

One-step Difunctionalization of [2.2]Metacyclophane via its Bis(tricarbonylchromium) Complex

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The preparation of 5,13-bisethoxycarbonyl-*anti,anti*-(μ -[2.2]metacyclophane)bis(tricarbonylchromium) (**5**) in a one-step reaction from ([2.2]metacyclophane)bis(tricarbonylchromium) **3** is reported for the first time. Its structure is evaluated on the basis of the ¹³C NMR spectrum and compared with other tricarbonylchromium complexes (**2**, **7**). The crystal structure of **5** has been determined. Crystal data: C₂₈H₂₄Cr₂O₁₀, *M*_r = 624.5; orange blocks; triclinic, space group *P* $\bar{1}$; *a* = 769.0(1), *b* = 957.4(1), *c* = 1068.7(1) pm; α = 98.76(1), β = 99.68(1), γ = 102.37(1)°; *V* = 743.0(3) Å³; *Z* = 1; *D*_c = 1.396 g cm⁻³; crystal dimensions, 0.15 × 0.15 × 0.25 mm³.

Complexation of arenes with the tricarbonylchromium group is a valuable contribution to arene chemistry.¹ [2.2]Metacyclophanes are favourable 'ligands', because the 'umpolung' of reactivity of the complexed benzene ring can be used for the synthesis of substitutedphanes, which otherwise are more difficult to prepare.^{2,3} Recently de Meijere investigated the polyolithiation of mono-Cr(CO)₃ complexes in the paracyclophane series.⁴ He found, that bislithiation can occur at the complexed benzene ring and the neighbouring bridge atom in one step, by use of a manifold excess of *n*-BuLi and prolonged reaction times.

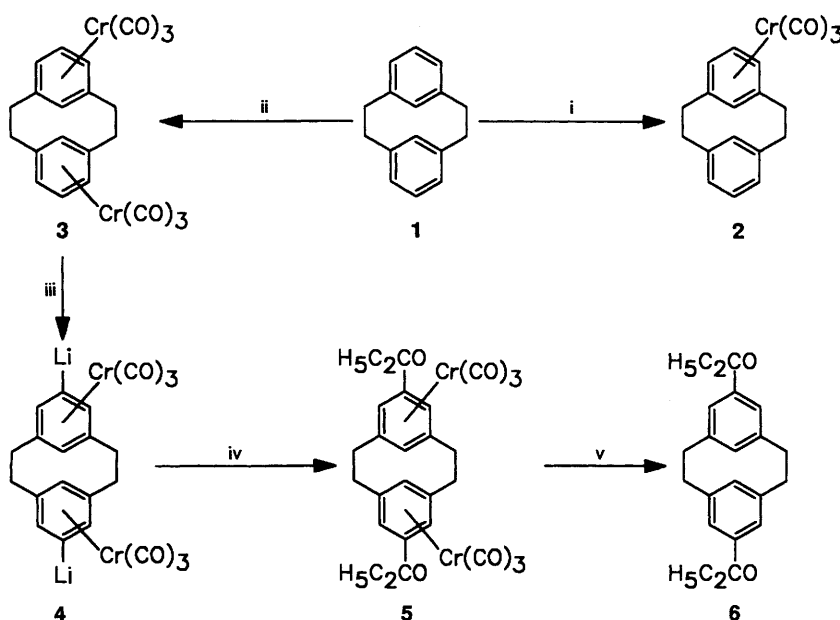
Results and Discussion

Synthesis.—Complexation of both benzene rings of [2.2]-metacyclophane (**1**) is achieved when two equivalents of Cr(CO)₃(NH₃)₃ are used, as we found recently.³ The bis-complex **3** is easily separated from starting material **1** and from the mono-complex **2** because of its insolubility in most organic solvents.

