

X-Ray Crystallographic Studies of Tricarbonylchromium Complexes of Calix[4]arene Conformers: On an Unusual Conformation Which Appears in Cone Conformers *

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Abstract. The structures of three arene-tricarbonylchromium complexes prepared from cone and 1,3-alternate-25,26,27,28-tetrapropoxycalix[4]arene(**1**) and Cr(CO)₆ were determined by single crystal X-ray studies. Crystal data for 1,3-alternate-**1**•Cr(CO)₃ are space group *P*2₁/*a*, *a*=19.496(3)Å, *b*=11.118(2)Å, *c*=19.121(2)Å, β =109.95°(1) and *V*=3895Å³. The structure was refined to *R*_w=0.068. Crystal data for cone-**1**•Cr(CO)₃ are space group *P*2₁/*a*, *a*=21.457(4)Å, *b*=12.184(1)Å, *c*=14.816(2)Å, β =91.61°(1) and *V*=3872Å³. The structure was refined to *R*_w=0.077. Crystal data for cone-**1**•2Cr(CO)₃ are space group *P*2₁/*a*, *a*=18.019(3)Å, *b*=41.347(4)Å, *c*=11.743(2)Å, β =97.39°(1) and *V*=8676Å³. The single crystal included two similar but slightly different structures but the data were successfully refined to *R*_w=0.092. The structure of 1,3-alternate-**1**•Cr(CO)₃ differs only slightly from that of the regular 1,3-alternate calix[4]arene. In contrast, cone-**1**•Cr(CO)₃ and cone-**1**•2Cr(CO)₃ show an unusual conformation with a pair of faced gable-like roofs, which is considerably distorted from the regular cone calix[4]arene. The origin of this distortion is discussed in combination with the spectral studies.

Key Words: Calixarenes, arenetricarbonylchromium, crystal structure.

1. Introduction

Calix[*n*]arenes are a class of cavity-shaped macrocycles composed of *n* molecules of phenol and *n* molecules of formaldehyde. X-ray crystallographic studies of calix[*n*]arene derivatives have been continuously reported by Atwood *et al.* [1-4], Andreetti *et al.* [4-8], and others [9-11]. We have also carried out the structure determination of partial-cone conformers and a 1,3-alternate conformer of calix[4]arene derivatives [12-14]. More recently, we have synthesized arene-tricarbonylchromium complexes from cone, 1,2-alternate and 1,3-alternate conformers of 25,26,27,28-tetrapropoxycalix[4]arene (**1**) [15]. The purpose of the study was to selectively introduce the desired functional group into the desired benzene nucleus because tricarbonylchromium [Cr(CO)₃] forms stable η^6 -arene complexes and the complexed benzene nucleus becomes extraordinarily "reactive" [16-20].

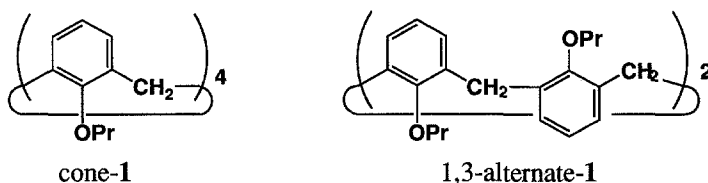
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This chemistry is also interesting from a stereochemical viewpoint: for example, (i) the molecular motion (*e.g.*, the rate of the oxygen-through-the-annulus rotation) of the benzene unit carrying a "heavy" $\text{Cr}(\text{CO})_3$ on its back should be different from that of the "free" benzene unit, (ii) introduction of $\text{Cr}(\text{CO})_3$ into the appropriate benzene unit in calix[4]arene conformers such as partial-cone and 1,2-alternate leads to the loss of molecular symmetry and therefore the products are optically-active [15] and (iii) the steric crowding increased by introduction of $\text{Cr}(\text{CO})_3$ should cause some steric distortion from regular calix[4]arene structures. In order to obtain basic insights into such stereochemical characteristics of calix[4]arene-tricarbonylchromium complexes we have carried out X-ray crystallographic studies on three complexes: cone-1• $\text{Cr}(\text{CO})_3$ (1:1 complex of **1** with a cone conformation), cone-1•2 $\text{Cr}(\text{CO})_3$ (distal 1:2 complex of **1** with a cone conformation) and 1,3-alternate-1• $\text{Cr}(\text{CO})_3$ (1:1 complex of **1** with a 1,3-alternate conformation). We find that the basic skeletons of calix[4]arene are surprisingly distorted by complexation with $\text{Cr}(\text{CO})_3$.



