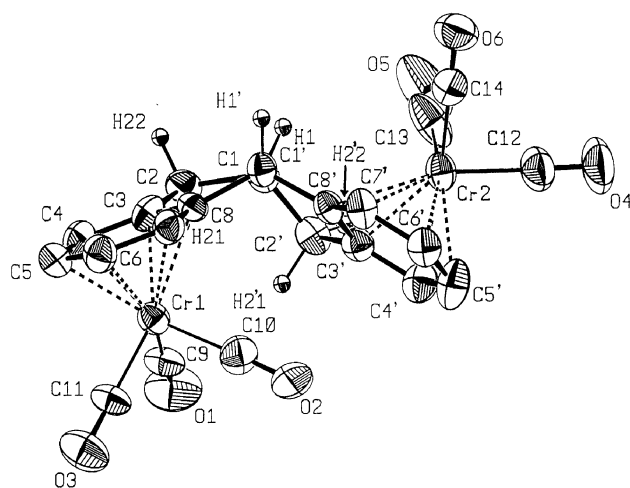


Fig. 6 Projection of the molecule of **B3** as viewed along the C(1)–C(1') bond

X-Ray measurements

Crystals of **B2** and **B3** suitable for X-ray analysis were obtained by isothermal slow evaporation under an inert atmosphere of concentrated solutions in a 1 : 1 : 1 mixture of acetone, methanol and methylene chloride. Crystals of **B1** were grown from methylene chloride–light petroleum by slow evaporation. In the case of **B4**, no suitable crystals have been obtained.

The results of the X-ray analysis for **B1**, **B2** and **B3** are shown in Figs. 4, 5 and 6, respectively. Crystal data and details of the intensity data collection for **B1**, **B2** and **B3** are reported in Table 4. In complexes **B1** and **B2**, the $\text{Cr}(\text{CO})_3$ units are bound to the convex (*anti*) and concave (*syn*) sides of the ligand, respectively. In complex **B3**, the two $\text{Cr}(\text{CO})_3$ units are bound to the concave and convex sides of the ligand. All bond lengths of the complexed benzene groups are longer (1.42 Å on average) than for the uncomplexed rings (1.39 Å); the bond angles $\text{Cr}-\text{C}=\text{O}$ deviate only slightly from 180° , and all $\text{C}-\text{Cr}-\text{C}$ bond angles are within the range $86\text{--}91^\circ$ (Table 5). No significant intermolecular contact distances are observed to affect the molecular structures.

Discussion

The results summarized in Table 1 indicate that the *anti*-complexation with one $\text{Cr}(\text{CO})_3$ on the convex side of the ligand is favoured as compared to the *syn*-complexation on the concave side. An *anti/syn* preference of *ca.* 2 can be estimated from the product ratio **B1/B2** in run 1 in which the lower $\text{Cr}(\text{CO})_6/\text{ligand}$ ratio and the shorter reaction time reduces the likelihood of bismetallation. The observed *anti/syn* ratio parallels the trend observed previously for the isomeric C_2 -diindan² and, even if with a higher *anti/syn* ratio, for a related centropolyindan having a pronounced convex/concave structure, *viz.*, 10-methyltribenzotriquinacene.⁶ Thus, it is reasonably ascribed to steric causes. The relative amounts of the two isomeric bis-complexes **B3** and **B4** produced in run 2 by using a markedly higher $\text{Cr}(\text{CO})_6/\text{ligand}$ ratio and longer reaction times clearly indicate a different reactivity of the two mono-complexes towards the second metallation. This is further supported by the observations of runs 3 and 4 (Table 1) in which **B1** was found to be relatively unreactive while **B2** did undergo substitution. Again, these results parallel earlier results^{2,5,6} in which an *anti*-mono-complex was found to be less reactive towards $\text{Cr}(\text{CO})_6$ than the corresponding *syn*-mono-complex.