Reaction of **3** with six equivalents of *n*-BuLi/TMEDA at -78 °C readily yields the bis(aryllithium)Cr(CO)₃ complex **4**. Formation of **4** is indicated by a change in the colour of the THF solution from yellow to deep green-blue; the corresponding solution of the mono(aryllithium)Cr(CO)₃-complex is red-brown.^{2,3} Quenching of the lithium salt **4** with ethyl chloroformate at -78 °C occurs immediately and yields an orange solution, containing the 5,13-disubstituted bis-complex **5** as the main product. None of the proposed by-products (4,12-di-, 4,14-di- and 5,12-disubstitution) could be isolated in pure form owing to closely similar chromatographic properties. The regioselectivity observed here is low because of the absence of bulky groups in the ethano bridges, which act as the directing factors in the functionalization of bridge-substituted [2.2]-metacyclophane-chromium complexes, as we pointed out recently.^{2,3}

Decomplexation of **5** is achieved simply by exposure of a THF solution to air and sunlight for one day (Scheme 1).

X-Ray Analysis.—Single crystals of **5** were prepared. The



Scheme 1 One-step difunctionalization of [2.2]metacyclophane **1** via its bis(tricarbonylchromium) complex **3**. Reagents: i, Cr(CO)₃(NH₃)₃ (1 equiv.) [yield 65%]; ii, Cr(CO)₃(NH₃)₃ (2 equiv.) [yield 33% **3** + 32% **2**]; iii, BuⁿLi-TMEDA, THF, -78 °C; iv, ClCO₂C₂H₅, THF, -78 °C [yield 19%]; v, hv, THF, 1 day [yield 92%].

