

## Syntheses and Spectral Characterizations of Tricarbonylchromium Complexes of Calix[4]arenes†

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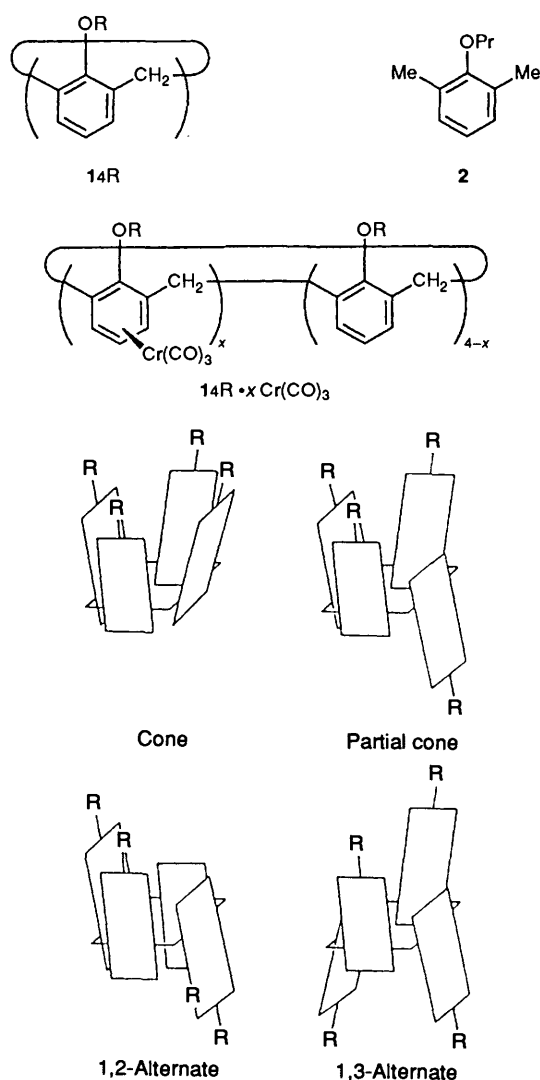
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The 1:1 arene-tricarbonylchromium complexes were synthesized for the first time from four conformational isomers of 25,26,27,28-tetrapropoxycalix[4]arene (**1<sub>4</sub>Pr**) and  $\text{Cr}(\text{CO})_6$ . The 1:2, 1:3 and 1:4 complexes of cone-**1<sub>4</sub>Pr** were also synthesized by increasing the ratio of  $\text{Cr}(\text{CO})_6$  against cone-**1<sub>4</sub>Pr**. The 1:2 complex was a mixture of two compounds, which were identified as distal and proximal isomers of cone-**1<sub>4</sub>Pr**- $2\text{Cr}(\text{CO})_3$ . The relative stability of the 1:1 complex was estimated *via* its oxidation by  $\text{CuCl}_2$ . The pseudo-first-order rate constants appeared to be in the order of 1,3-alternate-**1<sub>4</sub>Pr** > 1,2-alternate-**1<sub>4</sub>Pr** > cone-**1<sub>4</sub>Pr** > 2,6-dimethylanisole. The results indicate that the **1<sub>4</sub>Pr**- $\text{Cr}(\text{CO})_3$  complexes are less stable than the corresponding monomeric complex. The 1:1 complexes with partial-cone-**1<sub>4</sub>Pr** and 1,2-alternate-**1<sub>4</sub>Pr** were demonstrated to be a pair of racemates by  $^1\text{H}$  NMR spectroscopy using a chiral shift reagent (Pirkle's reagent).

Calix[*n*]arenes are cyclic oligomers which belong to the class of [*1<sub>n</sub>*]-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.<sup>1-4</sup> To design such functionalized calix[*n*]arenes, it is essential to develop methods for the selective introduction of desired functional groups into the desired benzene nuclei. In fact, a few groups have so far attempted to develop such synthetic methods,<sup>5-9</sup> but few general methodologies exist for this purpose.<sup>10</sup> It is known that tricarbonylchromium [ $\text{Cr}(\text{CO})_3$ ] forms stable  $\eta^6$ -arene complexes and the complexed benzene ring becomes extraordinarily 'reactive'.<sup>10-13</sup> We thus expected that the functional group would be selectively introduced into the benzene unit which was activated through complexation with  $\text{Cr}(\text{CO})_3$ . This chemistry is also interesting from a stereochemical viewpoint: introduction of  $\text{Cr}(\text{CO})_3$  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 syntheses and spectral characterizations of 1:1 complexes with four 25,26,27,28-tetrapropoxycalix[4]arene (**1<sub>4</sub>Pr**) conformers and 1:2, 1:3 and 1:4 **1<sub>4</sub>Pr**- $\text{Cr}(\text{CO})_3$  complexes with cone-**1<sub>4</sub>Pr** (**1<sub>4</sub>Pr** with a cone conformation). Compound **2** was used as a reference compound.