2. Experimental

2.1. MATERIALS

Preparations of cone-1• $\text{Cr}(\text{CO})_3$, cone-1•2 $\text{Cr}(\text{CO})_3$ and 1,3-alternate-1• $\text{Cr}(\text{CO})_3$ have been described previously[15]. Single crystals of these complexes were prepared by recrystallization from methanol-dichloromethane for the cone-1 complexes and from acetonitrile for the 1,3-alternate complex.

2.2. X-RAY CRYSTALLOGRAPHY

Integral intensities were collected by using $\text{Cu-K}\alpha$ radiation by the ω - 2θ scan technique up to $2\theta = 130^\circ$. Absorption correction was made routinely. The intensities of the reflections in 1,3-alternate-1• $\text{Cr}(\text{CO})_3$, cone-1• $\text{Cr}(\text{CO})_3$ and cone-1•2 $\text{Cr}(\text{CO})_3$ decreased by 0.01%, 0.02% and 0.07% per hour, respectively. The structures were solved by direct methods (MULTAN 11/82 [21] for the 1,3-alternate-1 complex and SIR88 [22] for the cone-1 complexes) and then refined by the full-matrix least-squares procedure with anisotropic thermal parameters. Hydrogen atoms were included in refinement except for cone-1•2 $\text{Cr}(\text{CO})_3$. Crystal data thus obtained are summarized in Table I.

Table I. Summary of crystal data and intensity collection for complexes of **1**.

Compound	Cone- 1 •Cr(CO) ₃	Cone- 1 •2Cr(CO) ₃	1,3-Alternate- 1 •Cr(CO) ₃
Formula	C ₄₃ H ₄₈ O ₇ Cr	C ₄₆ H ₄₈ O ₁₀ Cr ₂	C ₄₃ H ₄₈ O ₇ Cr
<i>F</i> _w	728.85	864.88	728.85
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> , Å	21.457(4)	18.019(3)	19.496(3)
<i>b</i> , Å	12.184(1)	41.347(4)	11.118(2)
<i>c</i> , Å	14.816(2)	11.743(2)	19.121(2)
β, deg	91.61(1)	97.39(1)	109.95(1)
<i>V</i> , Å ³	3872	8676	3895
<i>D</i> _{calc} , g cm ⁻³	1.250	1.324	1.243
<i>Z</i>	4	8	4
Crystal size, mm	0.5x0.3x0.3	0.4x0.4x0.4	0.4x0.2x0.15
μ, cm ⁻¹	28.4	46.5	28.2
<i>T</i> , K	293	296	293
Rflns collected	7228	15773	7217
Independent rflns	6650	14207	6396
Std rflns	110	108	144
No. of data used in refinement	4018 [<i>I</i> _o > 3σ(<i>I</i> _o)]	7177 [<i>I</i> _o > 3σ(<i>I</i> _o)]	3059 [<i>I</i> _o > 3σ(<i>I</i> _o)]
Range of <i>h</i> , <i>k</i> , <i>l</i>	-25,0,0 to 25,14,17	-21,0,0 to 21,48,13	-22,0,0 to 22,13,22
<i>R</i>	0.058	0.067	0.056
<i>R</i> _w	0.077	0.092	0.068

3. Results and Discussion

3.1. STRUCTURE OF 1,3-ALTERNATE-1•Cr(CO)₃

X-Ray crystallographic studies on calix[4]arenes with a 1,3-alternate conformation have still been very limited. Bott *et al.* [4] found that conformationally-mobile 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetramethoxycalix[4]arene forms complexes with alkyl aluminiums and adopts a 1,3-alternate conformation in that crystal. Fujimoto *et al.* [14] and Verboom *et al.* [23] have reported the X-ray structures of 5,11,17,23-tetra-*tert*-butyl-25,26-bis(ethoxycarbonylmethoxy)-26,28-bis(2-pyridylmethoxy)calix[4]arene and 25,26,27,28-tetraethoxycalix[4]arene, respectively. These studies consistently show that, as suggested by theoretical calculations [24,25], four phenyl units are more or less parallel to each other, the dihedral angles to the mean plane of the four methylene groups being close to 90°.

