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Molecular design using electrostatic interactions. Part 3: Synthesis and properties of chromium tricarbonyl complexes of cationic mono-, di- and tripodands

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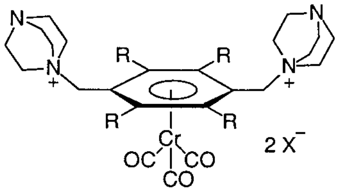
Abstract—Water soluble polycationic arene host systems have been prepared, using DABCO as the source of the cationic charge, in which the arene group is complexed to chromium tricarbonyl. Association constants for two salts were determined by NMR methods and the role of IR carbonyl band of the $Cr(CO)_3$ moeity as reporter group explored. The different properties of the salts in the solid state, in water and, where possible, organic solvents were examined and it was found that the nature of the anion had no effect on the carbonyl IR band in water, although it did in the solid state. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

A variety of metal-organic compounds have been shown to act as host molecules to bind a variety of organic substrates. The binding site may involve the metal, as in the metalloporphyrins described by Sanders and co-workers,[1,2] or through the organic ligand, as in the ruthenium pyrimidine derivatives of Constable and Fallahpour.[3] Beer and co-workers have shown that a variety of anions are strongly associated with cationic ruthenium complexes by a combination of electrostatic interactions and hydrogen bonding[4] and they have designed a system in which the potassium counterion adjusts the anion selectivity of the complex.[5] The importance of size and shape complementarity in the anion binding by ruthenium and iridium calixarenes has been demonstrated by Atwood and co-workers.[6,7] Chromium tricarbonyl based anion receptors have been reported [8] and the general area of recognition using inorganic complexes has been reviewed.[9]

We have previously described the preparation of a number of polycation podands based on benzene and naphthalene frameworks with pendant 1,4-diazabicyclo[2.2.2]octane (DABCO) substituents providing the positive charges.[10,11] Some of these complexes showed selectivity towards specific polyanions and some were able to select between ferri- and ferro-cyanide on the basis of charge matching,[10] although this was shown to be only one component in the selection process.[12] Since it appeared that the restriction of rotation of the pendant substituents increased the binding affinities of the polycation, we investigated the preparation of polycations with a metal complexed to the benzene ring which should restrict the access of the substituents to the opposite face. The metal component may also serve as a means of linking complexed molecules and of measuring ionic interactions. We chose chromium tricarbonyl complexes as these species are well known for benzenoid systems and can be prepared under a variety of conditions.



2. Results and discussion

2.1. Synthesis

Our initial attempts to prepare the chromium tricarbonyl complexes involved using the previously prepared polycations as substrates. A variety of conditions were explored but either starting materials or decomposition products were obtained. We then explored routes from the bromomethyl substituted chromium carbonyl compounds which were prepared by methods that are described elsewhere.[12] The appropriate bromomethyl substituted chromium complex was treated with DABCO in acetonitrile to give the desired cationic complex as the bromide salt. The reaction is illustrated in Scheme 1. By this means the complexes **1a**–**4a** were prepared in high yield. In the preparation of complex **2a**, we also isolated the partially substituted derivative **5**.

Keywords: chromium tricarbonyl complexes; polycations; benzenoid components; molecular recognition.

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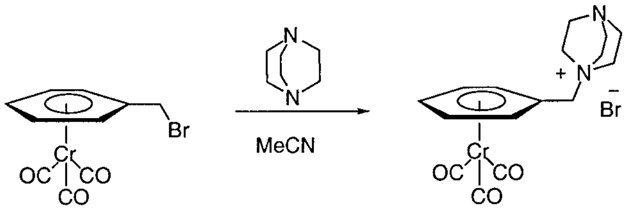
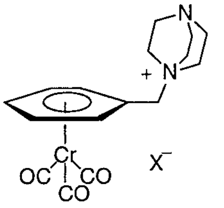
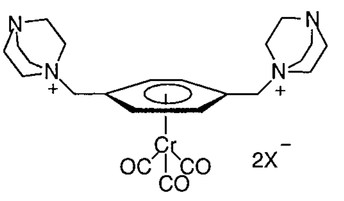


Scheme 1.

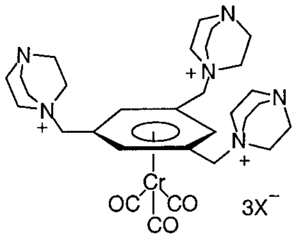
We also attempted to prepare the DABCO complex from (η^6-1,4-bisbromomethyl-2,3,5,6-tetramethybenzene)chromium tricarbonyl by the same reaction but only the non-complexed dication **6** was obtained.



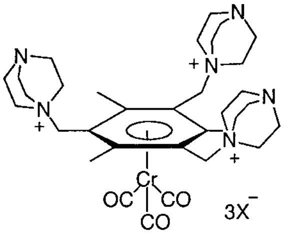
1a X = Br
b X = PF_6



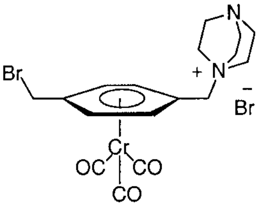
2a X = Br
b X = PF_6



3a X = Br
b X = PF_6



4a X = Br
b X = PF_6
c X = Cl
d X = I
e X = BPh_4



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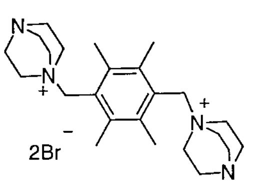
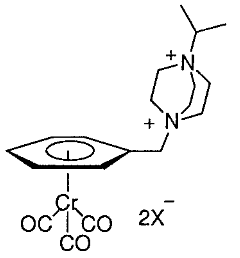


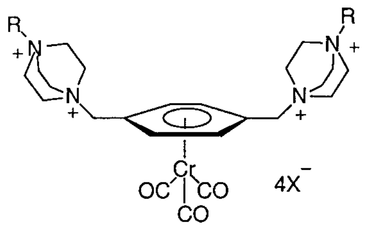
6

The bromide salts **1a**–**4a** were converted into the corresponding hexafluorophosphates by treatment of an aqueous solution of the bromide with a saturated aqueous solution of KPF_6. We also investigated the preparation of trication **4** with other counter ions. Reaction of 1,3,5-tris(chloromethyl)-2,4,6-trimethylbenzene with DABCO gave a low yield of the desired chloride **4c** contaminated with the starting chloride. The major absorptions in the IR spectrum were the carbonyl bands for **4c**. The iodide **4d** was prepared from the corresponding tris-iodomethyl derivative in 63% yield. The tetraphenylborate **4e** was prepared in 79% yield by ion exchange of the bromide **4a** with sodium tetraphenylborate. Similar attempts to prepare the tetrafluoroborate, trifluoroacetate, citrate and triflate only gave mixtures of the desired salt contaminated by the starting materials and the metal bromide. These mixed salts did, however, show the characteristic carbonyl bands in the IR spectrum.