### Results and Discussion

**1:1 1<sub>4</sub>Pr-Cr(CO)<sub>3</sub> Complexes.**—We first attempted the reaction of  $\text{Cr}(\text{CO})_6$  with 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetramethoxycalix[4]arene but the reaction scarcely took place and the  $\text{Cr}(\text{CO})_3$  complex could not be isolated. As established from the X-ray crystallographic studies, alkyl groups which are introduced into the hydroxy groups of a calix[4]arene with a cone conformation are turned outwards in order to reduce the steric crowding on the narrow lower rim.<sup>16,17</sup> Hence, the benzene  $\pi$ -system is covered not only by the *tert*-butyl group but also by the *O*-alkyl group. This steric crowding makes the interaction with the benzene  $\pi$ -system from the *exo*-annulus side difficult. For example, we have found that the association



constant for 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrapropoxycalix[4]arene with a cone conformation and tetracyanoethylene is smaller by about one order of magnitude than that for cone-**1<sub>4</sub>Pr**.<sup>18</sup> To avoid such steric complexity we decided to

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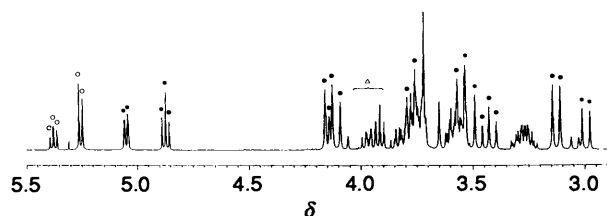


Fig. 1 Partial  $^1\text{H}$  NMR spectrum of Cr-complexed aromatic protons in partial-cone- $1_4\text{Pr-Cr}(\text{CO})_3$ ;  $[\text{partial-cone-}1_4\text{Pr-Cr}(\text{CO})_3] = 30 \text{ mmol dm}^{-3}$ ,  $30^\circ\text{C}$ ,  $\text{CDCl}_3$ .  $\circ$  Ring A is metallated;  $\bullet$  ring B or D is metallated;  $\triangle$  ring C is metallated

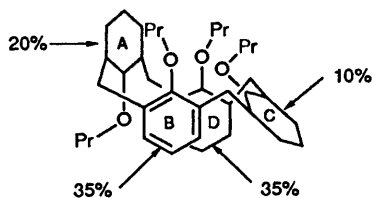


Fig. 2 Relative reactivity of the three inequivalent benzenes in partial-cone- $1_4\text{Pr}$  for mono-metallation

use calix[4]arene derivatives without *tert*-butyl groups at the 5,11,17,23-positions.

We first studied a  $\text{Cr}(\text{CO})_3$  complex with  $1_4\text{Me}$  and met with another difficulty. Although we could isolate the  $1_4\text{Me-Cr}(\text{CO})_3$  complex, the  $^1\text{H}$  NMR spectrum was too complex to assign. The complexity is related to conformational isomerism which takes place through the oxygen-through-the-annulus rotation of the methoxy groups.<sup>14,19,20</sup> To avoid this complexity we decided to employ conformationally-immobile  $1_4\text{Pr}$  because it has been established that the propyl group is too bulky to rotate through the annulus.<sup>14,20</sup>

The 1:1 reactions of  $\text{Cr}(\text{CO})_6$  and four different conformers of  $1_4\text{Pr}$  were carried out in a mixed solvent of dibutyl ether and THF at  $130^\circ\text{C}$  (oil-bath temperature). The progress of the reactions was followed by IR spectroscopy of samples withdrawn from the reaction mixture. The reaction rates for partial-cone, 1,2-alternate and 1,3-alternate were almost comparable (about 24 h) but that for cone was somewhat slower (about 30 h). In the formation of 1:1  $1_4\text{Pr-tetracyanoethylene}$  complexes we already noticed that the cone- $1_4\text{Pr}$  complex is most unstable.<sup>18</sup> In cone- $1_4\text{Pr}$  the propyl group is squeezed out of the lower rim onto the benzene ring, so that the benzene ring is partly covered by the propyl group. Thus, the CT complex with cone- $1_4\text{Pr}$  is destabilized because of the steric crowding. This explanation would be applicable to the low reactivity of cone- $1_4\text{Pr}$  towards  $\text{Cr}(\text{CO})_6$ .

