

Synthesis and Spectral Characterization of Tricarbonylchromium Complexes of Calix[4]arene Conformers

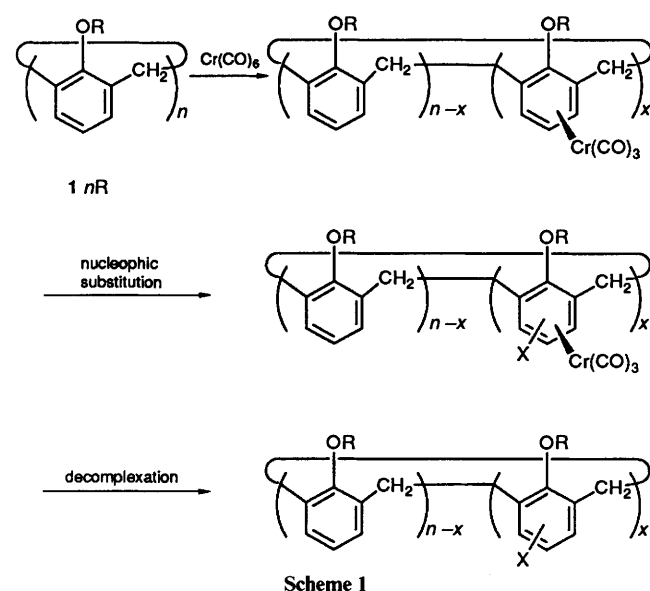
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Arene-tricarbonylchromium complexes were synthesized for the first time from cone, 1,2-alternate and 1,3-alternate conformers of 25,26,27,28-tetrapropoxycalix[4]arene.

Calix[*n*]arenes are cyclic oligomers which belong to the class of [*1_n*]-metacyclophanes. As calix[*n*]arenes have a cavity-shaped architecture, they are useful as building-blocks to design host-guest-type catalysts through appropriate modification of the edges.¹⁻⁴ To design such functionalized calix[*n*]arenes, it is indispensable to develop methods for the selective introduction of desired functional groups into the benzene nuclei. In fact, a few groups have so far attempted to develop such synthetic methods,⁵⁻⁹ but there exists no general methodology for selective introduction of functional groups. When taking into account that calix[*n*]arenes belong to the class of [*1_n*]metacyclophanes, we noticed that the formation of arene-tricarbonylchromium complexes may be utilized as a potential methodology for this purpose.¹⁰ It is known that tricarbonylchromium [Cr(CO)₃] forms stable η⁶-arene complexes and the complexed benzene ring becomes extraordinarily 'reactive'.¹⁰⁻¹³ We thus expected that the functional group would be selectively introduced into the benzene unit which was activated through complexation with Cr(CO)₃ (as shown in Scheme 1). This chemistry is also interesting from a stereochemical viewpoint: introduction of Cr(CO)₃ into the appropriate benzene ring in calix[4]arene conformers such as partial cone and 1,2-alternate leads to the loss of a plane of symmetry. One can thus expect the formation of ring-originating optically-active calix[4]arenes. As a prelude to this new chemistry we here report the first example of the synthesis and spectral characterization of Cr(CO)₃ complexes with three conformational isomers of 25,26,27,28-tetrapropoxycalix[4]arene (**1₄Pr**).

We first studied a Cr(CO)₃ complex with **1₄Me**, but the ¹H NMR spectrum of the product was too complex to assign. The complexity is related to conformational isomerism which takes place through the oxygen-through-the-annulus rotation.¹⁴⁻¹⁶



To avoid this complexity we employed conformationally-immobile **1₄Pr**.^{16,17} Conformational isomers of **1₄Pr** were synthesized in a manner similar to that described for their *p*-*tert*-butyl analogues.¹⁸

Cone-**1₄Pr** (0.30 g, 0.51 mmol) and Cr(CO)₆ (0.15 g, 0.52 mmol) were dissolved in a mixed solvent of dibutyl ether (27 cm³) and THF (3 cm³) and the solution was heated at 130 °C for 24 h. The solution was concentrated under reduced pressure, the oily residue being solidified by hexane. The solid product was purified by column chromatography [twice by silica gel and hexane-dichloromethane (5:1 v/v) and once by silica gel and benzene]. These operations were all carried out under the anaerobic (N₂) conditions: yellow prisms, m.p. 171.6–173.0 °C, yield 76% (Found: C, 71.05; H, 6.6. Calc. for C₄₃H₄₈CrO₇: C, 70.86; H, 6.64%). Cr(CO)₃ complexes with 1,2-alternate-**1₄Pr** and 1,3-alternate-**1₄Pr** were also synthesized in a similar manner from Cr(CO)₆ and corresponding conformers: 1,2-alternate-**1₄Pr**·Cr(CO)₃, m.p. (decomp.) 144 °C, yield 61% (Found: C, 70.8; H, 6.7. Calc. for C₄₃H₄₈CrO₇: C, 70.86; H, 6.64%). 1,3-Alternate-**1₄Pr**·Cr(CO)₃, m.p. 248.7–250.2 °C, yield 48% (Found: C, 70.6; H, 6.7. Calc. for C₄₃H₄₈CrO₇: C, 70.86; H, 6.64%). The elemental analysis data indicate that Cr(CO)₃ complexes with these three conformers are isolated as a 1:1 complex.† We also synthesized a Cr(CO)₃ complex with partial-cone-**1₄Pr**. We detected two major spots and several minor spots. This suggests that partial-cone-**1₄Pr**, which has three inequivalent benzene rings, results in the complex product distribution. We thus abandoned the isolation of this complex. As a noncyclic analogue we synthesized a Cr(CO)₃ complex with propyl 2,6-dimethylphenyl ether **2**: yellow prisms, m.p. 48.0–48.5 °C, yield 65% (Found: C, 55.8; H, 5.3. Calc. for C₁₄H₁₆CrO: C, 56.00; H, 5.37%).