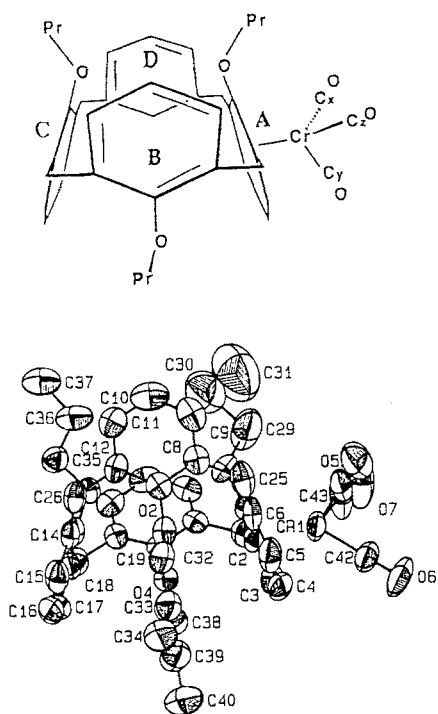


Fig. 1. Structure and ORTEP drawing of 1,3-alternate-1-Cr(CO)₃ with the thermal ellipsoids at the 50% probability level. Hydrogen atoms are deleted for clarity.

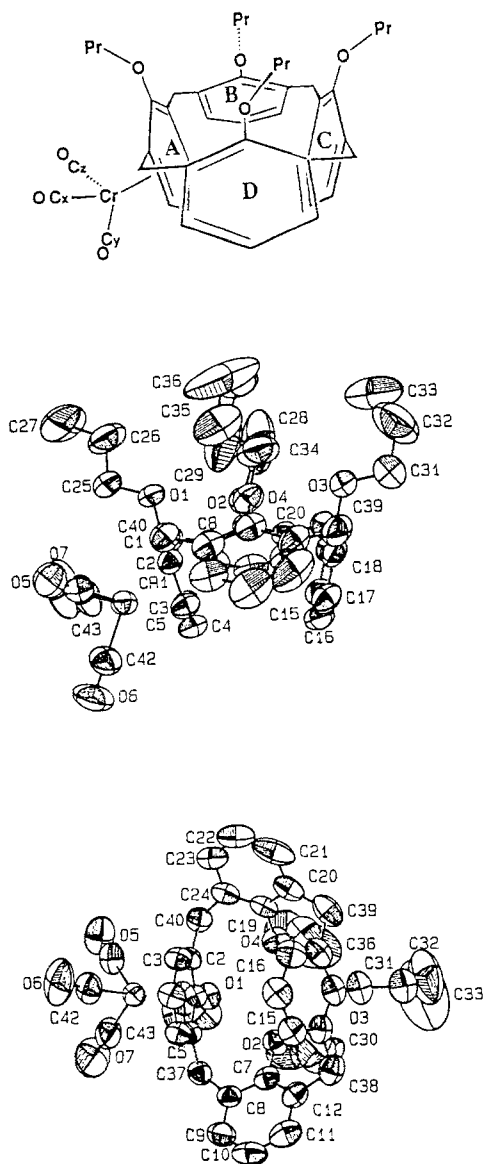


Fig. 2. Structure and ORTEP drawing of cone-1-Cr(CO)₃ with the thermal ellipsoids at the 50% probability level. Hydrogen atoms are deleted for clarity.