We could isolate the 1:1 complexes of cone-, 1,2-alternate- and 1,3-alternate- $1_4\text{Pr-Cr}(\text{CO})_3$  by column chromatography in 76, 61 and 48% yields, respectively. The synthesis of partial-cone- $1_4\text{Pr-Cr}(\text{CO})_3$  was more complicated. The TLC analysis indicated that the eluent from column chromatography contains three different isomers. The  $^1\text{H}$  NMR spectrum (Fig. 1) clarified that 20% of  $\text{Cr}(\text{CO})_3$  is bound to the inversed phenyl unit (ring A), 10% of  $\text{Cr}(\text{CO})_3$  is bound to the phenyl unit distal to the inversed phenyl unit (ring C) and 70% of  $\text{Cr}(\text{CO})_3$  is bound to the residual two phenyl units (rings B and D; Fig. 2). Provided that the regioselectivity is governed by kinetic control (*i.e.*, provided that the intramolecular isomerization governed by the thermodynamic control is not involved), it follows that rings B and D are most reactive towards  $\text{Cr}(\text{CO})_6$ . According to the X-ray crystallographic studies on partial-cone calix[4]arenes,<sup>14,16</sup> ring C is significantly flattened and therefore is most efficiently influenced by the steric crowding effect. Probably, this is the reason why ring C is least reactive. On the

other hand, it is known that rings B and D are more or less parallel to each other<sup>16</sup> and therefore less influenced by the steric crowding effect. The high reactivity of these rings is also rationalized in terms of the steric effect.

The  $^1\text{H}$  NMR spectra of the  $\text{Cr}(\text{CO})_3$  complexes for cone-, 1,2-alternate- and 1,3-alternate- $1_4\text{Pr}$  were measured at  $30^\circ\text{C}$  in  $\text{CDCl}_3$ . The chemical shifts of the calix[4]arene protons are recorded in Fig. 3. The assignment was completed with the aid of the  $^1\text{H-}^1\text{H}$  COSY method and the nuclear Overhauser effect. It is seen from Fig. 3 that the protons on the benzene ring complexed with  $\text{Cr}(\text{CO})_3$  appear at higher magnetic field. The largest up-field shift was observed for *m*-protons in cone- $1_4\text{Pr-Cr}(\text{CO})_3$  ( $\Delta\delta = -2.60$ ). 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- $1_4\text{Pr-Cr}(\text{CO})_3$ , the C- $\text{CH}_2$ -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- $1_4\text{Pr}$ ). 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- $\text{CH}_2$ -C protons in  $2\text{-Cr}(\text{CO})_3$  (1.80 ppm; 1.82 ppm in uncomplexed **2**). Thus, the up-field shift is explained 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.

$1_4\text{Pr-xCr}(\text{CO})_3$  Complexes.—Next, we synthesized polynuclear complexes with cone- $1_4\text{Pr}$  and estimated their structural characteristics. When cone- $1_4\text{Pr}$  and  $\text{Cr}(\text{CO})_3$  were mixed in a 1:1 molar ratio, the product (determined for the conformer mixture by  $^1\text{H}$  NMR spectroscopy) contained 75% of cone- $1_4\text{Pr-Cr}(\text{CO})_3$ , 9% of cone- $1_4\text{Pr-distal-}2\text{Cr}(\text{CO})_3$  and a trace amount (*ca.* 1%) of cone- $1_4\text{Pr-}3\text{Cr}(\text{CO})_3$ . How are the complexes produced if the reaction were to occur according to probability theory? We calculated the complex distribution for reactant quotient  $1_4\text{Pr}/\text{Cr}(\text{CO})_6 = 1.00$ . The mole fractions of mono-, di-, tri- and tetra-chromium complexes are expressed as  $4\alpha$ ,  $12\alpha^2 (=4\alpha \cdot 3\alpha)$ ,  $24\alpha^3 (=12\alpha^2 \cdot 2\alpha)$  and  $24\alpha^4 (=24\alpha^3 \cdot \alpha)$ , respectively, and that of unchanged  $1_4\text{Pr}$  as  $1 - 4\alpha$  where  $\alpha$  is the reaction probability. Based on the relationship  $4\alpha + 12\alpha^2 + 24\alpha^3 + 24\alpha^4 = 1$ , we obtained  $\alpha = 0.154$ . Hence, the molar proportions of the species are estimated to be  $1_4\text{Pr}:1_4\text{Pr-Cr}(\text{CO})_3:1_4\text{Pr-}2\text{Cr}(\text{CO})_3:1_4\text{Pr-}3\text{Cr}(\text{CO})_3:1_4\text{Pr-}4\text{Cr}(\text{CO})_3 = 0.389:0.335:0.199:0.075:0.002$ . Comparison of these proportions with those in Run 1 (Table 1) reveals that the yield of cone- $1_4\text{Pr-Cr}(\text{CO})_3$  is much higher than that produced in probability theory. The result implies that this reaction features the negative allostericity: that is, complexation of  $\text{Cr}(\text{CO})_6$  with one benzene nucleus suppresses further complexation of  $\text{Cr}(\text{CO})_6$ . As a result, the 1:1 cone- $1_4\text{Pr-Cr}(\text{CO})_3$  complex is afforded selectively. This concept is also applied to the 1:2 and 1:3 reactions (Runs 2 and 3 in Table 1): when cone- $1_4\text{Pr}$  and  $\text{Cr}(\text{CO})_6$  are mixed in a 1:2 and 1:3 molar ratio, cone- $1_4\text{Pr-}2\text{Cr}(\text{CO})_3$  and cone- $1_4\text{Pr-Cr}(\text{CO})_3$  result predominantly, respectively. On the other hand, when the ratio of  $\text{Cr}(\text{CO})_6$  fed in was increased higher than 4, the reaction mixture readily turned brown because of decomposition of  $\text{Cr}(\text{CO})_6$ . We thus were obliged to stop the reaction before it was completed (Run 4). We also attempted the 1:1 reaction of cone- $1_4\text{Pr-Cr}(\text{CO})_3$  and  $\text{Cr}(\text{CO})_6$  (Run 5). The complex distribution was similar to that of cone- $1_4\text{Pr}$  plus  $2\text{Cr}(\text{CO})_6$ , although the yield of cone- $1_4\text{Pr-Cr}(\text{CO})_3$  was increased a little and that of cone- $1_4\text{Pr-Cr}(\text{CO})_3$  was decreased a little.