A number of disubstituted DABCO cations were prepared in a similar manner to that described above for the monosubstituted cations. Reaction of (η^6-bromobenzyl)chromium tricarbonyl with *N*-2-propyl-DABCO in acetonitrile at room temperature gave the dication **7a** and this was converted to the hexafluorophosphate **7b** as described. Similarly, (η^6-1,4-bis[bromomethyl]benzene)chromium tricarbonyl was converted into the tetracation **8** as the tetrabromide or tetra-hexafluorophosphate. An attempt to prepare the corresponding methyl derivative from *N*-methyl-DABCO gave the product **9** in an impure form which we were unable to purify, and attempts to prepare the cations from (η^6-1,4-bis[bromomethyl]-2,3,5,6-tetramethyl-benzene)chromium tricarbonyl were unsuccessful. Similarly, all attempts to prepare the hexacationic analogues of **3** and **4** were unsuccessful.



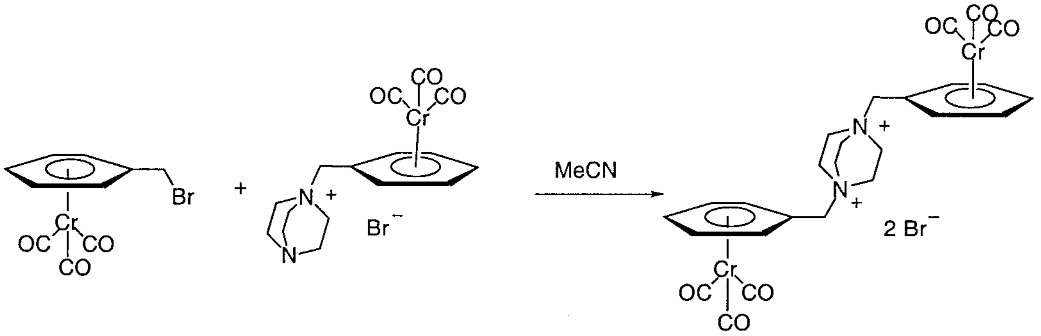
7a X = Br
7b X = PF_6



8a R = MeCHMe, X = Br
8b R = MeCHMe, X = PF_6
9 R = Me, X = Br

We also examined the preparation of systems in which η^6-arene chromium tricarbonyl complexes were linked by DABCO units. Complex **1a** was treated with (η^6-bromobenzyl)chromium tricarbonyl (**10**) in acetonitrile to give the complex **11** (Scheme 2).

Unsuccessful attempts were also made to convert (η^6-1,4-bis[bromomethyl]benzene)chromium tricarbonyl into the corresponding tri-phenylbenzene chromium tricarbonyl complex by reaction with **1a**. It may be possible to prepare



10 **1a** **11**

Scheme 2.

this compound from **2a** and **10** and we are currently exploring that route and are also investigating the preparation of analogues of **11** with different metals on the benzenoid components.

2.2. Complexation studies

Host–guest interactions were studied by monitoring the change in the chemical shift of the cation protons in the ^{1}H NMR spectrum with relative change in cation:anion concentration and the stoichiometry of the complex was determined by the method of continuous variation, as we have previously described.[10] The shifts of both the cation and anion protons were examined and it was found that only those for the cation in all cases gave curves for which there was no further shift at high guest ratios. Table 1 gives the maximum chemical shift change ($\Delta\delta$) of the specific cation proton and the calculated association constant.

The log K_a for the dication **2a** is considerably less than that determined for the non-complexed dication (3.55) with this dianion and suggests that the conformational effect of the $Cr(CO)_3$ group is outweighed by the directional effect required for the host:guest interaction, with approach from only one side now being possible. In the case of the complexed trianion **4a** the value with the trianion is considerably greater for the non-complexed trianion, but that value was taken for the anion shift as, in that case, it was not possible to calculate the association constant from the cation shifts.[10] The Job plot of **4a** and the dicarboxylate did not give a guest: host ratio of 1:1 and no association constant could be determined.

2.3. Infra-red studies

IR spectra of arene chromium tricarbonyl complexes show two intense carbonyl absorption bands between 1800 and 2050 cm^{-1}. These correspond to the carbonyl A_1 and E stretching vibrations of the $Cr(CO)_3$ group and are sensitive to the nature of the arene substituents. For (η^6-benzene)$Cr(CO)_3$ there is a lowering of frequency with electron-donating substituents and an increase in frequency for electron-withdrawing groups.[13–15] Thus, as the number of methyl groups substituting benzene is increased the frequency decreases incrementally, while with chlorine substituents there is an incremental increase.[16] With many

Table 1. ^{1}H NMR change of chemical shift of specific cation proton and log K_a for polycations with polyanions in water

Cation host	Anion guest	$\Delta\delta$ ppm	log K_a
2a	Na benzene-1,4-dicarboxylate	0.035 ± 0.002^a	2.64
4a	Na benzene-1,4-dicarboxylate	0.030 ± 0.002^b	*
4a	Na benzene-1,3,5-tricarboxylate	0.074 ± 0.001^b	2.89
4a	Na benzene-1,2,4,5-tetracarboxylate	0.019 ± 0.008^b	*

[a] Shift of benzylic protons, the aryl protons show a similar shift.

[b] Shift of methyl protons, benzylic protons obscured by water signals.