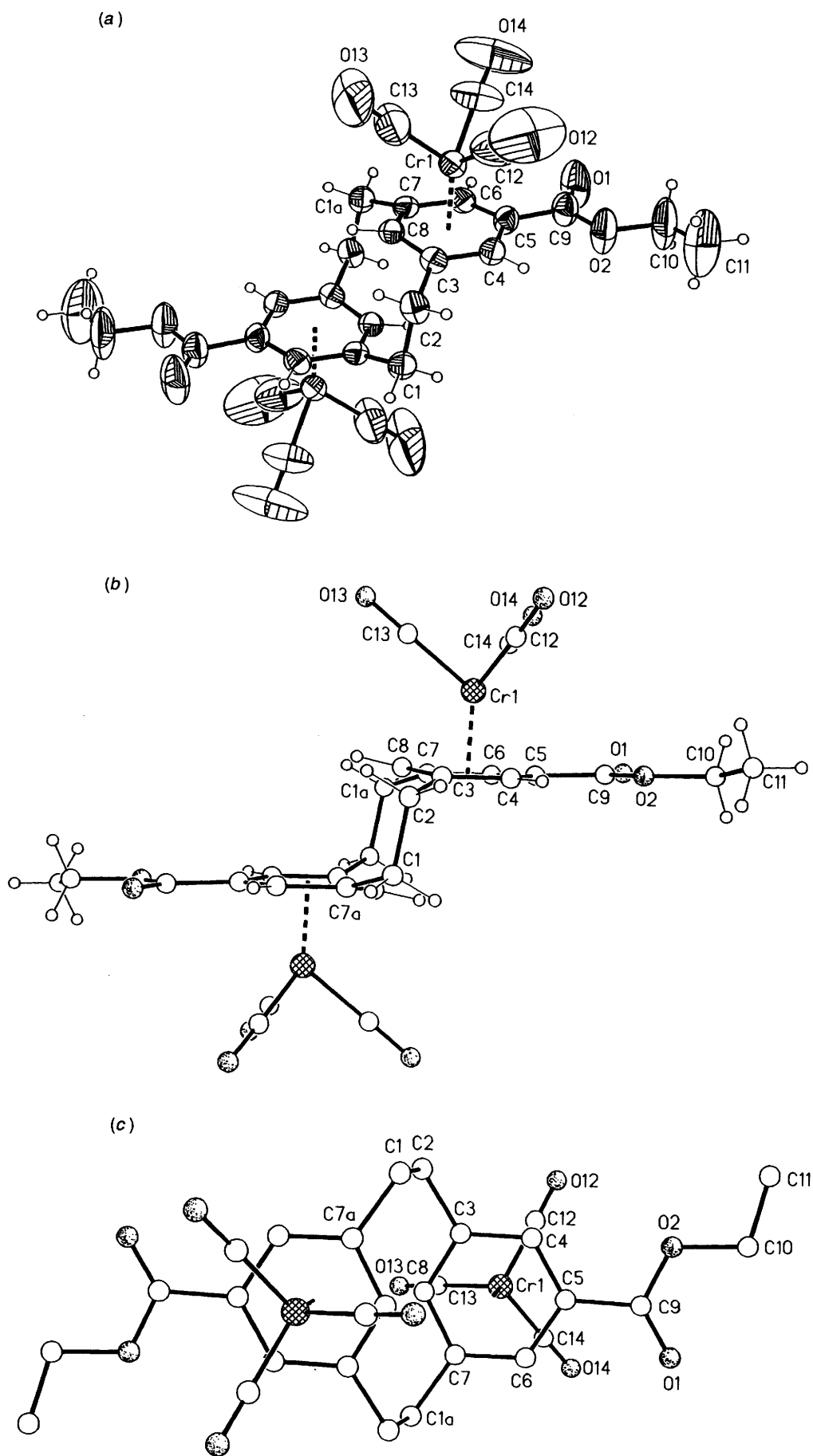


Fig. 1 X-Ray structure of compound 5: (a) and (b) side view; (c) top view

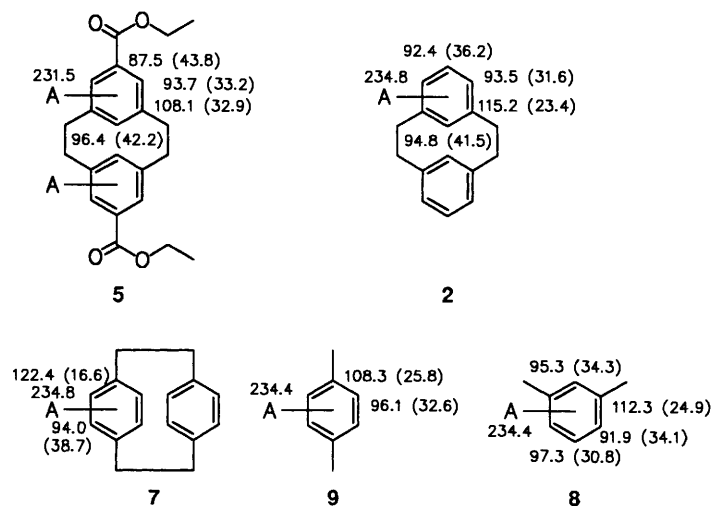


Fig. 2 ^{13}C NMR data for complexes and complexation shifts $\Delta\delta$ (in parentheses)

Table 1 Correlation between absorption of ligand carbons in the ^{13}C NMR spectrum and bending angle $^{\theta}$ (θ/deg) and distance to the chromium atom (d/pm); complexation shift: $\Delta\delta = -[\delta(\text{complex}) - \delta(\text{ligand})]$; complexation shift difference from the indicated reference: $\Delta\Delta\delta = \Delta\delta(\text{complex}) - \Delta\delta(\text{reference})$.^a ^{13}C NMR data for complex 7.⁸

Complex	C-atom	$\Delta\delta$	$\Delta\Delta\delta$	θ	d
2^a	C-8	+41.5	+7.2	10.2	217.3(3)
	C-5	+36.2	+5.4	3.5	221.8(4)
	C-3/C-7	+23.4	-1.5	0.0	228.3(3)/ 228.3(3)
	C-4/C-6	+31.6	-2.5	0.0	224.9(3)/ 224.9(3)
5^a	C-8	+42.2	+7.9	+12.0	215.4(4)
	C-5	+43.8	+13.0	+3.1	217.8(4)
	C-3/C-7	+32.9	+8.0	0.0	226.6(3)/ 227.2(4)
	C-4/C-6	+33.2	-0.9	0.0	221.6(3)/ 222.4(4)
7^b	C-3/C-6	+16.6	-9.2	-12.2	234.2
	C-4, -5, -7, -8	+38.7	+6.1	0.0	221.1

^a From *m*-xylene. ^b From *p*-xylene.