The ¹H NMR spectra of the Cr(CO)₃ complexes were measured at 30 °C in CDCl₃. The chemical shifts of the calix[4]arene protons are recorded in Fig. 1. The assignment was completed with the aid of the ¹H–¹H COSY method and the nuclear Overhauser effect. It is seen from Fig. 1 that the protons on the benzene ring complexed with Cr(CO)₃ appear at higher magnetic field. The largest up-field shift was observed for *m*-protons in cone-**1₄Pr**·Cr(CO)₃ (Δδ = –2.60). This shift is rationalized in terms of the decreased benzene ring-current which induces the decrease in the magnetic deshielding effect. In 1,2-alternate-**1₄Pr**·Cr(CO)₃, the C–CH₂–C methylene protons in one of four propyl groups appeared at unusually high magnetic field (0.37–0.47 ppm; 0.92 ppm in uncomplexed 1,2-alternate-**1₄Pr**). This is attributed to the conformational change in the calix[4]arene skeleton because such an up-field shift is not observed for the C–CH₂–C protons in **2**·Cr(CO)₃ (1.80 ppm; 1.82 ppm in uncomplexed **2**). Thus, the up-field shift is explained

† When cone-**1₄Pr** and Cr(CO)₆ were mixed in a 1:4 mole ratio, the main product was a 1:1 complex but the presence of the 1:2 complex was also confirmed by ¹H NMR spectroscopy.

