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On the Unusual Conformation of Calix[4]arene Which Appears in the Tricarbonylchromium Complexes

Hideshi IKI, Taketoshi KIKUCHI, Hirohisa TSUZUKI,† and Seiji SHINKAI*
Department of Organic Synthesis, Faculty of Engineering,
Kyushu University, Fukuoka 812
†Center of Advanced Instrumental Analysis, Kyushu University, Kasuga, Fukuoka 816

The structures of arene-tricarbonylchromium complexes prepared from cone-25,26,27,28-tetrapropoxycalix[4]arene and $Cr(CO)_6$ were studied by an X-ray crystallographic method: they showed an unusual conformation with a pair of faced gable-like roofs, which is extraordinarily transformed from a cone conformation.

The chemistry of calixarenes has recently become a very active area of endeavor because of their potential as polyfunctional ligands, catalysts, and host molecules.1) One of the unique characteristics is the conformational isomerism: in smallest calix[4]arenes four different forms can exist which we now refer to as "cone", "partial-cone", "1,2-alternate", and "1,3-alternate" conformations. The conformational isomerism in calix[4]arenes has been investigated by X-ray crystallographic analysis,2,3) NMR spectroscopy,1-3) and computational analysis.4,5) We recently established that interconversion among these four conformers, which occurs through the oxygen-through-the-annulus rotation, can be inhibited by the *O*-substituent bulkier than the ethyl group (*e.g.*, *n*-propyl group).6) By using the *n*-propyl group as a rotation inhibitor we can synthesize all possible conformers derivable from calix[4]arene.6)

More recently, we synthesized several arene-tricarbonylchromium complexes from 25,26,27,28-tetrapropoxycalix[4]arene conformers (**1**Pr).7) The purpose of the investigation was the selective introduction of a functional group into the desired benzene unit which was activated through complexation with $Cr(CO)_3$.8) We determined the structure of several **1**Pr•$Cr(CO)_3$ complexes by an X-ray crystallographic method. Interestingly, we found that among them, the complex structure derived from cone-**1**Pr was extraordinarily transformed from the usual cone conformation.

In **1**Pr•$Cr(CO)_3$, a $Cr(CO)_3$-carrying phenyl unit (benzene A) and a phenyl unit (benzene C) distal to benzene A are largely turned towards the *exo*-annulus direction whereas the two remaining phenyl units (benzenes B and D) are extremely flattened towards the *endo*-annulus direction (Fig. 1).9) 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).10) The single crystal of **1**Pr•distal-2$Cr(CO)_3$ included two similar but slightly different calix[4]arene structures in a 1:1 molar ratio (Fig. 2).11) In both structures, two $Cr(CO)_3$-carrying phenyl units (benzenes A and C) are largely turned towards the *exo*-annulus direction whereas the two remaining phenyl units (benzenes B and D) are extremely 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