X-ray analysis documents the typical stepwise conformation of the [2.2]metacyclophane skeleton with the two tricarbonylchromium groups complexing regioselectively the outer plane of each benzene ring [Fig. 1(a)–(c)]. Compound **5** possesses an inversion centre with the coplanar benzene rings being bent into shallow boat forms; the concave sides are complexed by the $\text{Cr}(\text{CO})_3$ groups.

The tricarbonylchromium groups in **5** show the expected staggered conformation with respect to the corresponding ester function [Fig. 1(c)].^{2,3}

The intraannular distance in the complex **5** (260 pm) is almost the same as in other [2.2]metacyclophanes.^{2,3} The distance of chromium to the planes of the distorted benzene rings, defined by C-3, C-4, C-6 and C-7,^{2,3} is slightly longer (174.8 pm) than that in benzene(tricarbonyl)chromium, where it amounts to 170 pm.⁵

^{13}C NMR Properties.—An interesting feature in the chemistry of tricarbonylchromium–arene complexes is the change in diamagnetic ring current of the complexed arene ring, causing a considerable highfield shift of ligand carbons and protons in the NMR spectra.⁶ While the effect of ring-current disruption in ^1H NMR spectroscopy has been extensively studied for transition-metal complexes of cyclophanes,^{6,7} Mori

recently showed a relationship between ^{13}C shifts and transition metal to ring-carbon distances.⁸

Qualitative examinations, owing to unknown structures of most of the complexes, support the assumption, that the complexation shift ($\Delta\delta$; Table 1) is dependent on the orbital interaction between the chromium atom and the ligand carbon. Extensive investigations in the [2.2]metacyclophane series revealed that complexation with tricarbonylchromium causes no substantial change in the distortion of the boat-like benzene rings;^{2,3} the same is observed in a ruthenium complex,⁹ and an iron complex¹⁰ shows a slightly different position of C-5, compared with that in the iron-free ligand. This is not the case for [2.2]paracyclophanes, as in this series some amount of π -compression of the hydrocarbon framework in the corresponding $\text{Cr}(\text{CO})_3$ complexes has been found.¹¹ A recent investigation of interactions between the chromium tricarbonyl complexes of substituted ligands shows, that π -donor substituents and the *ipso*-carbon to which they are attached are bent away from the $\text{Cr}(\text{CO})_3$ group.¹² Bulky substituents also cause distortion of the complexed benzene ring.¹² Hence the assumption of compensation of geometry in different types of cyclophane on complexation with transition metals should be treated with caution.

In Table 1 and Fig. 2 it is seen that C-5 and C-8 in complexes **5** and **2** are shielded more strongly by about 10–15 ppm ($\Delta\delta$ values) than the other ring atoms, in agreement with their shorter distance to the chromium atom. Subtraction of the complexation shift ($\Delta\delta$) of a reference complex indicates a difference in the shielding of that carbon atom on complexation relative to that in the uncomplexed cyclophane ($\Delta\Delta\delta$).^{7,8}

Large complexation shift differences $\Delta\Delta\delta$ indicate that orbital interaction between ligand-carbon and chromium atom are favourable (compared with the parent plane), owing to a short distance and the orbitals being oriented towards each other.⁸ The back-bonding of chromium to the ligand is affected mainly by these two factors and results in an angle-dependent charge density on chromium.¹³

Thus the tertiary carbon atoms C-5 and C-8 in **5** and **2** show positive $\Delta\Delta\delta$ values, while the quaternary carbon atoms C-3 and C-6 in the [2.2]paracyclophane complex **7**, where the chromium atom is bound to the convex side of the benzene ring, show negative $\Delta\Delta\delta$ values.⁸

