DALTON
FULL PAPER

Synthesis and structures of chromium tricarbonyl complexes of benzylic halides and benzylic alcohols†

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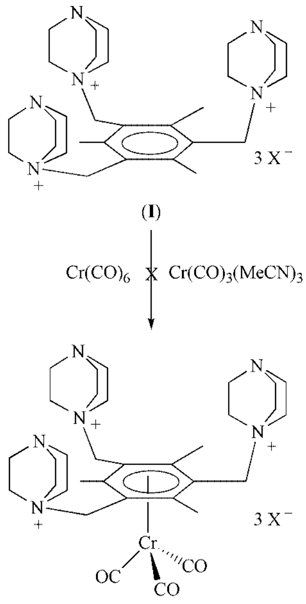
Chromium tricarbonyl complexes of mono-, bis- and tris-(hydroxymethyl) substituted benzene have been prepared *via* direct thermolysis of the alcohol and chromium hexacarbonyl in dibutyl ether–THF. Conversion into the corresponding benzyl halide complexes has been carried out using either PBr_3, HBr (aq), HBr in glacial acetic acid or BX_3 (X = Cl, Br or I). A comparative study showed that PBr_3 and BBr_3 give similar yields and purity and are superior to HBr. Crystallographic studies have been carried out on three benzyl alcohol complexes $[Cr\{\eta^6\text{-}C_6H_4(CH_2OH)_2\text{-}1,4\}(CO)_3]$, $[Cr\{\eta^6\text{-}C_6Me_4(CH_2OH)_2\text{-}1,4\}(CO)_3]$ and $[Cr\{\eta^6\text{-}C_6H_3(CH_2OH)_3\text{-}1,3,5\}(CO)_3]$ and on two benzyl bromide complexes $[Cr(\eta^6\text{-}C_6H_5CH_2Br)(CO)_3]$ and $[Cr\{\eta^6\text{-}C_6H_4(CH_2Br)_2\text{-}1,4\}(CO)_3]$.

Introduction

Arenechromium tricarbonyl complexes are important reagents in organic synthesis, their utility stemming from the change in properties of the arene upon metal co-ordination which also allows face-selective attack, the chromium tricarbonyl unit acting as a steric blocking group. One of the attractions of using these complexes is their easy preparation and since the first synthesis of benzene chromium tricarbonyl in 1958[1] a large number of related complexes have been prepared.[2] Synthesis is generally straightforward and results upon thermolysis of the arene and chromium hexacarbonyl (or the tris-acetonitrile complex) in a high boiling solvent(s). These conditions are tolerant to a wide range of substituents on the arene but work better for electron-donating rather than electron-withdrawing groups.

We have recently been concerned with the development of guest–host interactions between arenes carrying a high positive charge and a range of anions and have prepared a range of positively charged arenes *via* reaction of 1,4-diazabicyclo-[2.2.2]octane (DABCO) and benzyl halides.[3] For example, addition of three equivalents of DABCO to 2,4,6-tris(bromomethyl)mesitylene affords the trication **I**. In order to fix the conformation of the charged substituents such that they were all *syn* and to provide a charge sensitive probe to quantify the strength of the anion–cation interaction, we sought to complex a chromium tricarbonyl unit to the aryl ring. Unfortunately, the direct reaction between **I** and chromium hexacarbonyl or its tris(acetonitrile) derivative failed to yield the target arene-chromium tricarbonyl complex **II**,[4] a result which we attribute to the electron-deficient nature of the arene ring.



(I)

(II)

Taking one step back, we wondered if 2,4,6-tris(bromomethyl)mesitylene itself would co-ordinate to the chromium centre directly. Literature precedent suggests that this is not a feasible synthetic route as chromium(0) is known to reductively couple benzyl halides to produce linear coupling products and, when there is more than one benzyl halide substituent, cyclophanes. For example, Wey and Butenschön[5] have shown that $Cr(CO)_3(NH_3)_3$ reacts with 1,4-bis(chloromethyl)benzene to afford a mixture of reductively coupled products. A recent report by Dyson *et al.* suggests that direct reaction of 1,4-bis(bromomethyl)benzene and chromium hexacarbonyl produces $[Cr\{\eta^6\text{-}C_6H_4(CH_2Br)_2\text{-}1,4\}(CO)_3]$, which in turn is reduced by sodium in 1,4-dioxane to afford μ-([2.2]paracyclophane)-bis(tricarbonylchromium).[6] In our hands, the direct reaction of 1,4-bis(bromomethyl)benzene and chromium hexacarbonyl in 1,4-dioxane produced no evidence for the formation of $[Cr\{\eta^6\text{-}C_6H_4(CH_2Br)_2\text{-}1,4\}(CO)_3]$ **8**, although a mixture of cyclophanes was observed.[4]

The synthesis of arenechromium tricarbonyl complexes of benzyl halides is then not a trivial matter, indeed before we started this work only two examples were reported in the literature. The benzyl iodide complex $[Cr(\eta^6\text{-}C_6H_5CH_2I)(CO)_3]$ has been prepared from the reaction of $Hg[Cr(\eta^6\text{-}C_6H_5CH_2)(CO)_3]_2$ and iodine,[7] while $[Cr(\eta^6\text{-}C_6H_5CH_2Cl)(CO)_3]$[8] results upon addition of HCl to the benzyl alcohol complex $[Cr(\eta^6\text{-}C_6H_5\text{-}CH_2OH)(CO)_3]$ **1**.[9] The latter seemed attractive as benzyl alcohols are easily prepared and are known to react thermally with chromium hexacarbonyl to afford the desired complexes.

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† Supplementary data available: packing diagrams available from BLDSC (SUPP. NO. 57708, 6 pp.). See Instructions for Authors, Issue 1 (http://www.rsc.org/dalton).