Table 2. Carbonyl frequencies in the IR spectra of compounds of type (η^6-1,3,5-tris(XCH_2)-2,4,6-trimethylbenzene)chromium tricarbonyl in KBr

Complex	ν_{CO} (A_1) cm^{-1}	ν_{CO} (E) cm^{-1}
(η^6-hexamethylbenzene) chromium tricarbonyl[19]	1951 1929	1845
(η^6-1,3,5-tris($ClCH_2$)-2,4,6-trimethylbenzene)-chromium tricarbonyl[12]	1975 1957	1904 1882
(η^6-1,3,5-tris(ICH_2)-2,4,6-trimethylbenzene)-chromium tricarbonyl[12]	1980 1959	1903 1884 1871

Table 3. Carbonyl frequencies in the IR spectra of compounds containing CH_2DABCO substituents in KBr

Complex	CH_2–DABCO substituents	ν_{CO} (A_1) cm^{-1}	ν_{CO} (E) cm^{-1}
(η^6-toluene) chromium tricarbonyl	0	1953	1887
			1866
1a	1-	1971	1887
		1958	1859
11	1- (N, N′-DABCO)	1969	1904
			1896
(η^6-1,4-dimethylbenzene) chromium tricarbonyl	0	1958	1875
			1844
2a	1,4-	1979	1901
			1884
(η^6-mesitylene) chromium tricarbonyl	0	1963	1889
			1873
3a	1,3,5-	1989	1923
4a	1,3,5-	1981	1909

substituents, however, the incremental effects are non-linear.[15] Stephenson and co-workers have used the chromium tricarbonyl system as a reporting group, monitoring the change of frequency of the carbonyl bands of (h^6-benzene)chromium tricarbonyl in cyclohexane on addition of 1,2-dimethoxybenzene, new bands appearing as the concentration of the latter was increased.[17] Sodium ion complexation has been measured in related experiments involving benzannelated crown ethers.[18] We sought to use the change in the carbonyl stretching frequencies to monitor the binding of the counter ions to the polycation, supposing that the more strongly bound anion would decrease the positive charge on the DABCO units and thus make them less electron withdrawing. IR studies were carried out both in the solid state and in solution.

The increase in carbonyl frequency on introducing halogens to the 1,3,5-methyl groups of hexamethyl benzene is illustrated in Table 2. The effect of chlorine and iodine are very similar with a slightly greater increase in the A_1 band with iodine. Table 3 shows the change in carbonyl frequency on introducing DABCO-methyl groups on benzene and methylbenzenes. There is little difference in the E band carbonyl frequency between the chromium tricarbonyl complexes of toluene, benzyl DABCO **1a** and dibenzyl DABCO **11**, although the A band for the toluene complex is somewhat lower. Comparison of the chromium tricarbonyl complexes of 1,4-dimethylbenzene and **2a** shows that the addition of two charged DABCO units causes a significant increase in frequency of the A_1 band (21 cm^{-1}). The same effect is found with the complexes of mesitylene and **3a**, but the shift is larger (26 cm^{-1}). Introduction of the three 2,4,6 methyl groups on the 1,3,5-tris-(DABCOmethyl) framework, **4a**, causes a small decrease in frequency compared to **3a** (8 cm^{-1}). The changes to the E band are more difficult to interpret because of the splitting that occurs with this absorption.

Table 4. Carbonyl frequencies in the IR spectra of compounds containing disubstituted DABCO substituents in KBr

Complex	Phenyl–DABCO substituents	ν_{CO} (A_1) cm^{-1}	ν_{CO} (E) cm^{-1}
7a	1-CH_2–DABCO-2-Pr	1989	1922
		1974	1890
8a	1,4-bis(CH_2–DABCO-2-Pr)	1973	1897

The IR spectra of the disubstituted DABCO derivatives are shown in Table 4. Comparison of the disubstituted DABCO benzyl derivative **7a** (Table 4) with the monosubstituted analogue **1a** (Table 3) indicates that the disubstituted DABCO is having a greater electron withdrawing effect but comparison of **7a** and **8a** shows that the effect of increasing the number of such substituents is not additive.

Having examined the substituent effects on the position of the carbonyl absorptions in the IR spectrum, we then turned to an examination of the effect of the counter ion on the frequency of the carbonyl bands. A number of salts of the trication **4** were prepared, some contaminated with starting material (vide supra) but all showing characteristic carbonyl bands in the IR spectrum. Table 5 shows the salts and the frequencies of the carbonyl bands.

From the table it can be seen that there are three groups of salts with different frequencies for the A_1 band; (i) the halides and citrate, (ii) the tetraphenylborate and hexafluorophosphate, and (iii) the triflate and trifluoroacetate. The tetrafluoroborate A_1 carbonyl band is at a similar frequency to that observed with the halide anion, but its E band is at higher frequencies. These changes in frequency of the reporter carbonyl substituent can be interpreted in terms of host–guest interaction. The halides and citrate are most effective at quenching the positive charge on **4** and decrease the electron withdrawing effect of the DABCO substituents. The bulkier tetraphenylborate and hexafluorophosphate anions have the charge dispersed and are less effective, the A_1 carbonyl band shifting to higher frequency because of the greater electron withdrawing effect. The triflate and

Table 5. Carbonyl bands of the IR spectrum in KBr of salt **4** with various counter ions

Counter ion	ν_{CO} (A_1) cm^{-1}	ν_{CO} (E) cm^{-1}
Bromide	1981	1909
Iodide	1983	1911
Citrate	1984	1917, 1896
Tetrafluoroborate	1988	1933
Tetraphenylborate	1997	1943
Hexafluorophosphate	1997	1938, 1929
Triflate	2004	1957, 1939
Trifluoroacetate	2005	1949

trifluoroacetate ions with charge located on oxygen appear to be even less effective in charge quenching. The values of 2004 and 2005 cm^{-1} indicate that the arene ring in these derivatives is extremely electron deficient.[15] In all cases except citrate, three counterions are needed to quench the positive charges, and it appears likely that only the smaller ions can together approach the cationic centres without experiencing excessive coulombic repulsion. Only one citrate ion is required and coulombic repulsion between the anionic centres is, if anything, likely to be reduced.[20]

Since the $Cr(CO)_3$ group appeared to be acting as a reporter group for anion–cation interaction, we examined the IR spectra of **4a** with a number of benzene carboxylate anions in water. In all cases and with a variety of ratios of anion to cation, the mixtures showed, within experimental error, the same carbonyl frequencies as **4a** in water (1993, 1939 cm^{-1}). The water molecules are presumably solvating the anions and cations to such an extent that no change in the electron density of the arene occurs, even with benzene-1,3,5-tricarboxylate where the anion has the appropriate charge. This effect seems independent of the type of anion since the halide, BF_4^-, $CF_3CO_2^-$ and triflate salts in water all showed carbonyl bands at approximately the same frequencies. When the IR spectra of other polycations were examined in water, it was found that they showed similar changes of the carbonyl band frequencies as were observed in KBr. Thus **3a** has bands at 2002 and 1946 cm^{-1} compared to the bands at 1993 and 1939 cm^{-1} for **4a**. The three methyl groups on the benzene ring of **4a** are clearly donating electrons to the benzene system. A striking difference to the effect in water is seen in organic solvents. The hexafluorophosphate **4b** and tetraphenylborate **4e** salts are soluble in acetone and acetonitrile and the carbonyl bands in these solvents are at somewhat *lower* frequencies than in KBr (**4b** (acetone) 1988, 1926 cm^{-1}; (MeCN) 1991, 1930 cm^{-1}: **4e** (acetone) 1990, 1930 cm^{-1}; (MeCN) 1993, 1932 cm^{-1}). Clearly these solvents do not solvate the charged species and probably encourage tighter host: guest binding.