An interesting difference in $\Delta\Delta\delta$ values appears for the carbon atoms which lie in the plane of the benzene ring, namely the quaternary carbons C_q (C-3 and C-7) and tertiary carbons C_t (C-4 and C-6) in complexes **2** and **5**. Although the C_q –Cr distance is a little longer than the C_t –Cr distance, its $\Delta\Delta\delta$ value

Table 2 Atomic coordinates ($\times 10^4$) of compound 5

	x	y	z
C(1)	-2137(5)	-2286(4)	3464(3)
C(2)	-569(5)	-1718(4)	2776(3)
C(3)	105(4)	-83(3)	3216(3)
C(4)	-634(4)	883(4)	2564(3)
C(5)	-310(5)	2365(4)	3133(3)
C(6)	696(5)	2853(3)	4417(3)
C(7)	1452(4)	1923(3)	5094(3)
C(8)	1300(4)	490(3)	4423(3)
C(9)	-1011(6)	3426(4)	2441(4)
O(1)	-768(5)	4683(3)	2912(3)
O(2)	-1938(5)	2809(3)	1255(3)
C(10)	-2727(10)	3750(7)	486(6)
C(11)	-3419(14)	2926(11)	-804(7)
Cr(1)	2333(1)	1875(1)	3166(1)
C(12)	2457(8)	1474(8)	1481(6)
O(12)	2586(9)	1248(9)	428(5)
C(13)	4433(8)	1354(9)	3559(8)
O(13)	5779(8)	1053(12)	3834(10)
C(14)	3655(8)	3718(6)	3266(6)
O(14)	4444(9)	4879(5)	3300(7)

is larger (more positive) than that for C_t . Owing to the extreme out-of-plane distortion of the bridging carbons (C-1, C-2, C-9, C-10), the bridgehead carbons C_q should have a somewhat different hybridization (more sp^3 -like) compared with the tertiary carbons.¹⁴ This should result in a stronger orbital interaction with chromium thus giving larger $\Delta\Delta\delta$ values.

Conclusions

Introduction of two ethoxycarbonyl groups into the bis(tricarbonylchromium) complex of [2.2]metacyclophane in a one-step procedure was achieved. The semiquantitative correlation of the ^{13}C NMR shift with the carbon-to-metal distance underlines the importance of the orientation of the orbitals between chromium and ligand carbons of distorted benzene rings in explaining the highfield shift in the ^{13}C NMR spectra with complexation.⁸

Experimental

General Methods and Materials.—M.p.s were determined with a Kofler-Mikroskop-Heiztisch apparatus. 1H and ^{13}C NMR experiments were carried out with a Bruker WM-250 (250 MHz) apparatus. Mass spectrometry was carried out with a FAB-MS apparatus (Concept 1 H, Kratos, Manchester, GB) and a HPLC-MS apparatus (column: Lichrosorb Si₆₀₋₅ μ_m ; 125 \times 3 mm) connected to an HP 5989 A mass spectrometer (Hewlett-Packard, Palo Alto, USA). For thin layer chromatography silica gel [63–100 μ_m (Merck)] was used. Purification of argon was achieved with Oxisorb (Krämer & Martin).

anti,anti- $\{\mu$ -(5,13-Bisethoxycarbonyl[2.2]metacyclophane)}-bis(tricarbonylchromium) 5.—The reaction and work-up was carried out in the dark and argon was further purified with Oxisorb. Compound 3 (96 mg, 0.2 mmol) was placed in a three-necked round-bottomed flask under an inert gas atmosphere and dissolved in THF (10 cm³). The solution was cooled to $-78^\circ C$ and N,N,N',N' -tetramethylethylenediamine (TMEDA) (0.18 cm³, 1.2 mmol) and BuⁿLi (0.76 cm³, 1.2 mmol) were added. After 3 h, the deep blue-green solution was treated with ethyl chloroformate (0.16 ml, 1.2 mmol). Evaporation of solvents and chromatographic work-up yielded 24 mg (19%) of 5; orange crystals, $R_f = 0.08$ (CH₂Cl₂-cyclohexane 2:1; m.p. 216–218 $^\circ C$ (decomp.); m/z (FAB)-MS: 624 (M^+ , 30%), 540 (624 – 3CO, 50), 512 (624 – 4CO, 30), 484 (624 – 5CO, 70),