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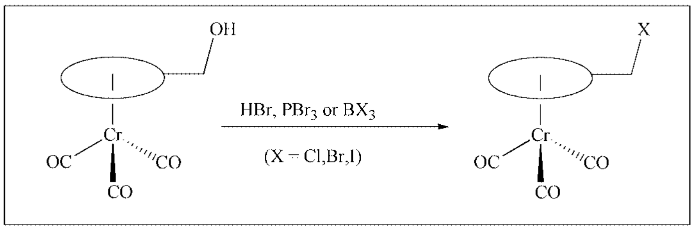

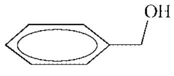

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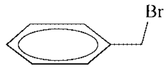

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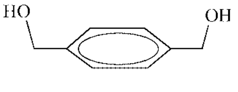

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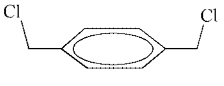

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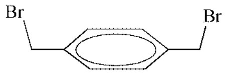

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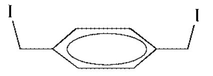

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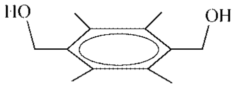

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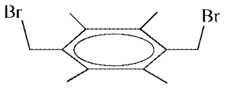

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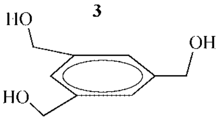

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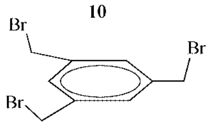

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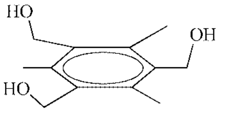

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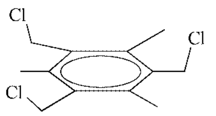

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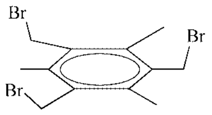

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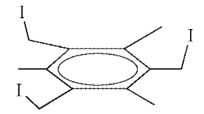

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Further, since we required the halide to be a good leaving group then benzyl bromide complexes were our targets. Herein we describe the synthesis of chromium tricarbonyl complexes of a number of benzyl bromides using either HBr or PBr$_3$ as the brominating agent. While this work was in progress Gibson and Schmid published a communication[10] in which they prepared primarily mono-substituted benzyl halide complexes but also [Cr{η^6-$C_6H_4(CH_2Br)_2$-1,4}$(CO)_3$] from the corresponding benzyl alcohols or ethers using boron trihalides. In order to prepare complexes of benzyl chlorides and iodides we have utilised their procedure and also carried out a comparative study of bromination using PBr$_3$, HBr and BBr$_3$ to determine the reagent of choice in this reaction.

Results and discussion

(i) Synthesis of benzylic alcohol complexes 1–5

While mono- and bis-hydroxymethyl substituted benzenes were commercially available, 1,3,5-tris(hydroxymethyl)benzene[11] and 2,4,6-tris(hydroxymethyl)mesitylene[12] had to be prepared from 1,3,5-benzenetricarboxylic acid[13] and 2,4,6-tris(acetoxymethyl)-mesitylene[12] respectively *via* modified literature procedures. The direct reaction of approximately equimolar amounts of benzylic alcohols and $Cr(CO)_6$ in dibutyl ether–THF (12:1) at 180–240 °C for 20–48 h resulted in the formation of the chromium tricarbonyl complexes **1**–**5** in *ca.* 90% yield. Characterisation was straightforward, the OH protons being observed as well resolved triplets in the ^{1}H NMR spectra. For the synthesis of **1**, Nicholls and Whiting[9] initially co-ordinated the methyl ester and then reduced this with LiAlH$_4$ to yield the co-ordinated benzyl alcohol. We also attempted the synthesis of **4** *via* this route. Co-ordination of trimethyl benzene-1,3,5-tricarboxylate to chromium did not, however, proceed cleanly and even after 48 h a 1:1 mixture of bound and unbound triester was observed. Further, treating this mixture with LiAlH$_4$ at −78 °C afforded a complex mixture by ^{1}H NMR spectroscopy which contained **4** together with partially reduced products. This result shows that the method of choice for the complexation of benzylic alcohol complexes of chromium tricarbonyl is the direct thermal reaction.

(ii) Synthesis of benzylic halide complexes 6–14

Addition of HBr (47%) to complex **1** gave [Cr(η^6-$C_6H_5CH_2Br$)-$(CO)_3$] **6** in 54% yield, however extension of this methodology to bis- and tris-hydroxymethyl benzene complexes was only partially successful. With the bis complex **2** the expected product was contaminated by the free benzyl bromide which we were unable to separate, while for the tris(alcohol) **4** a complex mixture resulted. The attempted use of 45% HBr in glacial acetic acid as a brominating agent also led to the formation of mixtures containing among other things the expected products and the free benzyl bromides even at 0 °C.

Since use of HBr did not provide pure samples of benzylic bromide complexes we decided to utilise the known brominating ability of phosphorus tribromide, which has successfully been used for the conversion of the free benzyl alcohols into the corresponding benzyl bromides.[11] Treatment of ether suspensions of complexes **1**–**5** with PBr$_3$ at 0 °C led to isolation of the desired benzyl bromide complexes in yields of 74–94% after purification. Spectroscopic and analytical data were consistent with the assigned structures, while no trace of unco-ordinated bromoarenes was detected. The conversion is believed to involve initial attack of the nucleophilic alcohol on PBr$_3$ affording a protonated alkyl dibromophosphite intermediate that is a good leaving group. An S$_N$2 step follows whereby HOPBr$_2$ is displaced by bromide.

Benzyl chloride (**7**, **12**) and iodide (**9**, **14**) complexes were also successfully prepared in good yields (81–88%) using BCl$_3$ and BI$_3$ to convert **2** and **5** respectively. We also assessed the relative abilities of PBr$_3$ and BBr$_3$ for the conversion of benzyl alcohol into benzyl bromide complexes (Table 1), and it is clear that there is little to choose between them but both are far better than HBr.