Although there are inherent problems in utilizing solid state structures to understand the reactivity in solution, the availability of molecular structures for **B1**, **B2** and **B3** does permit some comparisons to be made. In all cases, all bond lengths and angles are within normal ranges for (arene) $\text{Cr}(\text{CO})_3$ com-

Table 4 Summary of the crystal data and intensity collection for **B1**, **B2** and **B3**

	B1	B2	B3
Formula	C ₁₉ H ₁₄ CrO ₃	C ₁₉ H ₁₄ CrO ₃	C ₂₂ H ₁₄ Cr ₂ O ₆
<i>M</i>	342.3	342.3	478.3
Space group	<i>P2</i> ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.479(3)	11.807(6)	13.263(7)
<i>b</i> /Å	15.570(5)	8.451(5)	10.058(5)
<i>c</i> /Å	10.995(3)	7.906(4)	7.393(4)
α /°	90	77.3(2)	92.5(1)
β /°	99.4	77.2(2)	99.7(1)
γ /°	90	85.0(1)	93.7(1)
<i>V</i> /Å ³	1601.0	750.1	968.6
<i>Z</i>	4	2	2
Cryst. dimensions/mm	0.31 × 0.31 × 0.33	0.30 × 0.30 × 0.25	0.25 × 0.30 × 0.30
<i>D</i> _c /g cm ⁻³	1.42	1.52	1.64
μ /cm ⁻¹	7.6	7.16	14.61
<i>T</i> /K	297	298	298
Radiation (λ /Å)	Graphite-monochromated Mo-K α (λ = 0.7107)		
Take off angle/°	4	3	3
Scan speed/° min ⁻¹		2.0 in the 2 θ mode	
2 θ range/°	4.0 ≤ 2 θ ≤ 50	3.0 ≤ 2 θ ≤ 45	3.0 ≤ 2 θ ≤ 45
Unique reflections [<i>F</i> _o ² = 2 σ (<i>F</i> _o ²)]	1914	3625	3002
<i>R</i> (on <i>F</i> _o)	0.043	0.066	0.033

pounds. In **B2** and **B3** the *syn* Cr(CO)₃ group occupies a 'pocket' formed by two arene rings. As has been observed for similar compounds, the oxygen atom of one of the carbonyl groups of **B2**, C10–O2 (see Fig. 5), is positioned near the central normal of the second benzene ring at a distance of ca. 3.15 Å. The prevalence of this conformation within the whole class of centrodi- and centrotri-indan Cr(CO)₃ complexes suggests that there is a weak stabilizing interaction between the carbonyl and the adjacent aromatic electron cloud.^{2,5,6} Another short distance, also found for this class of compounds^{2,5,6} and believed to stabilize the structure, was observed between H2'1 and the middle point of the carbonyl C9–O1 (ca. 2.90 Å in **B2** and 2.80 Å in **B3**). These two weak interactions may be responsible for the deviation of the *syn*-Cr(CO)₃ tripod from an ideal staggered exo-conformation by ca. 5–7° as well as of its slippage by ca. 0.04–0.06 Å towards C4, C5 and C6.

Perhaps the most significant differences between the structures of the mono-complexed species are related to the twisting about the central C1–C1' bond as measured by the torsional angle H1–C1–C1'–H1'. This angle is 25.9° for **B1** and 27.5° for **B2** (and ca. 18° in the free ligand).⁴ As anticipated in the Introduction, the immediate cause for this twisting is the mutual repulsion of the two methine protons H1 and H1', and the *syn* methylene hydrogens H21 and H2'1. In the *anti*-mono-complex **B1** the H2'2 and H1' hydrogens are in a more 'equatorial' position relative to the complexed arene ring so relieving their repulsive interactions with H1 and the carbonyls. Moreover, the repulsive nonbonding interactions between the methylene *syn* hydrogens H21 and H2'1 are also strongly decreased. On the other hand, H1 results in a more 'axial' position, and this fact is expected to influence the conformation of the Cr(CO)₃ group. Actually, the orientation of the inorganic tripod Cr(CO)₃ in **B1** significantly deviates from the most common *exo* staggered conformation (10–11°) toward an eclipsed arrangement and the *anti* Cr(CO)₃ group in **B3** is almost in the eclipsed conformation (see Table 5). As a consequence of the twisting about the C1–C1' bond, both the H22 (*anti*) and the H1' protons are orientated axial to the non-complexed arene ring and strongly hinder complexation of an incoming chromium group to the free *anti* face (cf. preparative run 3). In contrast, the steric arrangement of the ligand as stabilized by the *anti* complexation does not appear to exclude the coordination of a second chromium group to the *syn* side of the second arene ring. This is in agreement with the results of the preparative run 4, even though a long reaction time is required to obtain a significant yield of **B3**.