Interestingly, we found in Runs 2, 4 and 5 that not only cone- $1_4\text{Pr-distal-}2\text{Cr}(\text{CO})_3$  which includes two  $\text{Cr}(\text{CO})_3$ 's at the distal benzene nuclei but also cone- $1_4\text{Pr-proximal-}2\text{Cr}(\text{CO})_3$  which includes two  $\text{Cr}(\text{CO})_3$ 's at the proximal benzene nuclei although the yields of the proximal-isomer are generally lower

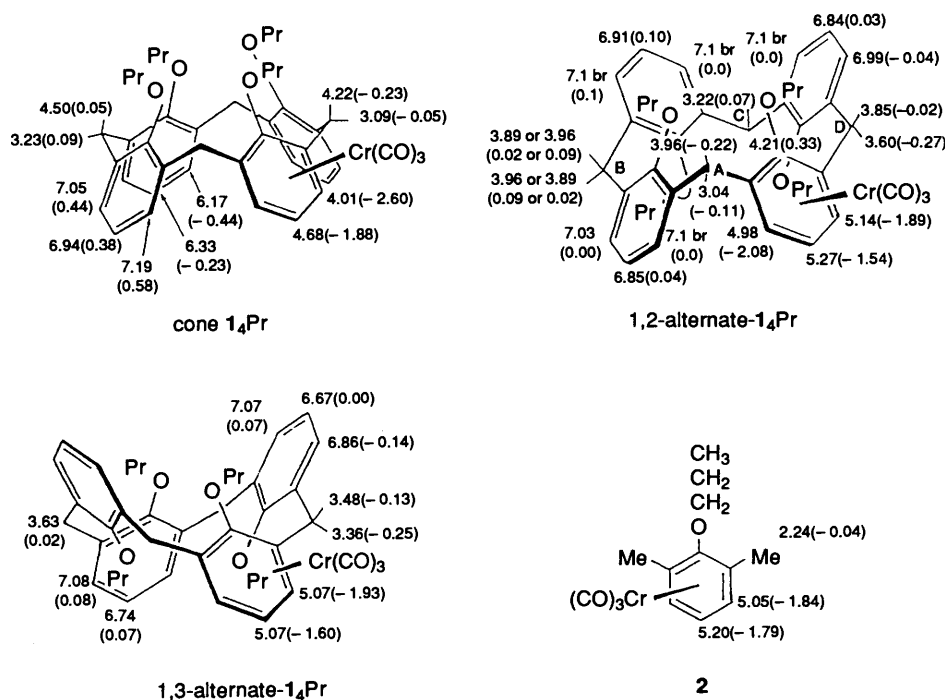


Fig. 3 Assignment of  $\text{Cr}(\text{CO})_3$  complexes. The numbers indicate the chemical shifts ( $\delta$ ): 30 °C,  $\text{CDCl}_3$ ,  $[\text{1}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3] = 10\text{--}30 \text{ mmol dm}^{-3}$ . The numbers in parentheses denote the shift from uncomplexed  $\text{1}_4\text{Pr}$  (+ to lower magnetic field, - to higher magnetic field). In 1,2-alternate- $\text{1}_4\text{Pr}$ , two  $\text{ArCH}_2\text{Ar}$  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.