3. Conclusions

The studies of the association constants of these complexes were rather disappointing as it proved difficult to compare similar ^1H NMR chemical shift parameters for the complexed and uncomplexed cations. From the results obtained, however, it does appear that complexing the phenyl ring with $Cr(CO)_3$ has rather a small effect on its association with anions, the enforcement of the preferred piano stool conformation presumably being offset by the blocking of the other face to the approach of the counter ion. The $Cr(CO)_3$ group did not provide a suitable IR reporter group in water whose solvation properties effectively screen the polycation host from the electron-donating effect of the guest. The $Cr(CO)_3$ group can, however, act as an IR reporter group in the solid-state, where small ions and ions with matching charge more effectively quench the cationic charge on the DABCO substituents. There is an indication that the group may also be an IR reporter in organic solvents but more data are required. It will be of interest to explore other metal carbonyls to see if they have similar properties and, more interestingly, to prepare cationic, water soluble complexes similar to **11** but in which the arene rings are complexed to different metals as a means of studying a variety of interactions in this medium. Such studies are currently ongoing.

4. Experimental

Unless otherwise stated, all manipulations involving a metal-complexation reaction or involving the metal complexes themselves, except crystallisation, were carried out under an atmosphere of nitrogen, using standard vacuum line, Schlenk and glove box techniques. All solvents and reagents were obtained from commercial sources, and the reagents were used without further purification, except chromium hexacarbonyl, which was sublimed before use. Solvents used in complex-forming reactions and reactions of complexes were distilled under an atmosphere of nitrogen over drying agents. Dibutyl ether and decalin were distilled over sodium, methanol over magnesium methoxide, dichloromethane and acetonitrile over calcium hydride, diethyl ether over sodium/potassium alloy, THF over potassium, and butyl acetate over magnesium sulfate. The dried solvents were degassed and stored in ampules over activated 4 Å sieves or sodium mirrors. Glassware was dried at 110°C prior to use. Melting points were obtained using either a Reichert hot stage melting point apparatus or an Electrothermal 6910 melting point apparatus and are uncorrected. Where melting points are not reported the complex decomposed over a wide temperature range.

NMR spectra were recorded on Varian VXR-400, Bruker AMX400 and Bruker AC300 spectrometers. Proton NMR spectra were recorded at 400 or 300 MHz and carbon-13 spectra were recorded at 100 and 75 MHz on Varian VXR-400 and Bruker AMX400 or AC300 spectrometers. The solvent was used as internal reference except for samples in D_2O when the spectrometer was referenced to sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate. ^{13}C–^{14}N couplings were observed on expanded spectra. Mass spectra were recorded on a VG ZAB-SE mass spectrometer for both EI and 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. IR spectra were recorded on a Nicolet 205 FTIR spectrophotometer and electronic spectra were recorded on a Shimadzu UV-160A spectrophotometer. For IR studies in water a CaF_2 cell was used and spectra were recorded between 2200–1600 cm^{-1}. Elemental analyses were carried out by the Microanalytical Section of the Chemistry Department, University College London.

4.1. General procedure for the preparation of mono-*N*-substituted DABCO complexes as their halides

A solution of DABCO (1.05 equiv.) in acetonitrile was added to a solution of the appropriate aromatic halide complex (1.0 equiv.) in acetonitrile under nitrogen. The reaction mixture was stirred at room temperature for a period of hours. If precipitation had not occurred, diethyl ether (100 mL) was added and the reaction mixture was then stirred for a period of hours. The solvents were removed by filtration under nitrogen and the residue was washed with diethyl ether (2×25 mL) and dried in vacuo to give the halide salt. Analytical samples were prepared by crystallisation from warm acetonitrile, solutions being cooled to 4°C.

4.2. General procedure for preparation of mono-*N*-substituted DABCO complexes as their hexafluorophosphates

The halide salt of the DABCO complex was dissolved in the minimum amount of degassed water, under nitrogen, and a degassed, saturated aqueous solution of potassium hexafluorophosphate was added, with stirring, until no further precipitation occurred. The mixture was left to stand for a period of hours, and the resulting yellow precipitate was collected by filtration, washed with water (50 mL) and dried in vacuo to give the hexafluorophosphate salt. Analytical samples were prepared by crystallisation from a mixture of acetonitrile and methanol.

4.2.1. (η^6-Benzyl-DABCO)chromium tricarbonyl bromide (1a). (η^6-Benzyl bromide)chromium tricarbonyl (1.13 g, 3.68 mmol) in acetonitrile (45 mL) and DABCO (0.43 g, 3.86 mmol) in acetonitrile (25 mL) were treated as described in the general procedure. The reaction mixture was stirred for 47 h (precipitation occurred). Diethyl ether (100 mL) was added to the reaction mixture and the resulting suspension was stirred for 1.5 h as described in the general procedure to yield **1a** as a yellow solid (1.34 g, 3.20 mmol, 87%); mp 185–186°C (dec.); ^{1}H NMR (d$_6$-acetone) δ 3.25 (t, 6H, J=7.2 Hz), 3.87 (t, 6H, J=7.2 Hz), 4.72 (s, 2H), 5.70 (t, 2H, J=6.4 Hz), 5.78 (t, 1H, J=6.4 Hz), 6.13 (d, 2H, J=6.4 Hz; (D$_2$O) δ 3.09 (t, 6H, J=7.2 Hz), 3.41 (t, 6H, J=7.3 Hz), 4.15 (s, 2H), 5.49 (t, 2H, J=6.1 Hz), 5.61–5.68 (m, 3H); ^{13}C NMR (D$_2$O) δ 45.0, 53.0, 67.6, 93.4, 94.3, 96.4, 99.1, 233.0; IR (KBr) 2991, 2970, 2951, 1971, 1958, 1887, 1859, 1457, 1409, 1380, 1084, 1060, 834, 667, 633, 545 cm^{-1}; (H$_2$O) 1978, 1909 cm^{-1}; MS (FAB) (*m/z*) 339 (79), 255 (9), 203 (100), 91 (11); $C_{16}H_{19}N_2O_3Cr$ requires 339.0801. Found 339.0790. $C_{16}H_{19}N_2O_3BrCr$ requires C, 45.84; H, 4.57; N, 6.68; Br, 19.06. Found: C, 45.16; H, 4.30; N, 6.38; Br, 19.41.