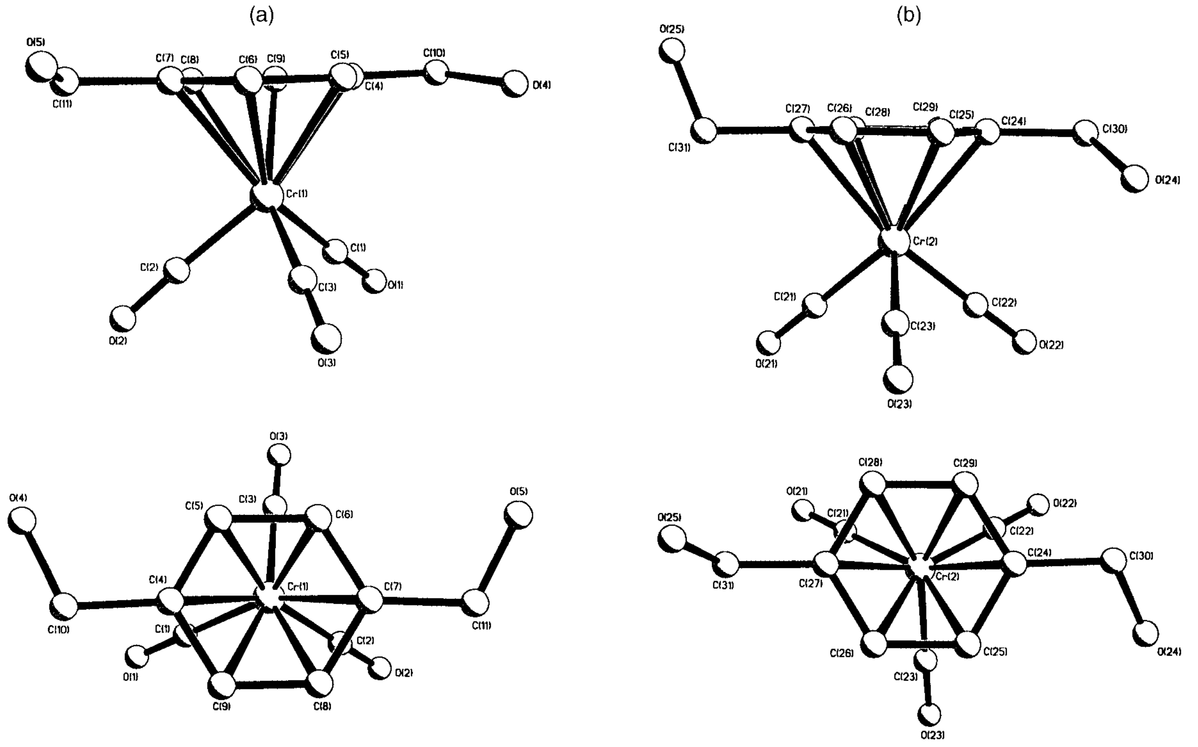


Fig. 1 Molecular structure of complex **2**: (a) molecule A, (b) molecule B.

Table 1 Yields (%) of benzyl bromide complexes as a function of brominating agent

Product	PBr_3	BBr_3	HBr(aq)
6	92	70	54[a]
8	94	88	64[a]
11	76	76	—[b]
13	91	86	20[c]

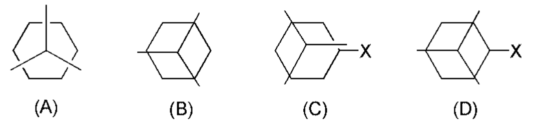
[a] Contains some free arene as shown by ^{1}H NMR. [b] Product formed in low yield as a complex mixture. [c] Formed as an inseparable 2 : 1 mixture of free and co-ordinated arene using HBr (acetic acid).

(iii) Crystal structures of benzyl alcohol and bromide complexes

Given the paucity of crystallographic data for both benzylic alcohol and benzylic bromide complexes of chromium tricarbonyl we have determined the structures of **2**–**4**, **6** and **8**, the results of which are summarised in Fig. 1–5 and Table 2. All complexes adopt the expected piano-stool structure, with the $Cr(CO)_3$ unit bound approximately symmetrically to the approximately planar arene ring. Two key points will be addressed concerning the intramolecular structures, namely the relative positions of the benzyl substituents to the arene plane and the $Cr(CO)_3$ unit and the relative positioning of arene substituents and carbonyl groups (eclipsed or staggered).

As can be seen from Table 2, the methylene carbon lies approximately in the plane of the arene (largest deviation is 0.22 Å) and can be oriented towards (−ve) or away from (+ve) the $Cr(CO)_3$ group. Hunter *et al.* have previously concluded[14] that π-donor substituents tend to bend away from the $Cr(CO)_3$ unit, while conversely π-acceptor groups bend towards it (but to a lesser extent). For the benzyl alcohols the methylene carbon can be orientated either towards or away from the $Cr(CO)_3$ unit suggesting that this moiety is neither strongly π-donating nor-withdrawing. This is exemplified by complex **2** for which there are two independent molecules in the asymmetric unit (Fig. 1). In molecule A the methylene carbons both point away from the $Cr(CO)_3$, while in molecule B they point towards it. In both benzyl bromide complexes the methylene carbon lies towards the metal centre indicating the electron-withdrawing nature of these substituents. The two independent molecules of **2** are further distinguished by the relative orientations of the OH groups. While both have a one up–one down configuration, deviations from the plane are much greater in molecule B (−0.636, 1.199 Å) than in A (−0.164, 0.259 Å). However, the major difference between the two molecules is seen in the orientations of the OH groups with respect to one another, molecule A being best described as *syn* and B as *anti* (Fig. 1b). In contrast, while the tetramethyl derivative **3** also shows two independent molecules in the asymmetric unit (Fig. 2), differences between them are subtle, for both the methylene carbons lie towards the metal and the OH groups away from it. In **4** (Fig. 3), the crystallographically imposed threefold symmetry renders the three benzyl alcohol units equivalent, the methylene carbon pointing away from the metal (0.067 Å) and the OH group towards it, albeit only slightly (−0.251 Å). For both benzyl bromide complexes (Fig. 4, 5) the large bromine atoms are orientated well away from the metal centre (**6**, 1.748; **8**, 1.817 and 1.836 Å).

The conformation of the chromium tricarbonyl tripod relative to the ring carbon atoms and substituents has previously been shown to be dependent upon the steric and electronic properties of the substituents, as well as the number on the ring.[15–17] Possible conformations are depicted below. Staggered (A) and eclipsed (B) conformations can be identified, while in the presence of a substituent the latter can be either be *syn* (C) or *anti* (D). A staggered conformation is rare for monosubstituted arenes;[18] electron-donating groups generally favour the *syn*-eclipsed (C) and electron-withdrawing the *anti*-eclipsed (D) conformation. The appropriate torsion angles for benzyl alcohol and bromide complexes are given in Table 2. All complexes display predominantly staggered arene–$Cr(CO)_3$ conformations except for the tris(alcohol) **4** which exhibits only a slight staggering (16.5°).