Table 1 Synthesis of cone- $\text{1}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3$  complexes<sup>a</sup>

Run	Starting material	$\text{Cr}(\text{CO})_3$ source	$\text{Cr}/\text{1}_4\text{Pr}$ ratio	Time (h)	Yield (%) of recovered $\text{1}_4\text{Pr}\cdot x\text{Cr}(\text{CO})_3$ <sup>b</sup>				
					$x = 0$	1	2 (distal)	2 (proximal)	3
1	$\text{1}_4\text{Pr}$	$\text{Cr}(\text{CO})_6$	1	30	15	75	9	trace	0
2	$\text{1}_4\text{Pr}$	$\text{Cr}(\text{CO})_6$	2	28	0	22	66	8	4
3	$\text{1}_4\text{Pr}$	$\text{Cr}(\text{CO})_6$	3	40	0	0	21	trace	53
4	$\text{1}_4\text{Pr}$	$\text{Cr}(\text{CO})_6$	8	27	0	17	37	7	14
5	$\text{1}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3$	$\text{Cr}(\text{CO})_6$	2	28	0	49	45	6	0
6 <sup>c</sup>	$\text{1}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3$	$(\text{MeCN})_3\text{Cr}(\text{CO})_3$	2	6	0	46	21	30	0
7 <sup>d</sup>	$\text{1}_4\text{Pr}$	$(\text{C}_{10}\text{H}_8)\text{Cr}(\text{CO})_3$	2	18	0	23	45	15	15

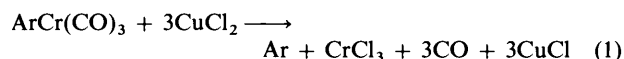
<sup>a</sup> Dibutyl ether (27  $\text{cm}^3$ )-THF (3  $\text{cm}^3$ ) at 130 °C. <sup>b</sup> Determined for the mixture by  $^1\text{H}$  NMR spectroscopy. <sup>c</sup> At 70 °C. <sup>d</sup> In refluxing THF.

than those of the distal-isomer. The production of proximal-isomers in addition to distal-isomers has also been found in diazo coupling reactions<sup>21</sup> and *O*-alkylation reactions.<sup>22–24</sup> Again according to probability theory, twice as much cone- $\text{1}_4\text{Pr}\cdot\text{proximal-2Cr}(\text{CO})_3$  should be produced as cone- $\text{1}_4\text{Pr}\cdot\text{distal-2Cr}(\text{CO})_3$ . The disagreement with the experimental results thus implies that the present reaction system shows the negative allosteric effect and the reactivity of the proximal benzene nuclei is more suppressed than that of the distal benzene nucleus. As mentioned above, the  $\pi$ -electron density of  $\text{Cr}(\text{CO})_3$ -complexed benzene nucleus is conspicuously decreased. Provided that the change influences the  $\pi$ -electron density of the proximal benzene nuclei through the  $\text{Ar-CH}_2\text{-Ar}$  bonds, it follows that their reactivity is suppressed. We consider that this is rather unlikely because the chemical shifts of the  $\text{Cr}(\text{CO})_3$ -complexed benzene protons move to higher magnetic field whereas those of the proximal benzene protons are scarcely affected. More conceivably, the proximal benzene nuclei are selectively deactivated because of the increased steric crowding.

We used  $(\text{MeCN})_3\text{Cr}(\text{CO})_3$  or (naphthalene) $\text{Cr}(\text{CO})_3$  instead of  $\text{Cr}(\text{CO})_6$  in order to accelerate the reaction (Runs 6 and

7). We found that the reaction is completed in 6 h at 70 °C for  $(\text{MeCN})_3\text{Cr}(\text{CO})_3$  and in 18 h at 66 °C for (naphthalene)- $\text{Cr}(\text{CO})_3$ , indicating the high reactivity of these reactants as a  $\text{Cr}(\text{CO})_3$  donor. It is interesting that the yield of cone- $\text{1}_4\text{Pr}\cdot\text{proximal-2Cr}(\text{CO})_3$  is found to be significantly enhanced in these runs. Probably, these highly-reactive reagents are less affected by the steric effect and give a proximal:distal ratio fairly close to 2.000 (the value required from probability theory).

**Relative Stability of  $\text{1}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3$ .**—In order to estimate the relative stability of  $\text{1}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3$  complexes, we conducted the oxidation by  $\text{CuCl}_2$  in  $\text{DMF-THF}$  (100:1 v/v) at 25 °C under the pseudo-first-order conditions  $\{[\text{1}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3] = [\text{2}\cdot\text{Cr}(\text{CO})_3] = 1.49 \times 10^{-5} \text{ mol dm}^{-3} < [\text{CuCl}_2] = 4.39 \times 10^{-4} \text{ mol dm}^{-3}$ ; eqn. (1).



The pseudo-first-order rate constant ( $k$ ) for  $\text{2}\cdot\text{Cr}(\text{CO})_3$  was estimated to be  $1.10 \times 10^{-2} (\pm 0.03 \times 10^{-2}) \text{ s}^{-1}$ . We found that