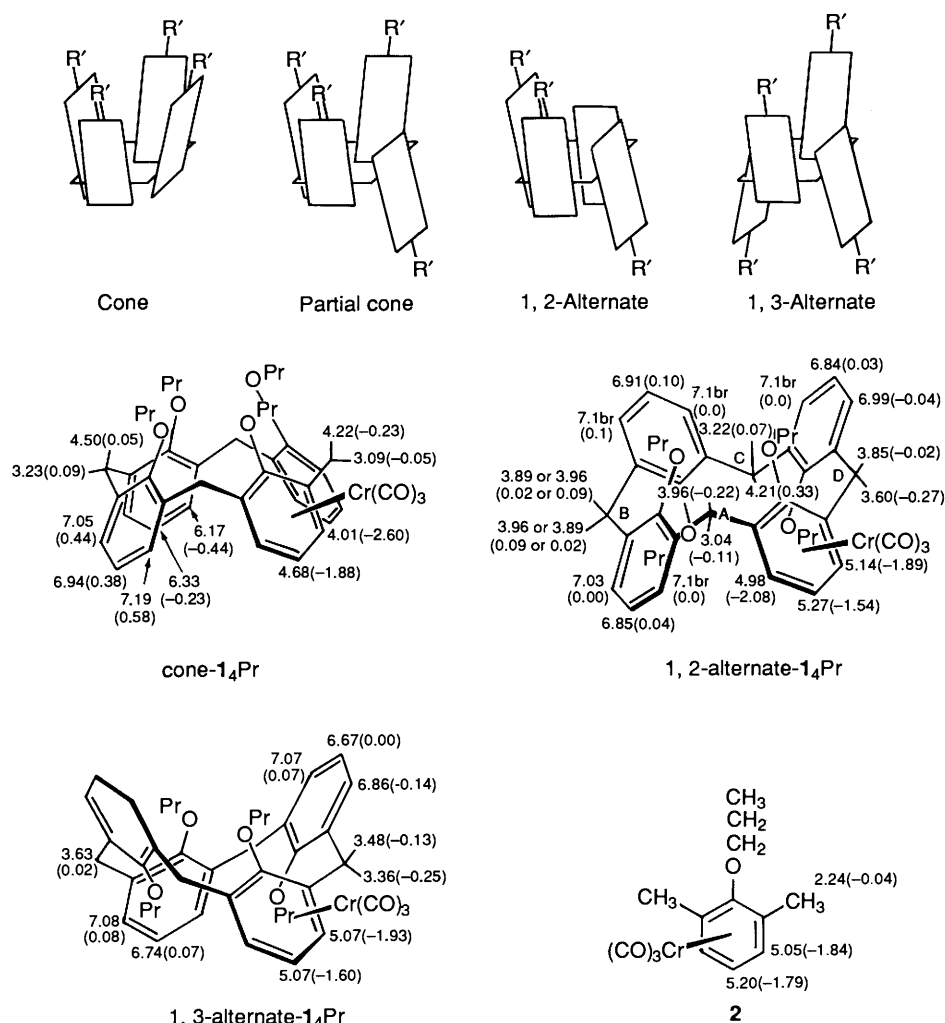


Fig. 1 Assignment of $\text{Cr}(\text{CO})_3$ complexes. The numbers indicate the chemical shifts (δ): 30 °C, CDCl_3 , $[\text{1}_4\text{Pr}] = 10\text{--}30 \text{ mmol dm}^{-3}$. The numbers in parentheses denote the shift from uncomplexed $\text{1}_4\text{Pr}$ (+ to lower magnetic field, - to higher magnetic field). In 1,2-alternate- $\text{1}_4\text{Pr}$, two ArCH_2Ar methylene protons at position B are not assigned precisely. In 1,3-alternate- $\text{1}_4\text{Pr}$, the *m*- and *p*-protons in the $\text{Cr}(\text{CO})_3$ -complexed benzene ring appeared as a singlet at 30 °C. At low temperature (-50 °C) or at high temperature (55 °C) it splits into a doublet and a triplet. This indicates that the chemical shifts for these protons are accidentally the same at 30 °C.

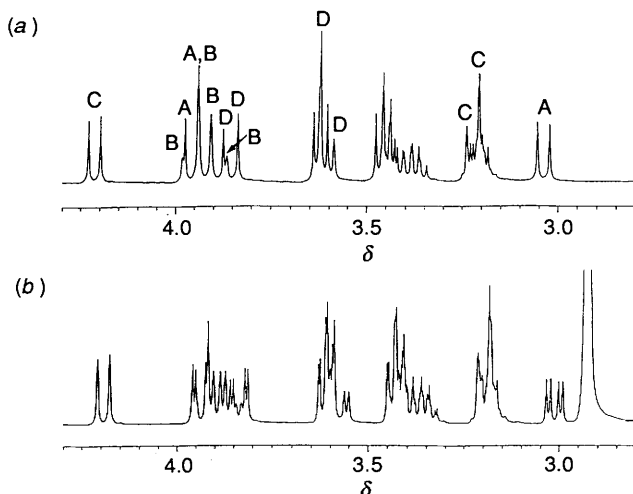


Fig. 2 Partial ^1H NMR spectra of 1,2-alternate- $\text{1}_4\text{Pr-Cr}(\text{CO})_3$ in the absence (a) and the presence (b) of Pirkle's reagent: 30 °C, CDCl_3 , $[\text{1,2-alternate-1}_4\text{Pr}] = 14 \text{ mmol dm}^{-3}$, $[\text{Pirkle's reagent}] = 140 \text{ mmol dm}^{-3}$. The peaks A-D correspond to the lettering shown in Fig. 1.

in relation to the 'flattening' of a phenyl unit, rendering the propyl group into the cavity composed of benzene rings. At present, we cannot specify which benzene ring is flattened.

Of further interest is the ^1H NMR spectrum of 1,2-alternate- $\text{1}_4\text{Pr-Cr}(\text{CO})_3$ in the presence of a chiral shift reagent, Pirkle's reagent [(*S*)-2,2,2-trifluoro-1-(9-anthryl)ethanol]. As shown in Fig. 2, most signals were split into pairs. This indicates that the complex has no plane of symmetry and consists of a pair of racemates. This is a novel example for ring-originating optical isomers.

In conclusion, the present study demonstrated for the first time that calix[4]arene isomers can form stable complexes with $\text{Cr}(\text{CO})_3$ unless they have bulky substituents (such as *tert*-butyl) at the *p*-position.* The results are readily applicable to the selective introduction of a new substituent into the benzene nucleus. Further extensions of these and related calix[*n*]arene- $\text{Cr}(\text{CO})_3$ complexes are now under intensive investigation. Of particular interest are (i) the nucleophilic substitution on the $\text{Cr}(\text{CO})_3$ -complexed benzene nucleus,† (ii) optical resolution of 1,2-alternate- $\text{1}_4\text{Pr-Cr}(\text{CO})_3$ and (iii) the molecular motion of the benzene unit carrying a 'heavy' $\text{Cr}(\text{CO})_3$ on its back.

* The synthesis of arene-tricarbonylchromium complexes from 25,26,27,28-tetrapropoxy-5,11,17,23-tetra-*tert*-butylcalix[4]arene was very difficult and the products were quite unstable. This is probably due to steric hindrance of *tert*-butyl groups.

† If the nucleophilic substitution occurs at the *m*-position, the product is optically-active even after decomposition of $\text{Cr}(\text{CO})_3$ complexes.¹⁹

Acknowledgements

We thank Mr. Hideki Horiuchi for technical assistance in making glasswares for the anaerobic treatment of $\text{Cr}(\text{CO})_3$ complexes.

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Paper 1/06209C

Received 10th December 1991

Accepted 20th January 1992