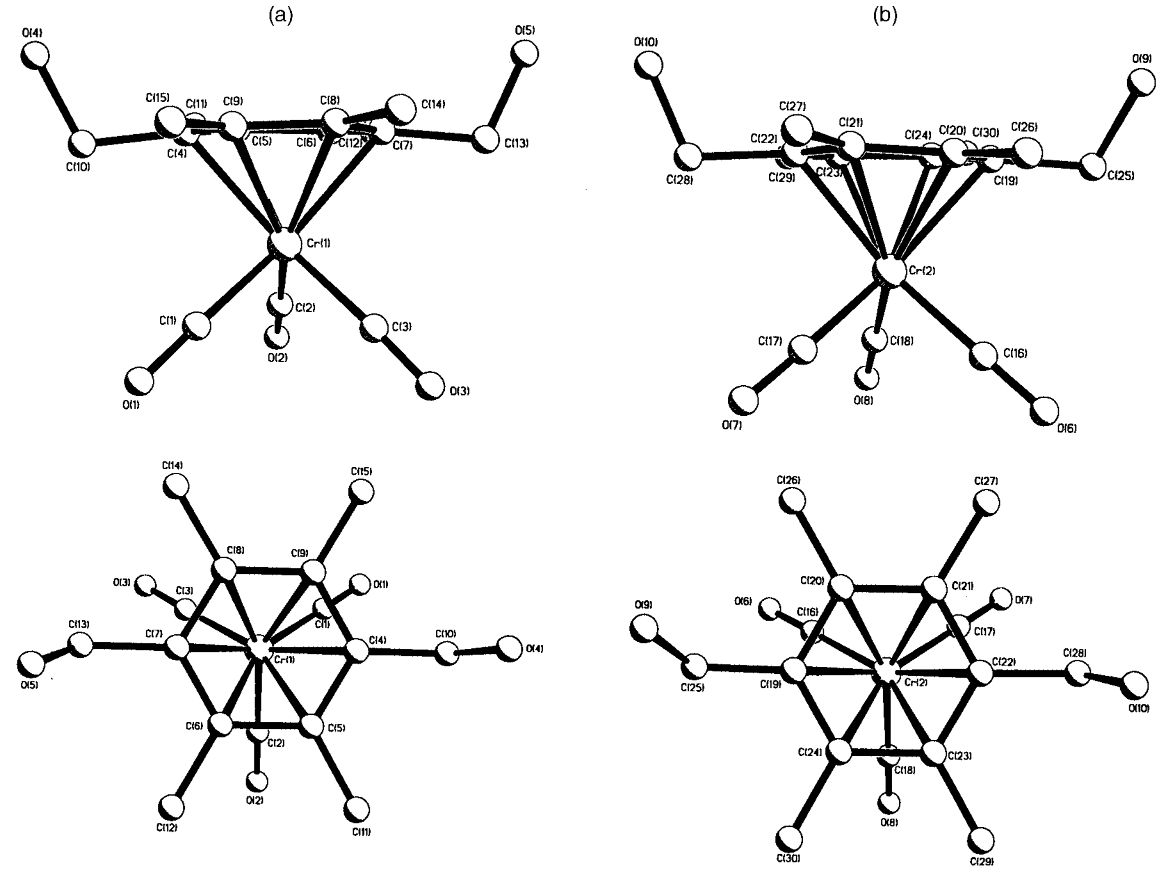


Fig. 2 Molecular structure of complex **3**: (a) molecule A, (b) molecule B.

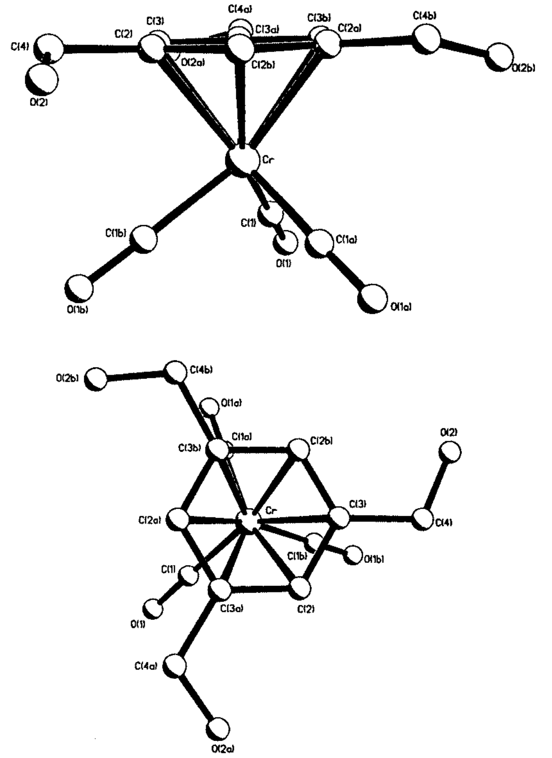


Fig. 3 Molecular structure of complex **4**.

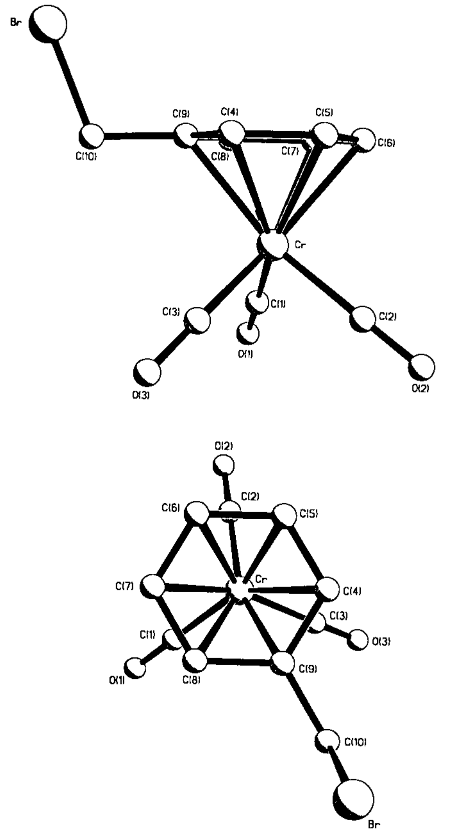


Fig. 4 Molecular structure of complex **6**.