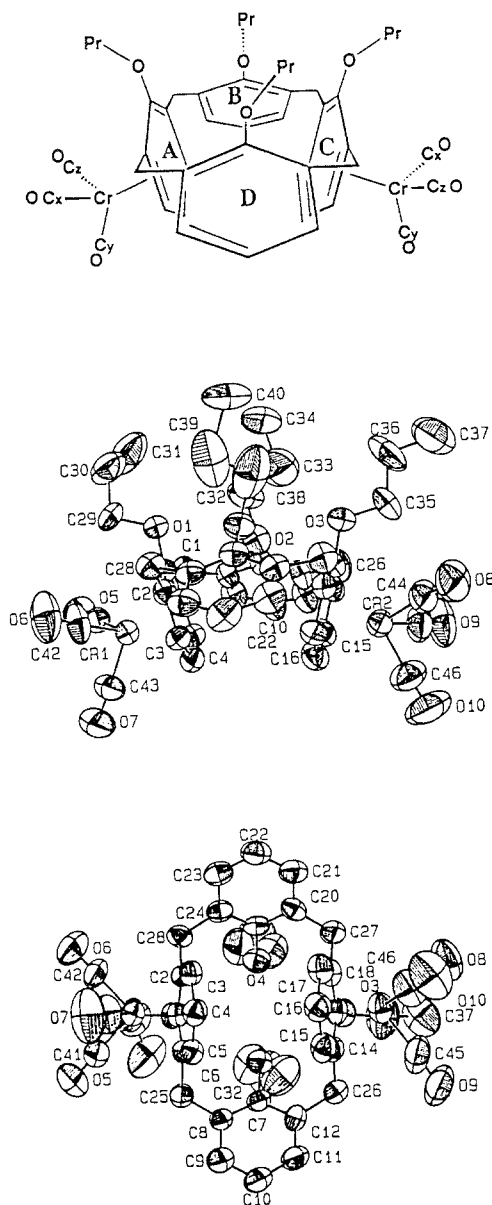


Fig. 3. Structure and ORTEP drawing of cone-1•2Cr(CO)₃ with the thermal ellipsoids at the 50% probability level. Hydrogen atoms are deleted for clarity.

The ORTEP drawing of 1,3-alternate-1•Cr(CO)₃ is shown in Fig. 1. Selected bond lengths and bond angles are summarized in Table II. In 1,3-alternate-1•Cr(CO)₃ the

dihedral angles of benzenes A, B, C and D against the mean plane of the four methylene groups are 105.2° , -115.2° , 113.3° and -111.5° , respectively.* The absolute values of the dihedral angles obtained from previous X-ray studies are 93.5 - 106.1° [4] and 75.6 - 77.8° [23] and those obtained from theoretical calculations are 91.75 - 91.93° [25]. One can thus conclude that the phenyl units in 1,3-alternate- $1\cdot\text{Cr}(\text{CO})_3$ are "flattened" to some extent. Conceivably, the steric crowding increased by introduction of the $\text{Cr}(\text{CO})_3$ group is relaxed by this conformational change. The bond angles for the ArCH_2Ar methylene groups were estimated to be 117.2 - 120.2° . These values are clearly greater than those for conventional 1,3-alternate calix[4]arenes (112.9 - 114.9° [4], 108.7 - 109.2° [23] and 115.1° [25]). This means that the flattening of the phenyl units inevitably causes the expansion of the ArCH_2Ar bond angles. It is also worthwhile mentioning that the $\text{O-CH}_2\text{-CH}_2\text{-CH}_3$ group in the $\text{Cr}(\text{CO})_3$ -complexed phenyl unit adopts a gauche conformation whereas those in the residual three phenyl units adopt an anti conformation. It seems that the gauche conformation acts to reduce the steric crowding.

In general, the structural change induced by $\text{Cr}(\text{CO})_3$ -complexation is relatively small, compared with those observed for cone- $1\cdot\text{Cr}(\text{CO})_3$ and cone- $1\cdot 2\text{Cr}(\text{CO})_3$ (*vide post*).

3.2. STRUCTURE OF CONE- $1\cdot\text{Cr}(\text{CO})_3$ AND CONE- $1\cdot 2\text{Cr}(\text{CO})_3$.

The ORTEP drawings of cone- $1\cdot\text{Cr}(\text{CO})_3$ and cone- $1\cdot 2\text{Cr}(\text{CO})_3$ are shown in Figs. 2 and 3. The single crystal of cone- $1\cdot 2\text{Cr}(\text{CO})_3$ included two similar but slightly different calix[4]arene structures in a 1:1 molar ratio. This explains $Z = 8$ for cone- $1\cdot 2\text{Cr}(\text{CO})_3$ in contrast to $Z = 4$ for cone- $1\cdot\text{Cr}(\text{CO})_3$.

At the first glance it seems from Figs. 2 and 3 that the structures of the $\text{Cr}(\text{CO})_3$ complexes differ appreciably from that of the regular cone conformation. In cone- $1\cdot\text{Cr}(\text{CO})_3$, a $\text{Cr}(\text{CO})_3$ -carrying phenyl unit (benzene A) and a phenyl unit (benzene C) distal to benzene A are turned towards the *exo*-annulus direction whereas the two remaining phenyl units (benzenes B and D) are flattened towards the *endo*-annulus direction (Fig. 2). The dihedral angles between the four phenyl rings and the mean plane of the four ArCH_2Ar methylene groups are 75.1° , 146.6° , 76.9° , and 144.3° (from A to D). In both structures of cone- $1\cdot 2\text{Cr}(\text{CO})_3$, two $\text{Cr}(\text{CO})_3$ -carrying phenyl units (benzenes A and C) are turned towards the *exo*-annulus direction whereas the two remaining phenyl units (benzenes B and D) are flattened towards the *endo*-annulus direction. The dihedral angles are 74.6° (76.6°), 152.1° (143.5°), 76.2° (72.4°) and 142.1° (142.7°) (from A to D: the angles in parentheses are those for the second structure). Thus, 1:1 and 1:2 cone- $1\cdot\text{Cr}(\text{CO})_3$ complexes may be described as having two benzene roofs confronting each other (we call it a "bis-roof" structure for convenience). Cone-calix[4]arenes have a

* The dihedral angle is defined as follows.