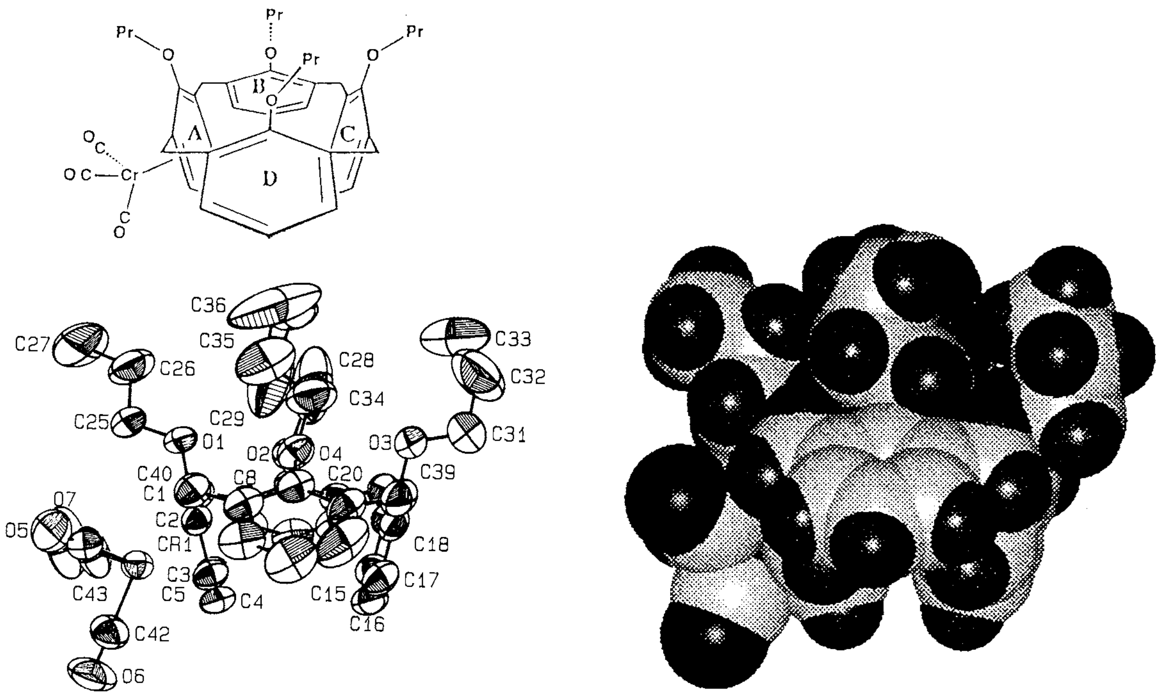

Fig. 1. Structure, ORTEP drawing and space-filling structure for 1Pr•$Cr(CO)_3$.

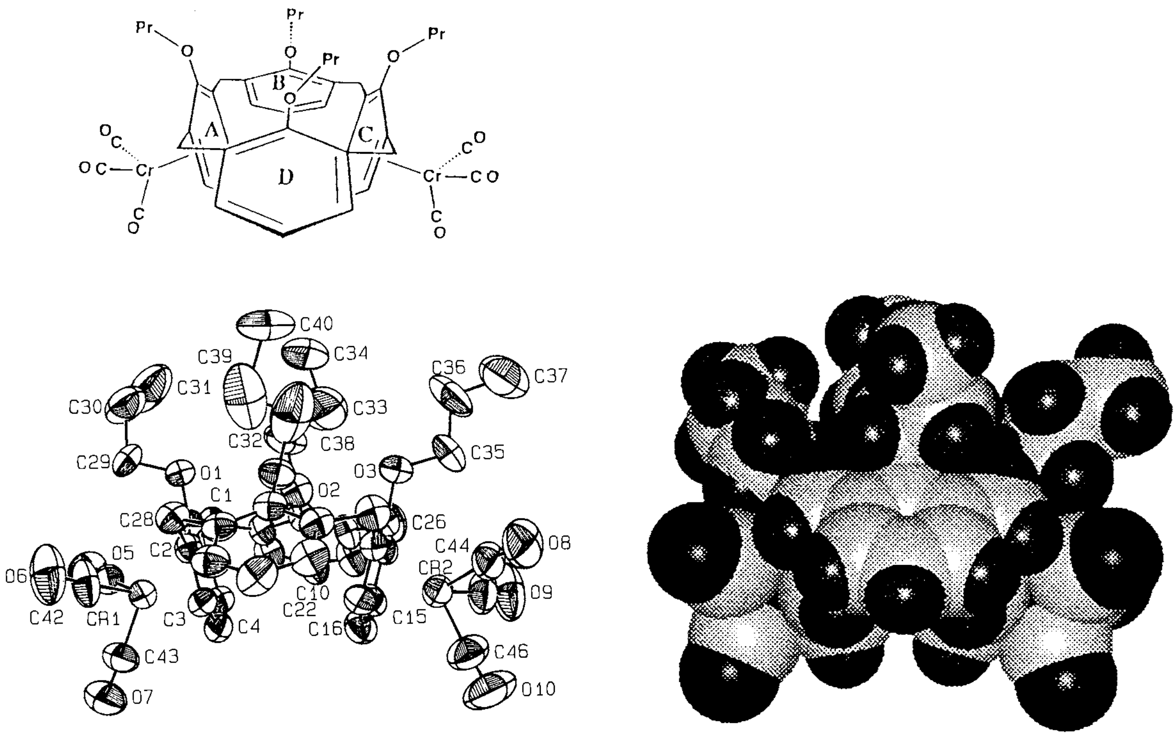

Fig. 2. Structure, ORTEP drawing and space-filling structure for 1Pr•distal-2$Cr(CO)_3$. A unit cell includes eight molecules with two slightly different structures in a 1:1 ratio. We here illustrate one of these two structure.