In all five structures intermolecular interactions are observed (Table 3). For benzyl alcohol complexes these are hydrogen bonds of the type OH · · · O between the OH groups and for the bis(alcohol) complexes **2** and **3** occur between molecules of the same type and between different molecules in the asymmetric unit. Oxygen–oxygen interactions are shortest for **4** (2.677 Å) and vary between 2.697 and 2.823 Å for **2** and **3**. Braga *et al.* have reported that columns of arenechromium tricarbonyl molecules can be held together by the interactions between arene units and the carbonyl ligands of neighbouring molecules.[19] This type of interaction is seen for both benzyl bromide complexes.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **2**–**4**, **6** and **8**

	2		**3**				
	Molecule A	Molecule B	Molecule A	Molecule B	**4**	**6**	**8**
Cr–C(*ipso*)	2.238(2)	2.217(2)	2.193(2)	2.205(2)	2.222(3)	2.204(4)	2.222(4)
	2.252(2)	2.230(2)	2.200(2)	2.192(2)			2.222(4)
Cr–C(*ortho*)$_{av}$	2.218(4)	2.213(4)	2.246(4)	2.241(4)	2.227(3)	2.202(9)	2.212(8)
Cr–C(centroid)	1.726	1.714	1.713	1.709	1.721	1.705	1.706
Cr–C(CO)$_{av}$	1.840(5)	1.847(5)	1.843(5)	1.844(5)	1.839(8)	1.839(10)	1.851(8)
Torsion angle[a]	25.4	30.1	32.5	28.5	16.5	38.4	34.6
C–C(ring)$_{av}$	1.408(7)	1.405(9)	1.428(7)	1.428(7)	1.409(7)	1.393(12)	1.413(12)
C–CH_2	1.515(3)	1.509(4)	1.517(3)	1.514(3)	1.508(4)	1.488(6)	1.490(5)
	1.510(3)	1.514(4)	1.519(3)	1.513(3)			1.497(5)
CH_2–X	1.418(3)	1.407(4)	1.438(2)	1.424(3)	1.406(5)	1.956(5)	1.969(4)
	1.418(4)	1.400(3)	1.440(3)	1.440(3)			1.973(4)
C(*ipso*)–CH_2–X	113.0(2)	113.3(2)	111.2(2)	110.7(2)	113.8(3)	110.4(3)	109.0(3)
	112.9(2)	112.2(2)	110.4(2)	110.6(2)			108.7(3)
[b]C(*ipso*)	0.0073(C4)	−0.0037(C24)	−0.0590(C4)	−0.0421(C19)	0.0012(C3)	−0.0070(C9)	0.0015(C6)
	0.0225(C7)	−0.0078(C27)	−0.0569(C7)	−0.0547(C22)			0.0011(C9)
[b](CH_2)	0.0299	−0.0047	−0.2158	−0.1100	0.0676	−0.0582	−0.0193
	0.0579	−0.0416	−0.1922	−0.1590			−0.0113
[b]X	−0.1647	−0.6363	1.0600	1.0951	−0.2516	1.7481	1.8172
	0.2596	1.1995	1.0715	1.1405			1.8369

[a] Angle between the metal, ring centroid, α-carbon and carbonyl carbon. [b] Distance above (+ve) or below (−ve, near the metal) the plane of the arene ring.

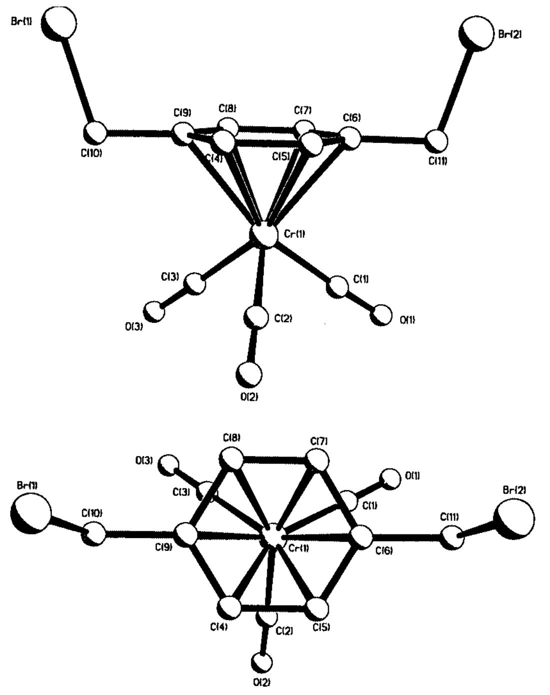


Fig. 5 Molecular structure of complex **8**.

In **6** bromine–oxygen contacts (3.153 Å) link the individual molecular units together, while in **8** both bromine–oxygen (3.344 Å) and bromine–bromine (3.639 Å) interactions result.

Conclusions

Reaction of chromium hexacarbonyl with benzyl alcohols, while being quite slow, affords a simple, high yielding, route to chromium tricarbonyl complexes. These in turn are useful intermediates towards benzylic halide complexes, which are inaccessible *via* the direct reaction. For benzyl bromides, PBr_3 and BBr_3 can both be used and are superior to HBr. The latter has previously been utilised but bromination is in competition with metal decomplexation leading to inseparable mixtures of complexed and uncomplexed products. The successful efficient synthesis of a range of benzylic bromide chromium tricarbonyl complexes has allowed us to study their reactions with nitrogen bases. Specifically, reaction with DABCO results in the generation of polycationic host molecules such as **II** the chemistry of which will be reported in a separate publication.[20]

Table 3 Intermolecular interactions in crystal structures

Compound	Bond formed	Bond length/Å
2	O(4)···O(5)	2.823
	O(4)···O(24)	2.792
	O(5)···O(25)	2.785
	O(24)···O(25)	2.736
3	O(4)···O(5)	2.719
	O(4)···O(10)	2.805
	O(5)···O(9)	2.717
	O(9)···O(10)	2.697
4	O(2)···O(2a)	2.677
6	Br···O(1)	3.153
8	Br(1)···Br(1a)	3.639
	Br(1)···O(3)	3.344

Experimental

General

Unless otherwise stated, all manipulations were carried out under an atmosphere of nitrogen, using standard vacuum line, Schlenk and glove-box techniques. Chromium hexacarbonyl was sublimed before use. Solvents were distilled under an atmosphere of nitrogen over drying agents and stored in ampoules over activated 4 Å sieves or sodium mirrors, after being degassed thoroughly. All halide complexes are light sensitive. Once made they were stored in a refrigerator in the glove-box. NMR spectra were recorded on Varian VXR-400, Bruker AMX400 and AC300 spectrometers, mass spectra on a VG ZAB-SE mass spectrometer for both electron impact (EI) and fast atom bombardment (FAB). High-resolution mass spectrometry was performed on a VG ZAB-SE mass spectrometer using FAB ionisation at the School of Pharmacy, University of London. Peak positions are given with percentage relative abundances in parentheses. Infrared spectra were recorded on a Nicolet 205 FTIR spectrophotometer. Elemental analyses were carried out by the Microanalytical Section of the Chemistry Department, University College London. Melting points were obtained using either a Reichert hot stage melting point apparatus or an Electrothermal 6910 melting point apparatus and are uncorrected.