4.2.2. (η^6-Benzyl-DABCO)chromium tricarbonyl hexafluorophosphate (1b). (η^6-Benzyl-DABCO)chromium tricarbonyl bromide (0.50 g, 1.19 mmol) was treated as described in the general procedure, being allowed to stand for 2.5 h, to give the hexafluorophosphate salt **1b** as a yellow solid (0.26 g, 0.54 mmol, 45%); mp 206–208°C (dec.); ^{1}H NMR (d$_6$-acetone) δ 3.32 (t, 6H, J=7.2 Hz), 3.75 (t, 6H, J=7.2 Hz), 4.49 (s, 2H), 5.74 (t, 2H, J=6.2 Hz), 5.85 (t, 1H, J=6.2 Hz), 5.96 (d, 2H, J=6.2 Hz); ^{13}C NMR (d$_6$-acetone) δ 45.7, 53.3, 67.2, 93.3, 95.3, 96.0, 99.0, 232.5; IR (KBr) 1986, 1972, 1897, 1887, 1464, 1084, 1060, 841, 662, 630, 558, 536 cm^{-1}; MS (FAB) (*m/z*) 339 (97), 227 (27), 203 (100); $C_{16}H_{19}N_2O_3Cr$ requires 339.0801. Found 339.0790. $C_{16}H_{19}N_2O_3F_6PCr$ requires C, 39.68; H, 3.95; N, 5.78. Found: C, 39.19; H, 3.93; N, 5.50.

4.2.3. (η^6-1,4-Bis{DABCO-*N*-methyl}benzene)chromium tricarbonyl dibromide (2a) and (η^6-1-{DABCO-*N*-methyl}-4-{bromomethyl}benzene)chromium tricarbonyl bromide (5). A solution of DABCO (1.17 g, 10.4 mmol) in acetonitrile (60 mL) was added to a solution of (η^6-1,4-bis{bromomethyl}benzene)chromium tricarbonyl (2.00 g, 5.00 mmol) in acetonitrile (40 mL) under nitrogen. The reaction mixture was stirred for 46 h during which time precipitate formed. Diethyl ether (250 mL) was added to the reaction mixture and the resulting suspension was stirred for 1 h. The solution was removed by filtration, leaving a precipitate which was washed with Et$_2$O and dried in vacuo to give **2a** as a yellow solid (2.20 g, 3.33 mmol, 67%); ^{1}H NMR (D$_2$O) δ 3.11 (t, 12H, J=6.8 Hz), 3.47 (t, 12H, J=6.8 Hz), 4.22 (s, 4H), 5.70 (s, 4H); ^{13}C NMR (D$_2$O) δ 45.1, 53.1, 67.0, 95.2, 97.0, 230.9; IR (KBr) 3458–3374, 1979, 1901, 1884, 1059, 620 cm^{-1}; MS (FAB) (*m/z*) 545 (2), 543 (2), 433 (99), 431 (100), 321 (35), 319 (34), 297 (70), 295 (75). $C_{23}H_{32}N_4O_3Br_2Cr{\cdot}2H_2O$ requires C, 41.83; H, 5.49; N, 8.48. Found: C, 42.27; H, 5.49; N, 8.81.

The filtrate was left to stand for 3 h, during which time yellow plates formed, and was then cooled to 4°C for 12 h. The mixture was filtered and the residue washed with cold Et$_2$O (25 mL) and dried in vacuo to give **5** as a yellow solid (0.34 g, 0.67 mmol, 13%); ^{1}H NMR (d$_6$-DMSO) δ 3.05 (t, 6H, J=6.9 Hz), 4.28 (s, 2H), 4.49 (s, 2H), 5.97 (d, 2H, J=6.8 Hz), 6.03 (d, 2H, J=6.8 Hz); ^{13}C NMR (d$_6$-DMSO) δ 32.0, 44.7, 51.8, 64.2, 94.5, 98.9, 109.1, 232.0; IR (KBr) 3040, 3002, 2959, 2881, 1968, 1919, 1915, 1886, 1231, 1201, 1158, 1077, 1053, 722, 692, 631, 608, 538, 522, 472 cm^{-1}; MS (FAB) (*m/z*) 948 (1), 946 (3), 944 (3), 942 (1), 809 (1), 807 (1), 433 (97), 431 (100). $C_{17}H_{20}N_2O_3Br_2Cr$ requires C, 39.87; H, 3.94; N, 5.47; Br, 31.20. Found: C, 40.59; H, 4.05; N, 5.60; Br, 29.40.

4.2.4. (η^6-1,4-Bis[DABCO-*N*-methyl] benzene)chromium tricarbonyl bis(hexafluoro-phosphate) (2b). (η^6-1,4 Bis[DABCO-*N*-methyl]benzene) chromium tricarbonyl dibromide **2a** (1.16 g, 1.86 mmol) was treated as described in the general procedure, being allowed to stand for 18 h, to give the hexafluorophosphate salt **2b** as a yellow solid (0.58 g, 0.77 mmol, 41%); mp 237–239°C (dec.); ^{1}H NMR (d$_6$-acetone) δ 3.29 (t, 12H, J=7.0 Hz), 3.68 (t, 12H, J=6.9 Hz), 4.54 (s, 4H), 6.07 (s 4H); ^{13}C NMR (d$_6$-acetone) δ 45.5, 53.3, 66.7, 96.3, 97.7, 230.9; IR (KBr) 1989, 1919, 1916, 1468, 1083, 1060, 839, 648, 620, 559, 532 cm^{-1}; $\lambda_{\max}$ (MeCN) 316 nm (11,300); MS (FAB) (*m/z*) 609 (83), 473 (100); $C_{23}H_{32}N_4O_3F_{12}P_2Cr$ requires 36.62; H, 4.27; N, 7.43. Found: C, 36.33; H, 4.37; N, 7.31.