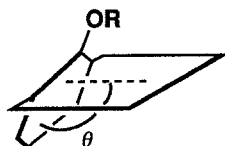


Table II Selected structural data for $1\cdot n\text{Cr}(\text{CO})_3$.

Compound ^{a)}		cone- $1\cdot\text{Cr}(\text{CO})_3$	cone- $1\cdot 2\text{Cr}(\text{CO})_3$ ^{b)}	1,3-alternate- $1\cdot\text{Cr}(\text{CO})_3$	
Dihedral angle θ , deg.	A	75.1(1)	74.6(1)[76.7(1)]	105.2(1)	
	B	146.6(1)	152.2(3)[143.5(3)]	-115.2(2)	
	C	76.21(9)	76.2(2)[72.4(2)]	113.3(1)	
	D	144.3(2)	142.1(2)[142.7(3)]	-111.5(1)	
Bond angle for the ArCH ₂ Ar methylene groups, deg.	A-CH ₂ -B	110.2(3)	108.7(5)[106.1(6)]	117.9(5)	
	B-CH ₂ -C	112.3(4)	109.3(6)[106.0(6)]	120.2(4)	
	C-CH ₂ -D	111.4(4)	106.6(6)[106.2(6)]	119.0(5)	
	D-CH ₂ -A	109.6(3)	107.2(5)[107.5(6)]	117.2(4)	
Distance, Å	Cr-C(1)	2.246(4)	2.252(6)[2.245(6)]	2.251(6)[2.250(7)]	2.263(4)
	Cr-C(2)	2.248(4)	2.273(6)[2.260(7)]	2.279(6)[2.264(7)]	2.282(5)
	Cr-C(3)	2.200(4)	2.251(7)[2.211(8)]	2.238(6)[2.228(7)]	2.202(6)
	Cr-C(4)	2.209(4)	2.220(6)[2.203(7)]	2.193(7)[2.212(7)]	2.179(6)
	Cr-C(5)	2.237(4)	2.237(6)[2.249(7)]	2.236(7)[2.233(7)]	2.205(6)
	Cr-C(6)	2.271(4)	2.239(6)[2.254(7)]	2.253(7)[2.256(7)]	2.260(4)
Torsion angle, deg. ^{c)}	C _x -Cr-C _g -C(2)	5.7	-0.2[-5.7]	-19.1[-13.7]	14.0
	C _y -Cr-C _g -C(4)	8.0	-4.0[-4.1]	-22.8[-12.8]	11.8
	C _z -Cr-C _g -C(6)	4.9	-2.0[-4.7]	-17.2[-10.5]	11.0
Distance between two <i>p</i> -carbons in benzenes A and C , Å		3.877(6)	3.81(1)[3.72(1)]	6.950(7)	
Distance between two <i>p</i> -carbons in benzenes B and D , Å		10.136(7)	10.25(1)[10.11(1)]	7.237(9)	

^{a)}Phenyl rings A-D and carbons x-z correspond to the lettering in shown in Figs. 1, 2 and 3.

^{b)}Numbers in [] are those for the second structure.

^{c)}C_g means an aromatic center of gravity.

skirt-like shape with an open upper side and a closed lower side. As a result, the four dihedral angles should be larger than 90°: for example, 135.48° and 96.68° for MM3-optimized 25,26,27,28-tetramethoxycalix[4]arene with C_{2v} symmetry [25] and 138°, 94°, 136° and 92° for X-ray-determined 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(ethoxycarbonylmethoxy)calix[4]arene [9].