The molecular structure of **B2** reveals that in the *syn* complex the H21 methylene hydrogen and the C1'–C8' bond are in a more equatorial position relative to the complexed ring, while H1' and H2'2 are still in the equatorial position relative to the *anti* face of the noncomplexed arene ring. As a consequence, the free *anti* side is sterically accessible for chromium complexation. Hence formation of the *syn,anti* bis-Cr(CO)₃ complex **B3** from **B2** should be sterically allowed as evidenced by the preparative run 4 (Table 1).

The molecular structure of the bis-complex **B3** confirms the structural arguments developed above as the environments of each of the two Cr(CO)₃ groups are very close to those observed for the corresponding Cr(CO)₃ groups in **B1** and **B2**. In fact, it might be argued that the *syn,anti* complexation in these compounds is synergistic, leading to **B3** as the favoured product. The torsion about the C1–C1' bond of **B3** is 23.1°. As in the mono complexes, the repulsive nonbonding interaction between the *syn* hydrogens H21 and H2'1 of the methylene groups is mostly relieved and the atoms are actually at ca. 2.33 Å from each other. The *anti* Cr(CO)₃ tripod is rotated from an idealized eclipsed conformation only by 5–6°, whereas the *syn* Cr(CO)₃ group deviates by only 4–5° from the staggered *exo* conformation. Short distances are observed between H1 and H2'1 and the middle point of the carbonyls C13–O5 (2.83 Å) and C9–O1 (2.80 Å), respectively. The oxygen atom O2 lies very close to the central normal to the plane of the adjacent *anti*-coordinated adjacent benzene ring at a distance of 3.10–3.15 Å which is significantly shorter than that observed for **B2** (3.30 Å), as expected. Again, this is in agreement with the behaviour of related bis- and tris-Cr(CO)₃ complexes of *centro*-polyindans in which the interaction takes place between a carbonyl of a *syn*-Cr(CO)₃ group and an *anti*-Cr(CO)₃-complexed benzene ring.^{4–6}

Experimental

General

All the reactions and complex manipulations were performed in an oxygen-free argon atmosphere. The solvents were carefully dried and deoxygenated before use. Cr(CO)₆ was sublimed twice under reduced pressure just before use. Solvent mixtures, reaction times and complexing agent/substrate ratios are given in Table 1. The percentages of complexation products were determined by integration of the corresponding signals in the ¹H NMR spectra of the crude reaction mixtures. In the preparative experiments, the pure products were obtained by flash