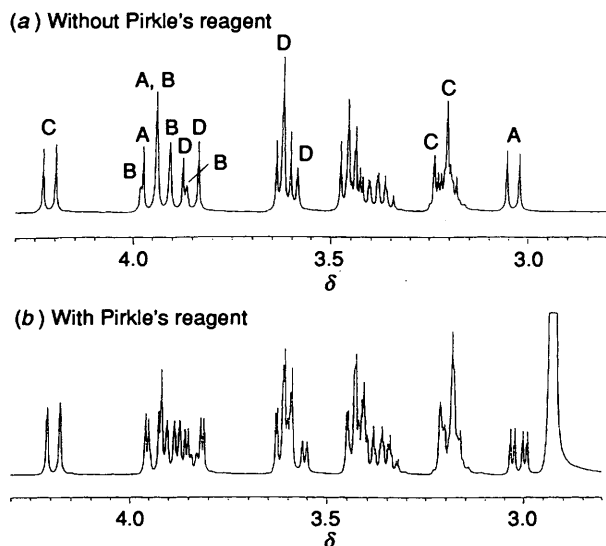


Fig. 4 Partial  $^1\text{H}$  NMR spectra of 1,2-alternate- $1_4\text{Pr-Cr}(\text{CO})_3$  in the absence (a) and the presence (b) of Pirkle's reagent:  $30^\circ\text{C}$ ,  $\text{CDCl}_3$ ,  $[1,2\text{-alternate-}1_4\text{Pr}] = 14 \text{ mmol dm}^{-3}$ ,  $[\text{Pirkle's reagent}] = 140 \text{ mmol dm}^{-3}$ . The peaks A–D correspond to the lettering shown in Fig. 1.

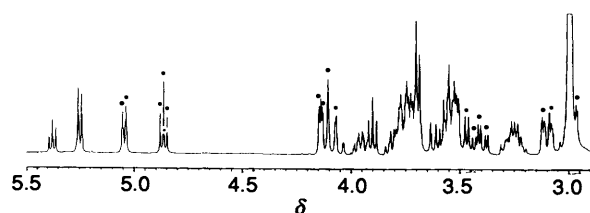


Fig. 5 Partial  $^1\text{H}$  NMR spectra of partial-cone- $1_4\text{Pr-Cr}(\text{CO})_3$  in the presence of Pirkle's reagent:  $30^\circ\text{C}$ ,  $\text{CDCl}_3$ ,  $[\text{partial-cone-}1_4\text{Pr-Cr}(\text{CO})_3] = 14 \text{ mmol dm}^{-3}$ ,  $[\text{Pirkle's reagent}] = 140 \text{ mmol dm}^{-3}$ . It is seen that only the protons in ring B and D are split into pairs (compare the spectrum with that in Fig. 1).

the  $k$  values for the  $1_4\text{Pr-Cr}(\text{CO})_3$  complexes are all larger than this value:  $k = 1.80 \times 10^{-2}$  ( $\pm 0.02 \times 10^{-2}$ )  $\text{s}^{-1}$  for cone- $1_4\text{Pr-Cr}(\text{CO})_3$ ,  $2.05 \times 10^{-2}$  ( $\pm 0.01 \times 10^{-2}$ )  $\text{s}^{-1}$  for 1,2-alternate- $1_4\text{Pr-Cr}(\text{CO})_3$  and  $2.51 \times 10^{-2}$  ( $\pm 0.05 \times 10^{-2}$ )  $\text{s}^{-1}$  for 1,3-alternate- $1_4\text{Pr-Cr}(\text{CO})_3$ . The most important finding from the kinetic study is that the calix[4]arene complexes are more easily oxidized than the corresponding monomer complex. Although the reaction mechanism for the oxidation of arene-tricarbonylchromium complexes is not well understood,<sup>25–28</sup> the initial electron transfer step  $\{\text{ArCr}(\text{CO})_3 + \text{Cu}^{2+} \longrightarrow [\text{ArCr}(\text{CO})_3]^+ + \text{Cu}^+\}$  should be involved in the rate-determining step. We noticed that in IR spectroscopy the CO stretching bands ( $\nu_{\text{CO}}$ ) for calix[4]arene–chromium complexes appear at lower frequency [e.g., 1868 and 1951  $\text{cm}^{-1}$  for cone- $1_4\text{Pr-Cr}(\text{CO})_3$ ] than those for  $2\text{-Cr}(\text{CO})_3$  (1880 and 1961  $\text{cm}^{-1}$ ). It is known that the  $\nu_{\text{CO}}$  frequency is correlated with the ionization potential and the shift to lower frequency region is caused by the increased  $\pi$ -donation ability.<sup>29</sup> Thus, the IR spectral data imply that benzene nuclei in calix[4]arenes show higher  $\pi$ -donation ability than does compound **2**. A similar trend was found for the calix[4]arene–tetracyanoethylene charge–transfer complexes. One can thus consider that  $\text{ArCr}(\text{CO})_3^+$  in calix[4]arene–chromium complexes is relatively more stabilized than that in  $2\text{-Cr}(\text{CO})_3$  leading to the relatively larger rate constants.

**Chiral Induction.**—Among four conformers of  $1_4\text{Pr}$ , chirality can be induced from partial-cone and 1,2-alternate through  $\text{Cr}(\text{CO})_3$ -complexation. In 1,2-alternate- $1_4\text{Pr}$ , introduction of one  $\text{Cr}(\text{CO})_3$  into any benzene unit makes the complex chiral.