Why do cone- $1\cdot\text{Cr}(\text{CO})_3$ and cone- $1\cdot 2\text{Cr}(\text{CO})_3$ adopt such an unusual "bis-roof" conformation? Careful examination of Figs. 2 and 3 reveals two structural characteristics of these complexes. The first characteristic is related to the position of Cr metal on the benzene ring. In conventional arene-tricarbonylchromium complexes Cr metal occupies the centro-position (C_g) on the benzene ring and the Cr-C_g line is perpendicular to the benzene plane [26-28]. In cone- $1\cdot\text{Cr}(\text{CO})_3$ and cone- $1\cdot\text{Cr}(\text{CO})_3$, on the other hand, Cr atom shifts to the *m*- or *p*-position side: in benzene **A** of cone- $1\cdot\text{Cr}(\text{CO})_3$, for example, the distances from Cr metal to 3-, 4- and 5-carbons are 2.20, 2.21 and 2.24 Å, respectively

whereas those from Cr-metal to 1-, 2- and 6-carbons are 2.25, 2.25 and 2.27 Å, respectively. A similar characteristic is also observed for cone-1•2Cr(CO)₃: in benzenes A and C the distances from Cr to 3-carbon are 2.20 (2.19) and 2.20 (2.21) Å, respectively whereas those from Cr to 1- and 2-carbons are 2.25 (2.25) and 2.27 (2.28) Å in benzene A and 2.25 (2.28) and 2.28 (2.26) Å in benzene C. We consider that this shift is induced by steric repulsion between Cr(CO)₃ and the propyl group. In fact, van der Waals radii of 4- and 16-carbons are nearly in contact with each other (Figs. 2 and 3). The second characteristic is related to the conformation of the propyl group. In tetrapropoxycalix[4]arenes the propyl groups tend to adopt the most stable *anti-zigzag* conformation. In cone-1•Cr(CO)₃ and cone-1•2Cr(CO)₃, in contrast, some propyl groups adopt a less stable *gauche* conformation. We consider that this conformation is favorable to relax the steric crowding around the propyl group [29].

Foregoing results support the view that the "bis-roof" structure is brought forth by the Cr(CO)₃-enhanced steric crowding on the lower rim. One of the characteristics of this structure is that the *p*-carbon in benzene A is very close to that in benzene C (only 3.88 Å for cone-1•Cr(CO)₃ and 3.81 (3.72) Å for cone-1•2Cr(CO)₃) whereas two *p*-carbons in benzenes B and D are very far (10.14 Å for cone-1•Cr(CO)₃ and 10.25 (10.10) Å for cone-1•2Cr(CO)₃). The unusual intramolecular proximity between confronting benzene units may be reflected by some spectral properties of the complexes. We examined the IR spectra (CH₂Cl₂ solvent) of cone-1•Cr(CO)₃ and cone-1•2Cr(CO)₃. We found that the $\nu_{C=O}$ bands for cone-1•Cr(CO)₃ (1951 and 1868 cm⁻¹) shift to lower wavenumber than those for cone-1•2Cr(CO)₃ (1961 and 1880 cm⁻¹). The shift to lower wavenumber means that the π -basicity in the Cr(CO)₃-carrying benzene unit in cone-1•Cr(CO)₃ is higher than that in cone-1•2Cr(CO)₃[30]. We consider that the difference is induced by the difference in the transannular interaction: that is, in cone-1•Cr(CO)₃ benzene A and benzene C act as an electron-acceptor and an electron-donor, respectively and interact with each other transannularly.

The above-mentioned characteristic is well reflected by the ¹H NMR spectra in solution (30 °C, CDCl₃) [15]. In cone-1•Cr(CO)₃, for example, the δ_H values for *m*-H and *p*-H in benzene C shift to higher magnetic field by 0.44 and 0.23 ppm, respectively, from those in tetrapropoxycalix[4]arene. This indicates that these protons move into the shielding area of benzene A. On the other hand, the δ_H values for *m*-H and *p*-H in benzenes B and D shift to lower magnetic field by 0.58 and 0.38 ppm, respectively. This indicates that these protons leave from the shielding area of benzene nuclei. We thus believe that cone-1•Cr(CO)₃ and cone-1•2Cr(CO)₃ adopt a "bis-roof" structure also in solution.

4. Conclusion

The purpose of the present study was, when it was commenced, regioselective introduction of functional groups into calix[4]arene nuclei. Through the study, however, we noticed that introduction of Cr(CO)₃ causes large conformational changes in a calix[4]arene skeleton and without the information on the conformational changes one cannot predict

the reactivities of nuclear substitution reactions. The X-ray crystallographic studies revealed that introduction of $\text{Cr}(\text{CO})_3$ increases the steric crowding and the conformational changes take place to enable the skeleton to relax the steric crowding. In particular, the "bis-roof" conformation observed for cone-1- $\text{Cr}(\text{CO})_3$ complexes is novel and can be classified into neither of the usual four conformations: cone, partial-cone, 1,2-alternate and 1,3-alternate. We believe that the structural information obtained here is useful for predicting the regioselective reaction course and the relative stability and steric crowding of calix[4]arene conformers.

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