4.2.5. (η^6-1,3,5-Tris{DABCO-*N*-methyl}benzene)chromium tricarbonyl tribromide (3a). η^6-1,3,5-Tris(bromomethyl)benzene chromium tricarbonyl (0.69 g, 1.40 mmol) in acetonitrile (45 mL) and DABCO (0.48 g, 4.24 mmol) in acetonitrile (30 mL) were treated as described in the general procedure. The reaction mixture was stirred for 95 h and no precipitation occurred. Diethyl ether (260 mL) was added to the reaction mixture and the resulting suspension was stirred for 1.5 h as described in the general procedure to yield **3a** as a pale orange solid (1.05 g, 1.27 mmol, 90%); mp 240–241°C (dec.); ^{1}H NMR (D$_2$O) δ 3.11 (br s, 18H), 3.55 (br s, 18H), 4.24 (s, 6H), 6.17 (s, 3H); ^{13}C NMR (D$_2$O) δ 45.1, 52.8, 66.6, 91.1, 102.7, 227.8; IR (KBr) 2963, 2925, 2891, 2852, 1989, 1923, 1639, 1462, 1262, 1083, 1058, 1026, 848, 800, 651, 613 cm^{-1}; MS (FAB) (*m/z*) 751 (19), 749 (39), 747 (19), 615 (14), 613 (32), 611 (16), 533 (14), 531 (16), 422 (41), 420 (37), 229 (56), 113 (100); $C_{30}H_{45}N_6O_3Br_2Cr$ requires 747.1325. Found 747.1348.

4.2.6. (η^6-1,3,5-Tris[DABCO-*N*-methyl]benzene)chromium tricarbonyl tris-(hexafluorophosphate) (3b). (η^6-1,3,5-Tris[DABCO-*N*-methyl]benzene)chromium tricarbonyl tribromide **3a** (0.35 g, 0.42 mmol) was treated as described in the general procedure, being allowed to stand for 2 h, to give the hexafluorophosphate salt **3b** as a pale orange solid (0.23 g, 0.22 mmol, 53%); ^{1}H NMR (d$_6$-acetone) δ 3.27 (br t, 18H, *J*=6.7 Hz), 3.68 (br t, 18H, *J*=6.7 Hz), 4.52 (s, 6H), 6.52 (s, 3H); ^{13}C NMR (d$_6$-acetone) δ 45.4, 53.1, 66.6, 92.0, 103.3, 227.5; IR (KBr) 2964, 2010, 1999, 1961, 1932, 1630, 1467, 1412, 1369, 1325, 1086, 1059, 998, 836, 648, 611, 559 cm^{-1}; MS (FAB) (*m/z*) 879 (61), 597 (21) 486 (42), 431 (24), 340 (10), 300 (21), 229 (51), 112 (100); $C_{30}H_{45}N_6O_3F_{12}P_2Cr$ requires 879.2242. Found: 879.2255. $C_{30}H_{45}N_6O_3F_{18}P_3Cr$ requires 35.17; H, 4.43; N, 8.20. Found: C, 34.36; H, 4.73; N, 7.93.

4.2.7. (η^6-1,3,5-Tris[DABCO-*N*-methyl]-2,4,6-trimethylbenzene)chromium tricarbonyl tribromide (4a). (η^6-1,3,5-Tris(bromomethyl)-2,4,6-trimethylbenzene)chromium tricarbonyl (1.57 g, 2.93 mmol) in acetonitrile (150 mL) and DABCO (3.29 g, 29.4 mmol) in acetonitrile (60 mL) were treated as described in the general procedure. The reaction mixture was stirred for 96 h when precipitation had occurred. The precipitate was removed by filtration under nitrogen, washed with MeCN (2×35 mL) and dried in vacuo to give **4a** as an orange solid (2.50 g; yield assuming 3H$_2$O, 2.70 mmol, 92%); mp 228–230°C (dec.); ^{1}H NMR (D$_2$O) δ 2.66 (s, 9H), 3.09 (t, 18H, *J*=6.9 Hz), 3.58 (t, 18H, *J*=6.9 Hz), 4.66 (s, 2H); ^{13}C NMR (D$_2$O) δ 23.1, 45.3, 53.2, 64.3, 94.9, 113.3, 228.4; IR (KBr) 3551–3392, 2950, 2859, 1981, 1909, 1464, 1262, 1060, 1024 cm^{-1}; λ_{max} (H$_2$O) 326 nm (12,300); MS (FAB) (*m/z*) 793 (8), 791 (17), 789 (9), 600 (10), 598 (9), 545 (7), 541 (6), 271 (41), 159 (41), 113 (100); $C_{33}H_{51}N_6O_3Br_3Cr\cdot 3H_2O$ requires C, 42.82, H, 6.21; N, 9.08; Br, 25.90. Found C, 42.66; H, 6.25; N, 8.94; Br, 25.21.

4.2.8. (η^6-1,3,5-Tris[DABCO-*N*-methyl]-2,4,6-trimethylbenzene)chromium tricarbonyl tris-(hexafluorophosphate) (4b). (η^6-1,3,5- Tris[DABCO-*N*-methyl]-2,4,6-trimethylbenzene)chromium tricarbonyl tribromide **4a** (0.20 g, 0.23 mmol) was treated as described in the general procedure, being allowed to stand for 2 h, to give the hexafluorophosphate salt **4b** as an orange solid (0.21 g, 0.20 mmol, 86%); mp 265–266°C (dec.); ^{1}H NMR (d$_6$-acetone) δ 3.06 (s, 9H), 3.23 (t, 18H, *J*=6.9 Hz), 3.72 (t, 18H, *J*=6.9 Hz), 5.03 (s, 6H); ^{13}C NMR (d$_6$-acetone) δ 22.7, 45.8, 53.4, 63.7, 95.4, 115.2, 228.5; IR (KBr) 2953, 2902, 1997, 1938, 1929, 1638, 1510, 1469, 1376, 1262, 1062, 1026, 998, 842, 661, 610, 559 cm^{-1}; (acetone) 1988, 1926 cm^{-1}; (MeCN) 1991, 1930 cm^{-1}; λ_{max} 325 nm (11,800); MS (FAB) (*m/z*) 921 (42), 785 (75) 136 (50), 113 (100); $C_{33}H_{51}N_6O_3F_{12}P_2Cr$ requires 921.2711. Found: 921.2742.

4.2.9. (η^6-1,3,5-Tris[DABCO-*N*-methyl]-2,4,6-trimethylbenzene)chromium tricarbonyl triiodide (4d). (η^6-1,3,5-Tris(iodomethyl)-2,4,6-trimethylbenzene)chromium tricarbonyl (0.20 g, 0.30 mmol) in acetonitrile (70 mL) and DABCO (0.33 g, 2.96 mmol) in acetonitrile (30 mL) were treated as described in the general procedure. The reaction mixture was stirred for 96 h when no precipitation had occurred. Diethyl ether (100 mL) was added, the mixture stirred and the product isolated as in the general procedure to give **4d** as an orange solid (0.19 g, 0.19 mmol, 63%); ^{1}H NMR (D$_2$O) δ 2.69 (s, 9H), 3.10 (br s, 18H), 3.60 (br s, 18H); IR (KBr) 2997, 2959, 2887, 1983, 1911, 1623, 1510, 1490, 1462, 1431, 1407, 1374, 1320, 1261, 1190, 1059, 1023, 994, 885, 857, 801, 659, 611, 537, 472 cm^{-1}; MS (FAB) (*m/z*) 887 (0.3), 751 (0.2), 524 (3), 397 (5) 128 (12), 113 (91), 39 (100); $C_{33}H_{51}N_6O_3I_2Cr$ requires 885.1517. Found 885.1504.