In partial-cone- $1_4\text{Pr}$ , on the other hand, introduction to the benzene unit B or D (see Fig. 2) makes the complex chiral whereas introduction to the benzene unit A or C cannot produce such molecular asymmetry. In order to find evidence for such molecular asymmetry, we measured the  $^1\text{H}$  NMR spectra in the presence of Pirkle's reagent [ $(S)$ -2,2,2-trifluoro-1-(9-anthryl)ethanol]. As shown in Fig. 4, most signals in the 1,2-alternate- $1_4\text{Pr-Cr}(\text{CO})_3$  complex were split into pairs. In the partial-cone- $1_4\text{Pr-Cr}(\text{CO})_3$  complex, on the other hand, only the protons which are assigned to ring B- or ring D-complexed isomers were split into pairs (Fig. 5). 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.

**Conclusions.**—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*-positions. 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 racemic 1,2-alternate- and partial-cone- $1_4\text{Pr-Cr}(\text{CO})_3$  and (iii) the molecular motion of the benzene unit carrying a 'heavy'  $\text{Cr}(\text{CO})_3$  on its back.

## Experimental

**Materials.**—Conformational isomers of  $1_4\text{Pr}$  were synthesized in a manner and in yields similar to those described for their *p-tert*-butyl analogues.<sup>14,15</sup> Their analytical data are recorded below.

25,26,27,28-Tetrapropoxycalix[4]arene.—Cone- $1_4\text{Pr}$ : m.p.  $190.5\text{--}192.3^\circ\text{C}$ ;  $\delta_{\text{H}}(\text{CDCl}_3; 30^\circ\text{C})$  0.99 (12 H, t,  $\text{CH}_3$ ), 1.92 (8 H, m,  $\text{CCH}_2\text{C}$ ), 3.14 and 4.45 (2 H each, d and d,  $\text{ArCH}_2\text{Ar}$ ), 3.84 (8 H, t,  $\text{OCH}_2$ ) and 6.54–6.62 (12 H, m, ArH) (Found: C, 80.9; H, 8.1.  $\text{C}_{40}\text{H}_{48}\text{O}_4$  requires C, 81.04; H, 8.16%).

Partial-cone- $1_4\text{Pr}$ : m.p.  $200.3\text{--}201.7^\circ\text{C}$ ;  $\delta_{\text{H}}(\text{CDCl}_3; 30^\circ\text{C})$  0.70, 1.06 and 1.09 (12 H, t each,  $\text{CH}_3$ ), 1.39, 1.86 and 1.94 (2 H, 4 H and 2 H respectively, q each,  $\text{CCH}_2\text{C}$ ), 3.04, 3.65 and 4.07 (2 H, 4 H and 2 H respectively, d, s and d,  $\text{ArCH}_2\text{Ar}$ ), 3.31, 3.54 and 3.76 (2 H, 2 H and 4 H respectively, m each,  $\text{OCH}_2$ ), 6.25, 6.42, 6.86, 6.89, 6.94, 7.08 and 7.22 (2 H, 2 H, 1 H, 1 H, 2 H, 2 H and 2 H respectively, dd, t, t, t, dd, d and d, ArH) (Found: C, 81.0; H, 8.15.  $\text{C}_{40}\text{H}_{48}\text{O}_4$  requires C, 81.04; H, 8.16%).

1,3-Alternately- $1_4\text{Pr}$ : m.p.  $251.2\text{--}252.2^\circ\text{C}$ ;  $\delta_{\text{H}}(\text{CDCl}_3; 30^\circ\text{C})$  0.92 (12 H, t,  $\text{CH}_3$ ), 1.64 (8 H, m,  $\text{CCH}_2\text{C}$ ), 3.61 (8 H, s,  $\text{ArCH}_2\text{Ar}$ ), 6.67 and 7.00 (4 H, and 8 H respectively, t and d, ArH) (Found: C, 80.9; H, 8.15.  $\text{C}_{40}\text{H}_{48}\text{O}_4$  requires C, 81.06; H, 8.16%).

1,2-Alternately- $1_4\text{Pr}$ : m.p.  $154.8\text{--}155.6^\circ\text{C}$ ;  $\delta_{\text{H}}(\text{CDCl}_3; 30^\circ\text{C})$  0.61 (12 H, t,  $\text{CH}_3$ ), 0.92 and 1.20 (4 H, each, m each,  $\text{CCH}_2\text{C}$ ), 3.15, 3.87 and 4.18 (2 H, 4 H and 2 H respectively, d, s and d,  $\text{ArCH}_2\text{Ar}$ ), 3.34 (8 H, m,  $\text{OCH}_2$ ), 6.81, 7.03 and 7.06 (4 H, each t, dd and d respectively, ArH) (Found: C, 80.9; H, 8.05.  $\text{C}_{40}\text{H}_{48}\text{O}_4$  requires C, 81.04; H, 8.16%).