Synthesis of benzyl alcohol complexes 1–5

In a Schlenk vessel fitted with a gas inlet adapter and reflux condenser with bubbler were placed chromium hexacarbonyl, dibutyl ether and THF. The alcohol was then added. The apparatus was thoroughly purged with nitrogen and nitrogen allowed to flow slowly throughout the reaction. The mixture was heated under reflux with stirring at between 180 and 240 °C for 20–48 h. The resulting solution was cooled to room temperature and filtered under nitrogen over Fuller's earth which was then washed with THF. The combined filtrate and washings were concentrated under reduced pressure to yield the product as a bright yellow solid. For the tris(hydroxymethyl substituted benzenes) some yellow solid and sometimes a small amount of brown solid was deposited on the wall of the Schlenk vessel. The solution was removed by filtration under nitrogen and the yellow and brown solids were dried briefly *in vacuo* before being dissolved in THF. The yellow solution that resulted was filtered under nitrogen to leave the insoluble fine brown solid behind. The filtrate was concentrated *in vacuo* to yield the desired product as a yellow solid. Crystals for X-ray crystallography were obtained by recrystallisation from a mixture of dibutyl ether–THF or hexane at 4 °C.

Complex **1** 90% yield. ^{1}H NMR (d_6-acetone): δ 4.44 (d, 2 H, *J* 5.6, ArCH_2), 4.64 (t, 1 H, *J* 5.6 Hz, OH), 5.50–5.54 (m, 1 H, Ar) and 5.62–5.71 (m, 4 H, Ar). ^{13}C NMR (CDCl$_3$): δ 63.3, 90.8, 91.6, 92.9, 93.0 and 232.7: IR (CH$_2$Cl$_2$): 3600–3000w, 1950s, 1878s and 1866s cm^{-1}. MS (FAB): *m*/*z* 244 (M$^+$). Complex **2** 98% yield. ^{1}H NMR (d_6-acetone): δ 4.41 (d, 4 H, *J* 5.6, ArCH_2), 4.63 (t, 2 H, *J* 5.6 Hz, OH) and 5.71 (s, 4 H, Ar). ^{13}C NMR (d_6-acetone): δ 62.7, 93.3, 113.1 and 234.4. IR: (CH$_2$Cl$_2$) 1968s and 1891s; (MeCN) 1964s and 1883s; (THF) 3577w, 3501w, 3411w, 1964s and 1887s cm^{-1}. MS (FAB): *m*/*z* 274 (M$^+$). Calc. for $C_{11}H_{10}CrO_5$: C 48.19, H 3.68. Found: C 48.09, H 3.59%. Complex **3** 95% yield. ^{1}H NMR (d_6-acetone): δ 2.31 (s, 12 H, ArCH_3), 4.52 (t, 2 H, *J* 4.7, OH) and 4.62 (d, 4 H, *J* 4.7 Hz, ArCH_2). ^{13}C NMR (d_6-acetone): δ 15.7, 59.4, 108.8, 128.9 and 235.3. IR: (KBr) 3600–3100m, 2954w, 2906w, 2853w, 1966s, 1959s, 1895s, 1869s, 1386w, 1262w, 1081w, 1020w, 999m, 814w, 665m, 627m and 533w; (CH$_2$Cl$_2$) 3750–3500m, 1980s, 1956s, 1879s and 1603w; (THF) 3650–3250m, 1979s, 1952s, 1874s and 1714w cm^{-1}. MS (FAB): *m*/*z* 330 (M$^+$). HRMS ($C_{15}H_{18}CrO_5$, [M]): calc. *m*/*z* 330.0539, found 330.0547. Calc. for $C_{15}H_{18}CrO_5$: C 54.55, H 5.49. Found: C 53.68, H 5.19%. Complex **4** 87% yield. mp 150 °C (decomp.); ^{1}H NMR (d_6-acetone): δ 4.49 (d, 6 H, *J* 5.2, ArCH_2), 4.65 (t, 3 H, *J* 5.6 Hz, OH) and 5.58 (s, 3 H, Ar). ^{13}C NMR (d_6-acetone): δ 63.1, 90.0, 114.7 and 234.5. IR (THF): 3437s, 1961s, 1884s and 1608w cm^{-1}. MS (FAB): *m*/*z* 304 (M$^+$). Calc. for $C_{12}H_{12}CrO_6$: C 47.38, H 3.98. Found: C 47.40, H 3.96%: Complex **5** 88% yield. Mp 210–212 °C (decomp.). ^{1}H NMR (d_6-acetone): δ 2.50 (s, 9 H, ArCH_3) and 4.44 (s, 6 H, ArCH_2). ^{13}C NMR (d_6-acetone): δ 14.9, 59.1, 105.8, 113.4 and 234.8. IR (THF): 3500–3300m, 1954s and 1877s cm^{-1}. MS (FAB): *m*/*z* 346 (M$^+$). Calc. for $C_{15}H_{18}CrO_6$: C 52.03, H 5.24. Found: C 51.54, H 5.09%

Synthesis of complexes 6–14

(a) Bromination using PBr$_3$. A solution of phosphorus tribromide in diethyl ether was slowly added to a solution (or suspension) of the alcohol complex in diethyl ether cooled to 0 °C, under nitrogen. The reaction mixture was stirred at 0 °C for between 2 and 2.5 h and then stirred at room temperature for 2.5–18 h. Water was added to quench the reaction, which resulted in the formation of two layers. The mixture was transferred to a separating funnel and the aqueous layer removed. The ether layer was washed with water and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the filtrate transferred to a Schlenk vessel, where the solvent was removed under reduced pressure to give the corresponding bromide complex as a deep yellow–orange solid.