4.2.10. (η^6-1,3,5-Tris[DABCO-*N*-methyl]-2,4,6-trimethylbenzene)chromium tricarbonyl tris-(tetraphenylborate) (4e). Sodium tetraphenylborate (5% in water, 78 mL, 11.40 mmol) was added, with stirring, to a solution of **4a** (0.32 g, 0.37 mmol) in water (20 mL). On addition a fine, pale brown precipitate was formed. The mixture was stirred for 5 min and was then allowed to stand for 5 h, after which time the precipitate was removed by filtration, washed with water (100 mL) and dried in vacuo to give **4e** as a pale brown solid (0.46 g, 0.29 mmol, 79%); mp 209–212°C (dec.); ^{1}H NMR (d$_6$-acetone) δ 3.07 (br m, 34H), 3.61 (br s, 13H), 4.97 (s, 4H), 6.82 (t, 13H, *J*=6.9 Hz), 6.97 (t, 23H, *J*=7.1 Hz), 7.36 (s, 24H); ^{13}C NMR (d$_6$-acetone) δ 22.9, 46.0, 53.9, 64.2, 95.1, 114.8, 122.3, 126.0, 136.8, 164.1, 164.5, 165.0, 165.5, 228.5; IR (KBr) 3054, 3035, 2999, 2953, 1997, 1943, 1617, 1579, 1480, 1461, 1428, 1372, 1263, 1060, 1029, 990, 848, 745, 711, 651, 609, 533, 466 cm^{-1}; (acetone) 1990, 1930 cm^{-1}; (MeCN) 1993, 1932 cm^{-1}; MS (FAB) (*m/z*) 1271 (3), 1269 (3), 1133 (3), 702 (16), 112 (100); $C_{81}H_{91}N_6O_3B_2Cr$ requires 1269.6744. Found: 1269.6793.

4.3. General procedures for the preparation of *N*,*N*′-disubstituted DABCO complexes as their halide salts

The appropriate mono-*N*-substituted DABCO derivative was added to a solution of the appropriate aromatic halide complex in acetonitrile under nitrogen. The reaction mixture was either stirred at room temperature for between 2–11 days or it was stirred at between 35–40°C for ca. 70 h during which time precipitation occurred. The precipitate was removed by filtration under nitrogen, washed with acetonitrile and dried in vacuo to give the product as an orange solid.

4.4. General procedure for the preparation of *N*,*N*′-disubstituted DABCO complexes as their hexafluorophosphate salts

The halide salt was dissolved in a minimum amount of degassed water, the solution stirred and a degassed, saturated aqueous solution of potassium hexafluorophosphate was then added until no further precipitation was seen to occur. The reaction mixture was left to stand at room temperature for between 1–18 h, and the precipitate was then isolated by filtration under nitrogen. The precipitate was washed with water and dried in vacuo to give the hexafluorophosphate salt as a yellow or orange solid.

4.4.1. (η^6-{*N*′-2-Propyl-DABCO-*N*-methyl}benzene)-chromium tricarbonyl dibromide (7a). (η^6-Bromobenzyl)chromium tricarbonyl (0.40 g, 1.30 mmol) and *N*-2-propyl-DABCO bromide (0.52 g, 2.21 mmol) in acetonitrile (50 mL) were treated at room temperature as described in the general procedure. The reaction mixture was stirred for 70 h, and the resulting precipitate was collected by filtration under nitrogen, washed with acetonitrile (2×40 mL) and dried in vacuo to give **7a** as a yellow solid (0.35 g, 0.65 mmol, 49%); ^{1}H NMR (D_2O) δ 1.35 (d, 6H, J=6.4 Hz), 3.85 (br, s, 7H), 3.99 (br, s, 6H), 4.47 (s, 2H), 5.50 (t, 2H, J=6.1 Hz), 5.66 (t, 1H, J=6.0 Hz), 5.71 (d, 2H, J=6.0 Hz); ^{13}C NMR (D_2O) δ 16.2, 49.2, 51.9, 68.0, 69.5, 92.3, 93.2, 96.6, 98.7, 232.5; IR (KBr) 2986, 2968, 1989, 1974, 1922, 1890, 1462, 1416, 1396, 1262, 1117, 1088, 1059, 1020, 837, 805, 657, 622, 531, 476 cm^{-1}; MS (FAB) (*m*/*z*) 463 (2), 461 (2), 381 (3), 325 (7), 281 (5), 245 (10), 203 (14), 155 (100); $C_{19}H_{26}N_2O_3BrCr$ requires 461.0532. Found: 461.0517.

4.4.2. (η^6-[*N*′-2-Propyl-DABCO-*N*-methyl]benzene)chromium tricarbonyl bis-(hexafluorophosphate) (7b). (η^6-[*N*′-2-Propyl-DABCO-*N*-methyl]benzene)chromium tricarbonyl dibromide (0.19 g, 0.35 mmol) was treated as described in the general procedure, being allowed to stand for 1 h, to give the hexafluorophosphate salt **7b** as a yellow solid (0.14 g, 0.21 mmol, 59%); mp 238–239°C (dec.); ^{1}H NMR (d_6-acetone) δ 1.61 (d, 6H, J=6.2 Hz), 4.21 (septet, 1H, J= 6.2 Hz), 4.30 (t, 6H, J=7.1 Hz), 4.47 (t, 6H, J=7.1 Hz), 4.91 (s, 2H), 5.73 (t, 2H, J=6.4 Hz), 5.89 (t, 1H, J=6.4 Hz), 6.06 (d, 2H, J=6.4 Hz); ^{13}C NMR (d_6-acetone) δ 16.0, 49.4, 52.2 (t, J ^{13}C–^{14}N)=10.6 Hz), 67.5, 69.1, 93.0, 93.5, 96.5, 98.9, 232.1; IR (KBr) 2961, 2002, 1980, 1919, 1894, 1619, 1479, 1118, 1084, 837, 657, 618, 559 cm^{-1}; MS (FAB) (*m*/*z*) 527 (17), 391 (10), 245 (13), 155 (100); $C_{19}H_{26}N_2O_3F_6PCr$ requires 527.0990. Found: 527.0985.