parentheses are those for the second structure). Thus, 1:1 and 1:2 **1Pr**/$Cr(CO)_3$ 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 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} symmetry5) and 121-125° for X-ray-determined 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrapropoxycalix[4]arene.12)

Why do **1Pr**•$Cr(CO)_3$ and **1Pr**•distal-2$Cr(CO)_3$ adopt such an unusual "bis-roof" conformation? Careful examination of Figs. 1 and 2 taught us 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.13) In **1Pr**•$Cr(CO)_3$ and **1Pr**•distal-2$Cr(CO)_3$, on the other hand, Cr metal shifts to the *m*- or *p*-position side: in benzene A of **1Pr**•$Cr(CO)_3$, 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. The similar characteristic is also observed for **1Pr**•distal-2$Cr(CO)_3$. 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 these atoms are nearly in contact with each other (Figs. 1 and 2). 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 **1Pr**•$Cr(CO)_3$ and **1Pr**•distal-2$Cr(CO)_3$, 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.

Foregoing results consistently 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 *p*-carbon in benzene A is very close to that in benzene C (only 3.88 Å for **1Pr**•$Cr(CO)_3$ and 3.81 (3.72) Å for **1Pr**•distal-2$Cr(CO)_3$) whereas two *p*-carbons in benzenes B and D are very far (10.14 Å for **1Pr**•$Cr(CO)_3$ and 10.25 (10.10) Å for **1Pr**•distal-2$Cr(CO)_3$). The unusual intramolecular proximity between faced benzene units may be reflected by some spectral properties of the complexes. We examined the IR spectra (CH_2Cl_2 solvent) of **1Pr**•$Cr(CO)_3$ and **1Pr**•distal-2$Cr(CO)_3$. We found that the $\nu_{c=o}$ bands for **1Pr**•$Cr(CO)_3$ (1951 and 1868 cm^{-1}) shift to lower wavenumber than those for **1Pr**•distal-2$Cr(CO)_3$ (1961 and 1880 cm^{-1}). The shift to lower wavenumber means that the π-basicity in the $Cr(CO)_3$-carrying benzene unit in **1Pr**•$Cr(CO)_3$ is higher than that in **1Pr**•distal-2$Cr(CO)_3$.14) We consider that the difference is induced by the difference in the transannular interaction: that is, in **1Pr**•$Cr(CO)_3$ 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 (30 °C, $CDCl_3$).7) In **1Pr**•$Cr(CO)_3$, for example, the δ_H 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 d_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 **1Pr**•$Cr(CO)_3$ and **1Pr**•distal-2$Cr(CO)_3$ adopt a "bis-roof" structure also in solution.

In conclusion, the present study demonstrated the presence of an unusual conformation of calix[4]arenes having faced two benzene roofs. We are now interested in inclusion properties of these "bis-roof" calix[4]arenes because they possess a novel inclusion cavity inside the calix[4]arene ring.

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9) Recrystallized from chloroform-ethanol. Crystal data: chemical formula $C_{43}H_{48}CrO_7$; *Fw* 728.85, crystal system, monoclinic; space group $P2_1/a$; $Z = 4$; $D_c = 1.250$ g cm^{-3}; cell dimensions, $a = 21.457$ (4) Å, $b = 12.184$ (1) Å, $c = 14.816$ (2) Å, b = 91.61 (1) deg; $R = 0.058$, $R_w = 0.077$ for 6396 independent reflections.

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11) Recrystallized from dichloromethane-methanol. Crystal data: chemical formula $C_{46}H_{48}Cr_2O_{10}$; *Fw* 864.88, crystal system, monoclinic; space group $P2_1/a$; $Z = 8$; $D_c = 1.324$ g cm^{-3}; cell dimensions, $a = 18.019$ (3) Å, $b = 41.347$ (4) Å, $c = 11.743$ (2) Å, b = 97.39 (1) deg; $R = 0.067$, $R_w = 0.092$ for 14207 independent reflections.

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