(b) Halogenation using BX$_3$ (X = Cl, Br or I). Boron trihalide (1 M, in dichloromethane) was added *via* syringe to a solution (or suspension) of the alcohol complex in dichloromethane under nitrogen at −78 °C and the resulting solution stirred for between 1.5 and 3 h. The reaction mixture was quenched with a saturated aqueous solution of sodium hydrogencarbonate and the mixture allowed to warm to room temperature. Water was added and the organic layer collected in air. The water layer was washed twice with dry diethyl ether and the washings were combined with the dichloromethane layer. This organic phase was then dried over anhydrous magnesium sulfate. The drying agent was removed by filtration through Celite and the filtrate transferred to a Schlenk vessel, where the solvents were removed under reduced pressure to give the corresponding halide complex as a deep yellow–orange solid.

(c) Bromination using hydrogen bromide (aqueous). A solution (or suspension) of the alcohol complex in dry benzene under nitrogen was shaken in a Schlenk vessel with aqueous hydrogen bromide (47%) for 10 min. The benzene layer was separated, washed twice with water (in air), and dried over anhydrous sodium sulfate. The drying agent was removed by filtration and the solution was transferred to a Schlenk vessel where it was concentrated *in vacuo* to give a yellow–orange solid, or a viscous oil, which was often a mixture of products.

(d) Bromination using hydrogen bromide (in glacial acetic acid). A solution (or suspension) of the alcohol complex in dry benzene under nitrogen was shaken in a Schlenk vessel with hydrogen bromide (in glacial acetic acid, 45%) at 0 °C for between 7 and 15 min. The reaction mixture was transferred to a separating funnel containing ice–water slush, in air. The water layer was removed and the benzene layer washed with water and dried over anhydrous sodium sulfate. The drying agent was removed by filtration, and the filtrate transferred to a Schlenk vessel where the solvent was removed under reduced pressure to leave either a yellow–orange solid or a viscous oil, which was often a mixture of products.

Complex **6**. (a) 92%; (b) 70%; (c) 54%; (d) impure pale orange viscous. Crystals suitable for X-ray diffraction were grown from diethyl ether–light petroleum (bp 40–60 °C). mp 73–75 °C. ^{1}H NMR (CDCl$_3$): δ 4.17 (s, 2 H, ArCH_2) and 5.38 (s, 5 H, Ar); (d_6-acetone) δ 4.42 (s, 2 H, ArCH_2), 5.66–5.73 (m, 3 H, Ar) and 5.76–5.79 (m, 2 H, Ar). ^{13}C NMR (d_6-acetone): δ 31.9, 91.6, 92.3, 93.2, 105.5 and 232.0. IR (CH$_2$Cl$_2$): 1975s and 1900s cm^{-1}. MS (FAB): *m*/*z* 306 (M$^+$). Calc. for $C_{10}H_7BrCrO_3$: C 39.12, H 2.30, Br 26.02. Found: C 38.76, H 2.22, Br 25.83%. Complex **7**. Yield (b) 88%. mp 90–95 °C. ^{1}H NMR (d_6-acetone): δ 4.54 (s, 4 H, ArCH_2) and 5.85 (s, 4 H, Ar). ^{13}C NMR (d_6-acetone): δ 45.0, 94.6, 107.7 and 232.8. IR (CH$_2$Cl$_2$): 1978s and 1906s cm^{-1}. MS (FAB): *m*/*z* 310 (M$^+$). Calc. for $C_{11}H_8Cl_2CrO_3$: C 42.47, H 2.59, Cl 22.79. Found, C 42.37, H 2.43, Cl 22.45%. Complex **8**. Yield (a) 94%; (b) 88%; (c) 64%; (d) orange solid shown to be a 2 : 1 mixture of **8** and free arene, 60%. mp 130–131 °C (decomp.). ^{1}H NMR (d_6-acetone): δ 4.45 (s, 4 H, ArCH_2) and 5.85 (s, 4 H, Ar). ^{13}C NMR (d_6-acetone): δ 32.1, 95.1, 107.5 and 232.9. IR: (KBr) 1964s, 1894s and 1880s; (CH$_2$Cl$_2$) 1977s and 1907s, IR (MeCN) 1974s and 1901s; (hexane) 1985s and 1924s cm^{-1}. MS (FAB) *m*/*z* 398 (M). Calc. for $C_{11}H_8Br_2CrO_3$: C 33.03, H 2.02, Br 39.95. Found: C 32.84, H 1.71, Br 39.56%. Complex **9**. Yield (b) 82%. mp 125–128 °C (decomp.). ^{1}H NMR (d_6-acetone): δ 4.39 (s, 4 H, ArCH_2) and 5.81 (s, 4 H, Ar). ^{13}C NMR (d_6-acetone): δ 3.7, 95.0, 109.3 and 233.4. IR (CH$_2$Cl$_2$): 1974s and 1905s cm^{-1}. MS (FAB): *m*/*z* 494 (M$^+$). Calc. for $C_{11}H_8CrI_2O_3$: C

Table 4 Selected crystallographic data for complexes **2**–**4**, **6** and **8**

	2	3	4	6	8
Formula	$C_{22}H_{20}Cr_2O_{10}$	$C_{15}H_{18}CrO_5$	$C_{12}H_{12}CrO_6$	$C_{10}H_7BrCrO_3$	$C_{11}H_8Br_2CrO_3$
Formula weight	578.38	330.29	304.22	307.07	399.99
Crystal system	Monoclinic	Triclinic	Trigonal	Triclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$R3$	$P\bar{1}$	$P2_1/n$
a/Å	12.882(3)	8.727(1)	12.698(2)	6.772(1)	10.0413(3)
b/Å	13.217(3)	11.925(1)	12.698(2)	8.541(2)	12.5369(6)
c/Å	14.087(3)	14.714(1)	6.858(1)	9.622(2)	10.7044(5)
α/°		69.767(5)		83.31(3)	
β/°	112.52(3)	82.210(6)		88.37(3)	105.026(2)
γ/°		84.463(5)		88.67(3)	
V/Å^3	2215.6	1421.4	957.6	552.4	1301.47
Z	4	4	3	2	4
μ(Mo-Kα)/cm^{-1}	10.38	8.23	9.15	46.33	70.10
Data measured	3903	6355	432	2530	2537
Unique data used	3898	6355	428	2525	2537
No. parameters	307	391	58	136	155
R (all data)	0.037 (0.044)	0.044 (0.057)	0.023 (0.024)	0.046 (0.066)	0.039 (0.098)
R_w (all data)	0.101 (0.110)	0.112 (0.121)	0.059 (0.065)	0.124 (0.149)	0.044 (0.1001)