4.4.3. (η^6-1,4-Bis{*N*′-2-propyl-DABCO-*N*-methyl}benzene)chromium tricarbonyl tetrabromide (8a). *N*-(2-Propyl)-DABCO bromide (0.54 g, 2.30 mmol), (η^6-1,4-bis{bromomethyl}benzene)chromium tricarbonyl (0.37 g, 0.93 mmol) and acetonitrile (50 mL) were stirred at room temperature for 47 h as described in the general procedure. The precipitate removed by filtration under nitrogen, washed with acetonitrile (2×30 mL) and dried in vacuo to leave **8a** as a yellow solid (0.30 g, 0.34 mmol, 37%); ^{1}H NMR (D_2O) δ 1.35 (d, 12H, J=6.5 Hz) 3.72 (m, 2H), 3.85 (br s, 12H), 3.95 (br s, 12H), 4.39 (s, 2H), 4.46 (s, 2H), 5.51 (d, 2H, J= 6.5 Hz), 5.78 (d 2H, J=6.5 Hz); ^{13}C NMR (D_2O) δ 16.2, 49.3, 51.9, 62.4, 67.5, 69.5, 91.4, 98.6, 114.0, 117.8, 232.3; IR (KBr) 2985, 1973, 1897, 1627, 1475, 1464, 1415, 1398, 1119, 1084, 1061, 856, 839, 673, 648, 622, 530, cm^{-1}; MS (FAB) (*m*/*z*) 793 (2), 791 (3), 789 (5), 787 (2), 655 (9), 653 (8), 421 (29), 419 (62), 417 (34), 339 (46), 297 (40), 295 (42), 156 (100); $C_{29}H_{46}N_4O_3Br_3Cr$ requires 787.0525. Found: 787.0498.

4.4.4. (η^6-1,4-Bis{*N*′-2-propyl-DABCO-*N*-methyl}benzene)chromium tricarbonyl tetrakis(hexafluorophosphate) (8b). (η^6-1,4-Bis[*N*′-2-propyl-DABCO-*N*-methyl]-benzene)chromium tricarbonyl tetrabromide (**8a**) (0.15 g, 0.17 mmol) was treated as described in the general procedure, being allowed to stand for 18 h, to give the hexafluorophosphate salt **8b** as a yellow solid (0.05 g, 0.04 mmol, 26%); ^{1}H NMR (d_6-acetone) δ 1.60 (d, 12H, J=6.5 Hz), 4.22 (m, 2H), 4.31 (t, 12H, J=6.7 Hz), 4.48 (t, 12H, J= 6.7 Hz), 4.52 (s, 2H), 4.89 (s, 2H), 5.73 (d, 2H, J=6.6 Hz), 6.12 (d, 2H, J=6.6 Hz); ^{13}C NMR (d_6-acetone) δ 16.0, 49.4, 52.1, 62.2, 67.1, 69.1, 90.8, 92.0, 99.0, 116.4, 232.0; IR (KBr) 3069, 2971, 2957, 2913, 1983, 1903, 1891, 1643, 1428, 1401, 1118, 1046, 841, 622, 559 cm^{-1}; MS (FAB) (*m*/*z*) 849 (2), 557 (10), 155 (100).

4.4.5. (η^6-1,4-Bis{*N*′-methyl-DABCO-*N*-methyl}benzene)chromium tricarbonyl tetrabromide (9). *N*-Methyl-DABCO bromide (1.11 g, 5.38 mmol), (η^6-1,4-bis{bromomethyl}benzene)-chromium tricarbonyl (0.43 g, 1.08 mmol) and acetonitrile (80 mL) were stirred for 23 h at 35–40°C as described in the general procedure. The reaction mixture was allowed to cool to room temperature and the precipitate removed by filtration under nitrogen, washed with acetonitrile (2×30 mL) and dried in vacuo to give **9** as a yellow solid (0.41 g, 0.50 mmol, 47%). Further attempts to purify this further were unsuccessful. ^{1}H NMR (D_2O) δ 3.23 (br s, 6H), 3.87 (br s, 18H), 4.36 (s, 2H), 4.45 (s, 2 Hz), 5.47 (t, 2H, J=6.5 Hz), 5.75 (t, 2H, J=6.4 Hz); ^{13}C NMR (D_2O) δ 44.7, 51.8, 54.1, 62.4, 67.8, 91.3, 98.6, 114.0, 119.9, 232.2; IR (KBr) 3006, 1971, 1903, 1888, 1628, 1470, 1383, 1261, 1122, 1059, 1020, 850, 654, 623, 531 cm^{-1}; MS (FAB) (*m*/*z*) 738 (0.1), 736 (0.1), 600 (0.2), 598 (0.9), 596 (0.7), 389 (4), 393 (4), 335 (3), 127 (100).

4.4.6. *N*,*N*′-Bis(η^6-benzyl chromium tricarbonyl)-1,4-diazabicyclo[2.2.2]octane dibromide (11). Acetonitrile (95 mL) was added to a mixture of (η^6-benzyl bromide)-chromium tricarbonyl (0.45 g, 1.47 mmol) and (η^6-benzyl-DABCO)chromium tricarbonyl bromide (0.53 g, 1.27 mmol), under nitrogen. The reaction mixture was stirred at room temperature for 3 days, during which time a yellow precipitate formed. The precipitate was removed by filtration, washed with acetonitrile and dried in vacuo to give **11** as a yellow solid (0.26 g, 0.36 mmol, 28%); mp 189–192°C (dec.); ^{1}H NMR (d_6-DMSO) δ 3.99 (s, 12H), 4.59 (s, 4H), 5.84 (t, 4H, J=6.2 Hz), 5.92 (t, 2H, J=6.3 Hz), 5.98 (d, 4H, J=6.3 Hz); ^{13}C NMR (d_6-DMSO) δ 50.4, 64.8, 93.8, 95.2, 96.5, 99.2, 232.4; IR (KBr) 3562–3428, 2976, 1969, 1904, 1876, 1256, 1211, 1091, 852, 838, 798, 656, 627, 608, 543, 477 cm^{-1}; MS (FAB) (*m*/*z*) 759 (6), 757 (5), 339 (37), 227 (44), 203 (100); $C_{32}H_{38}N_4O_6BrCr_2$ requires 757.0785. Found: 757.0793.

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