Table 5 Selected geometrical parameters for **B1**, **B2** and **B3**

	B1	B2	B3
Bond distances/Å			
Cr1–C3		2.240(5)	2.226(9)
Cr1–C4		2.219(3)	2.213(9)
Cr1–C5		2.205(5)	2.204(9)
Cr1–C6		2.218(4)	2.211(9)
Cr1–C7		2.240(4)	2.215(9)
Cr1–C8		2.270(3)	2.247(8)
Cr1–C9		1.834(4)	1.841(9)
Cr1–C10		1.857(4)	1.825(9)
Cr1–C11		1.829(4)	1.843(9)
O1–C9		1.155(4)	1.15(1)
O2–C10		1.138(4)	1.16(1)
O3–C11		1.161(4)	1.15(1)
Cr2–C3'	2.225(3)		2.239(8)
Cr2–C4'	2.226(4)		2.254(9)
Cr2–C5'	2.220(4)		2.210(9)
Cr2–C6'	2.217(4)		2.227(9)
Cr2–C7'	2.227(4)		2.230(8)
Cr2–C8'	2.242(4)		2.233(8)
Cr2–C12	1.846(4)		1.84(1)
Cr2–C13	1.839(4)		1.830(9)
Cr2–C14	1.838(4)		1.832(9)
O4–C12	1.162(6)		1.15(1)
O5–C13	1.156(5)		1.16(2)
O6–C14	1.152(5)		1.17(1)
M(1)–H21' ^a	>3.0	2.90	2.80
M(5)–H1' ^a	2.94		2.83
Bond angles/°			
C9–Cr1–C10		88.6(4)	88.8(5)
C9–Cr1–C11		90.0(2)	88.7(4)
C10–Cr1–C11		87.4(3)	88.2(4)
Cr1–C9–O1		177.2(4)	178.2(9)
Cr1–C10–O2		176.8(3)	177.5(8)
Cr1–C11–O3		178.5(5)	180.0(9)
C12–Cr2–C13	91.3(2)		88.6(6)
C12–Cr2–C14	89.9(2)		87.4(5)
C13–Cr2–C14	85.5(2)		87.1(5)
Cr2–C12–O4	177.8(4)		179.0(9)
Cr2–C13–O5	177.1(4)		179.0(9)
Cr2–C14–O6	177.5(4)		178.0(9)
Torsion angles/° ^b			
C3–P(1)–Cr1–C9		–23.4	–33.2
C5–P(1)–Cr1–C11		–24.0	–35.0
C7–P(1)–Cr1–C10		–24.2	–34.8
C3'–P(2)–Cr2–C13	–19.2		5.7
C5'–P(2)–Cr2–C12	–21.0		7.3
C7'–P(2)–Cr2–C14	–20.7		5.6
H1–C1–C1'–H1'	25.9	27.5	23.1

^a M(*n*) represents the middle point of the carbonyl group C=O(*n*). ^b P(*n*) represents the centre of the phenyl ring bonded to Cr(*n*).

chromatography of the residue on silica (diethyl ether–pentane mixtures as eluent) after removal of the solvents. All the complexes appear as yellow, air-stable microcrystalline powders. Melting points are uncorrected. The microanalyses were performed by Mr L. Turiaco, Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova and the data obtained were in agreement within 0.3% with those calculated for both C and H. The IR spectra were recorded as tetrahydrofuran (THF) solutions with a Perkin-Elmer 580B spectrophotometer and the 70 eV electron impact mass spectra were measured with a VG 16 MicroMass spectrometer.

Complex anti-Cr(CO)₃-4b,9,9a,10-tetrahydroindeno[1,2-*a*]-indene, B1. Mp = 138–140 °C (decomp.) (Found: C, 66.6; H, 4.3. C₁₉H₁₄CrO₃ requires: C, 66.7; H, 4.1%); $\nu_{\max}/\text{cm}^{-1}$ 1961vs and 1885vs (C=O); m/z 342 (M⁺, 13.6), 286 (M⁺ – 2 CO, 18.4), 258 (M⁺ – 3 CO, 100), 206 [M⁺ – (Cr, 3 CO), 4.1] and 52 (Cr⁺, 85.0%).

Complex syn-Cr(CO)₃-4b,9,9a,10-tetrahydroindeno[1,2-*a*]-indene, B2. Mp = 181–183 °C (decomp.) (Found: C, 66.5; H, 4.4. C₁₉H₁₄CrO₃ requires: C, 66.7; H, 4.1%); $\nu_{\max}/\text{cm}^{-1}$ 1964vs, 1893vs and 1885vs (C=O); m/z 342 (M⁺, 8.4), 286 (M⁺ – 2 CO, 8.3), 258 (M⁺ – 3 CO, 100), 206 [M⁺ – (Cr, 3 CO), 5.5] and 52 (Cr⁺, 76.7%).

Complex syn,anti-[Cr(CO)₃]₂-4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene, B3. Mp = 188–190 °C (decomp.) (Found: C, 55.1; H, 3.1. C₂₂H₁₄Cr₂O₆ requires: C, 55.2; H, 3.0%); $\nu_{\max}/\text{cm}^{-1}$ 1962vs and 1888vs (C=O); m/z 478 (M⁺, 21.1), 422 (M⁺ – 2 CO, 3.4), 394 (M⁺ – 3 CO, 15.3), 366 (M⁺ – 4 CO, 23.1), 342 [M⁺ – (Cr, 3 CO), 2.4], 338 (M⁺ – 5 CO, 42.2), 310 (M⁺ – 6 CO, 25.9), 286 [M⁺ – (Cr, 5 CO), 2.7], 258 [M⁺ – (Cr, 6 CO), 100], 206 [M⁺ – (2Cr, 6 CO), 5.8] and 52 (Cr⁺, 91.8%).