26.75, H 1.63, I 51.38. Found: C 27.10, H 1.46, I 51.39%. Complex **10**. Yield (b) 74%. ^{1}H NMR (d$_6$-acetone): δ 2.36 (s, 12 H, ArCH_3) and 4.74 (s, 4 H, ArCH_2). ^{13}C NMR (d$_6$-acetone): δ 15.7, 31.1, 104.9, 108.0 and 234.1. IR: (KBr) 2964w, 2925w, 2875w, 2855w, 1955s, 1877s, 1868s, 1639w, 1387w, 1262w, 1214m, 1089w, 1021w, 808w, 679w, 659m, 624m, 599w, 584w, 529m, 517w and 475w; (CH_2Cl_2) 1960s and 1886s cm^{-1}. MS (FAB): m/z 454 (M). Calc. for $C_{15}H_{16}Br_2CrO_3$: C 39.50, H 3.54, Br 35.04. Found: C 39.31, H 3.49, Br 35.19%. Complex **11**. Yield (a) 76%; (b) 76%; (c) orange viscous oil which was a mixture of many compounds; (d) orange viscous oil which was not solely the bromide complex. mp 94–97 °C. ^{1}H NMR (d$_6$-acetone): δ 4.48 (s, 6 H, ArCH_2) and 5.99 (s, 3 H, Ar). ^{13}C NMR (d$_6$-acetone): δ 31.9, 95.1, 107.6 and 232.2. IR (CH_2Cl_2): 1980s, 1913s and 1606w cm^{-1}. MS (FAB): m/z 490 (M$^+$). Calc. for $C_{12}H_9Br_3CrO_3$: C 29.24, H 1.84, Br 48.63. Found: C 29.45, H 1.65, Br 48.58%. Complex **12**. Yield (b) 81%. ^{1}H NMR (d$_6$-acetone): δ 2.60 (s, 9 H, ArCH_3) and 4.71 (s, 6 H, ArCH_2). ^{13}C NMR (d$_6$-acetone): δ 15.0, 42.0, 101.6, 112.5 and 232.5. IR: (KBr) 1975s, 1957s, 1904s, 1882s, 1428w, 1381w, 1313w, 1289w, 1223w, 1004w, 791w, 667m, 618m, 598w, 538w and 482m; (CH_2Cl_2) 1966s, 1899s, 1422m, 1278s and 1255s cm^{-1}. MS (FAB): m/z 400 (M$^+$). Calc. for $C_{15}H_{15}Cl_3CrO_3$: C 44.86, H 3.76, Cl 26.48. Found: C 45.31, H 3.85, Cl 26.35%. Complex **13**. Yield (a) 91%; (b) 86%; (d) orange solid approximately 2:1 mixture of free arene and **13** (59%). mp 155–158 °C (decomp.). ^{1}H NMR: ($CDCl_3$) δ 2.50 (s, 9 H, ArCH_3) and 4.29 (s, 6 H, ArCH_2); (d$_6$-acetone): δ 2.57 (s, 9 H, ArCH_3) and 4.62 (s, 6 H, ArCH_2). ^{13}C NMR (d$_6$-acetone): δ 14.8, 29.9, 111.9, 121.0 and 232.4. IR (CH_2Cl_2) 1968s, 1900s and 1606m cm^{-1}. MS (FAB): m/z 532 (M$^+$). Calc. for $C_{15}H_{15}Br_3CrO_3$: C 33.68, H 2.83, Br 44.81. Found: C 33.28, H 2.73, Br 44.56%. Complex **14**. Yield (b) 82%. mp 132–134 °C. ^{1}H NMR (d$_6$-acetone): δ 2.43 (s, 9 H, ArCH_3) and 4.49 (s, 6 H, ArCH_2). ^{13}C NMR (d$_6$-acetone): δ 3.2, 14.8, 103.1, 109.9 and 232.7. IR: (KBr) 1980m, 1959s, 1903s, 1884s, 1871s, 1638w, 1618w, 1438w, 1380w, 1262w, 1150m, 1020vw, 805w, 765w, 660m, 617m, 532w and 469m (CH_2Cl_2) 1964s, 1896m and 1606m cm^{-1}. MS (FAB): m/z 676 (M$^+$). Calc. for $C_{15}H_{15}CrI_3O_3$; C 26.65, H 2.24, I 56.32. Found, C 26.86, H 2.06, I 56.40%.

X-ray crystallography

Suitable single crystals of complexes **2**, **4** and **6** were mounted on a glass fibre at 295 K and all geometric and intensity data were taken from these samples using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-Kα radiation ($\lambda = 0.71073$ Å). Lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of a number of reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure reflections in the range $5 \le 2\theta \le 50°$ and three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz-polarisation effects, and empirically for absorption. The unique data with $I \ge 3.0\sigma(I)$ were used, being solved by direct methods and developed using alternating cycles of least-squares refinement and Fourier-difference synthesis. The non-hydrogen atoms were refined anisotropically while hydrogens were placed in idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08$ Å^2).

Crystals of complexes **3** and **8** were mounted on a thin glass fibre using silicon grease and cooled on the diffractometer to 100 K using an Oxford Cryostream low temperature attachment. Data were collected in wide-slicing mode using a Nonius Kappa CCD diffractometer, with a detector to crystal distance of 30 mm. Crystals were indexed from five preliminary frames each of 2σ width in a set corrected for Lorentz-polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Structures were solved by direct methods and developed *via* alternating least squares cycles and Fourier difference synthesis with the aid of the XSeed interface. All non-hydrogen atoms were modelled anisotropically. Hydrogen atoms were placed in calculated positions and allowed to ride on the atoms to which they were attached with an isotropic thermal parameter 1.2 times that of the parent atom. All calculations were carried out with either a Silicon Graphics Indy R5000 workstation or an IBM compatible PC. Packing diagrams for all crystal structures have been deposited as Supporting Information.

CCDC reference number 186/1988.

See http://www.rsc.org/suppdata/dt/b0/b002142n/ for crystallographic files in .cif format.

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