456 (624 – 6CO, 50), 404 (624 – 6CO and –1Cr, 100) and 352 (624 – 6CO and –2Cr, 3); δ_H (250 MHz; CDCl₃) 1.42 (s, 3 H, CH₃), 2.21 (d, 4 H, H_{ax}), 3.02 (d, 4 H, H_{eq}), 3.8 (s, 2 H, 8-, 16-H), 4.42 (q, 4 H, OCH₂) and 6.02 (s, 4 H, Ar-H); δ_C (250 MHz) 14.4 (2 CH₃), 37.8 (2 C₂H₄), 62.3 (2 OCH₂), 87.5 (C-5, -13), 93.7 (C-4, -6, -12, -14), 96.4 (C-8, -16), 108.1 (C-3, -7, -11, -15), 165.6 (ester CO) and 231.5 [Cr(CO)₃].

5,13-Bisethoxycarbonyl[2.2]metacyclophane 6.—Compound 5 (20 mg, 0.032 mmol) was dissolved in THF (20 cm³) and exposed to sunlight for 1 day. Recrystallisation gave 10 mg (92%) of 6; colourless crystals; m.p. 178–180 $^\circ C$ (methanol); m/z (70 eV) 352 (M^+ , 50%); δ_H (250 MHz; CDCl₃) 1.4 (s, 6 H, CH₃), 2.19 (d, 4 H, H_{ax}), 3.2 (d, 4 H, H_{eq}), 4.4 (q, 4 H, OCH₂), 4.42 (s, 2 H, 8-, 16-H) and 7.78 (d, 4 H, Ar-H); δ_C (250 MHz) 14.4 (2 CH₃), 40.5 (2 C₂H₄), 61.0 (2 OCH₂), 126.9 (C-4, -6, -12, -14), 131.3 (C-5, -13), 138.6 (C-8, -16), 141.0 (C-3, -7, -11, -15) and 167 (ester CO).

Crystal-structure Determination.—**Sample preparation.** Orange crystals, suitable for X-ray diffraction, were obtained by diffusion of methanol into a chloroform solution of 5.

Data collection and processing. Enraf-Nonius CAD4 diffractometer; ω/θ -scans, scan range (1.00 + 0.35 $\tan\theta$) $^\circ$, $2\theta_{max} = 50^\circ$ ($h: -9 \rightarrow 9, k: -11 \rightarrow 11, l: 0 \rightarrow 12$); 2782 measured reflections, 2628 unique ($R_{int} = 0.008$); 2006 observed reflections [$F > 4\sigma(F)$]; 181 refined parameters; $R = 0.047$ [$R_w = 0.048, w^{-1} = \sigma^2(F) + 0.0008F^2$]; largest difference peak 0.35 e \AA^{-3} ; Mo-K α ($\lambda = 0.71073 \text{\AA}$); $\mu = 0.784 \text{ mm}^{-1}$; $F(000) = 320$; $T = 298 \text{ K}$.

Structure analysis and refinement. The structure was solved and refined with SHELXTL-Plus¹⁵ by Patterson methods; non-H-atoms were refined anisotropically (full-matrix least-squares); H-atoms were refined using a riding model with fixed isotropic U . The atomic coordinates are given in Table 2.

Supplementary data. Lists of bond angles and bond lengths involving the non-H-atoms, anisotropic thermal parameters, and hydrogen coordinates have been deposited at the Cambridge Crystallographic Data Centre.* Lists of the observed and calculated structure factors may be obtained from the authors (M. N.).

Single crystals of two other chromium complexes, the synthesis of which we have already published, can now be obtained; structural data is available on request from us.

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* For details of the CCDC deposition scheme, see 'Instructions for Authors (1992)', *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1.

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