Complex anti,anti-[Cr(CO)₃]₂-4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene, B4. Mp = 178–180 °C (decomp.) (Found: C, 55.0; H, 3.2. C₂₂H₁₄Cr₂O₆ requires: C, 55.2; H, 3.0%); $\nu_{\max}/\text{cm}^{-1}$ 1970vs, 1959vs, 1890vs and 1888sh (C=O); m/z 478 (M⁺, 23.1), 422 (M⁺ – 2 CO, 3.4), 394 (M⁺ – 3 CO, 30.6), 366 (M⁺ – 4 CO, 12.9), 342 [M⁺ – (Cr, 3 CO), 2.7], 338 (M⁺ – 5 CO, 50.3), 310 (M⁺ – 6 CO, 26.5), 286 [M⁺ – (Cr, 5 CO), 4.8], 258 [M⁺ – (Cr, 6 CO), 97.3], 206 [M⁺ – (2Cr, 6 CO), 4.8] and 52 (Cr⁺, 100%).

Collection of NMR data

Appropriate 20–40 mmol dm^{–3} solutions for both ¹H and ¹³C NMR spectroscopic measurements were obtained by using carefully dried, oxygen-free [²H₆]acetone. The proton spectra were recorded on a Bruker AM-400 spectrometer operating at 400.133 MHz; the ¹H chemical shift values, taken against internal SiMe₄, are given in Table 2. The proton-decoupled 100.614 MHz ¹³C NMR spectra were obtained with the same solutions by using a 6 s delayed Waltz-like CPD decoupling technique with full recovery of the Overhauser line enhancement to get satisfactory signal-to-noise ratios after 256–512 accumulations on a 64 K word size. Two-dimensional NMR spectra were processed on a Bruker X-32 workstation. Hetero-correlated spectra were obtained with the pulse sequence of Bodenhausen and Ruben⁷ modified with a spin-lock purge pulse by Otting and Wütrich.⁸ Quadrature detection along ω_1 was achieved using the TPPI method.^{9,10} Typically, data matrices of 128 FIDs by 2 K complex points were collected, for total acquisition times of 12–14 h. Spin-lock pulses of 2 ms were employed. Before transformation, the data points were multiplied by shifted sine or sine squared window functions and zero filled to 1 K × 1 K real points. The ¹³C chemical shifts are listed in Table 3.

Collection of X-ray diffraction data

X-Ray-quality crystals of **B1** were obtained by slow evaporation from methylene chloride solutions, while **B2** and **B3** were grown from saturated solutions in an 1:1:1 mixture of acetone, methanol and methylene chloride. Single crystals of **B1** were mounted on a Nicolet R3 diffractometer, whereas a Philips PW-100 computer-controlled four-circle diffractometer with graphite monochromator was used for **B2** and **B3**. Standard centring and autoindexing procedures indicated a monoclinic lattice for **B1** and triclinic lattices for both **B2** and **B3**. The space group *P* $\bar{1}$ was initially assigned to **B2** and **B3** and later confirmed by a well-behaved refinement process; in the case of **B1**, the *P*2₁/*n* space group was uniquely determined by systematic absences in the diffraction data. The orientation matrix and accurate unit cell dimensions were determined from angular settings of 25 high-angle reflections. The intensities were corrected for Lorentz and polarization effects and for absorption by empirical methods (ψ -scan). Crystallographic data are collected in Table 4. In all cases, the structures were solved from Patterson syntheses and completed from difference maps. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were treated as idealized con-

tributions. Blocked-cascade least-square refinements were used. They converged to the conventional *R* indexes reported in Table 4. A unitary weighting scheme was used. Scattering factors for the atoms were taken from Cromer and Waber;¹¹ the scattering factors for Cr were corrected for the real and the imaginary parts of anomalous dispersion using Cromer's values.¹² All computations were carried out on a Cyber 76 computer using the SHELX-76 program.¹³ Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/56.

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