**General Procedure for the Synthesis of  $1_4\text{Pr-Cr}(\text{CO})_3$  Complexes.**— $\text{Cr}(\text{CO})_3$  complexes with conformers of  $1_4\text{Pr}$  were synthesized from  $\text{Cr}(\text{CO})_6$  and the corresponding conformer.  $1_4\text{Pr}$  (0.30 g, 0.51 mmol) and  $\text{Cr}(\text{CO})_6$  (0.15 g, 0.52 mmol) were dissolved in a mixed solvent of dibutyl ether (27  $\text{cm}^3$ ) and THF (3  $\text{cm}^3$ ) and the solution was heated at  $130^\circ\text{C}$ . The progress of the reaction was monitored either by IR spectroscopy [to detect unchanged  $\text{Cr}(\text{CO})_6$ ] or by TLC (to detect unchanged  $1_4\text{Pr}$ ). We found that the reaction is complete after 24 h. The solution

**Table 2**  $^1\text{H}$  NMR chemical shifts,<sup>a</sup>  $\delta$ , of cone- $\text{I}_4\text{Pr}\cdot x\text{Cr}(\text{CO})_3$ 

$\text{H}^b$	$x$				
	1	2 (distal)	2 (proximal)	3	4 <sup>c</sup>
<i>p</i> -Ar*-H	4.68 (-1.88)	4.80 (-1.76)		5.35 (-1.21)	5.22 (-1.34)
<i>m</i> -Ar*-H	4.00 (-2.61)	4.07 (-2.54)		5.04 (-1.57)	4.80 (-1.81)
<i>p</i> -Ar*-H			5.07 (-1.49)	4.92 (-1.64)	
<i>m</i> -Ar*-H			4.63 (-1.98)	4.38 (-2.23)	
<i>m</i> -Ar*-H			4.63 (-1.98)	4.23 (-2.38)	
<i>p</i> -Ar-H	6.33 (-0.23)	7.00 (0.44)		7.01 (0.45)	
<i>m</i> -Ar-H	6.17 (-0.44)	7.17 (0.56)		7.15 (0.54)	
<i>p</i> -Ar-H	6.94 (0.38)		6.71 (0.15)		
<i>m</i> -Ar-H	7.19 (0.58)		6.77 (0.16)		
<i>m</i> -Ar-H	7.05 (0.44)		6.77 (0.16)		
<i>exo</i> -Ar*CH <sub>2</sub> Ar*			2.89 (-0.25)	2.98 (-0.16)	2.99 (-0.15)
<i>endo</i> -Ar*CH <sub>2</sub> Ar*			4.06 (-0.39)	4.11 (-0.34)	4.09 (-0.36)
<i>exo</i> -Ar*CH <sub>2</sub> Ar	3.09 (-0.05)	3.19 (0.05)	3.08 (-0.06)	3.18 (0.04)	
<i>endo</i> -Ar*CH <sub>2</sub> Ar	4.22 (-0.23)	4.28 (-0.17)	4.28 (-0.17)	4.27 (-0.18)	
<i>exo</i> -ArCH <sub>2</sub> Ar	3.23 (0.09)		3.24 (0.10)		
<i>endo</i> -ArCH <sub>2</sub> Ar	4.50 (0.05)		4.49 (0.04)		
-CH <sub>3</sub>	1.11 (0.12)	1.13 (0.14)	1.21 (0.22)	1.11 (0.12)	1.01 (0.02)
	1.11 (0.12)	0.84 (-0.15)	0.96 (-0.03)	0.94 (-0.05)	
	0.86 (-0.13)			0.83 (-0.16)	
-CH <sub>2</sub> CH <sub>3</sub>	1.90 (-0.02) <sup>d</sup>	1.94 (0.02)	2.03 (0.11)	1.94 (0.02)	2.00 (0.08)
		1.85 (-0.07)	1.84 (-0.08)	1.77 (-0.15)	
-OCH <sub>2</sub>	4.00 (0.16) <sup>d</sup>	4.02 (0.18)	4.10 (0.26)	4.19 (0.35)	4.04 (0.20)
	3.90 (0.06)	3.94 (0.10)	3.99 (0.15)	3.94 (0.10)	
	3.71 (-0.13)		3.82 (-0.02)		

<sup>a</sup>  $T = 303$  K, solvent  $\text{CDCl}_3$ , internal standard  $\text{Me}_4\text{Si}$ ; the numbers in parentheses denote the shift from uncomplexed  $\text{I}_4\text{Pr}$  (+ to lower magnetic field, - to higher magnetic field). <sup>b</sup> Ar\* means  $\text{ArCr}(\text{CO})_3$ . <sup>c</sup> Solvent  $\text{CDCl}_3:\text{CD}_2\text{Cl}_2 = 3:1$ . <sup>d</sup> Multiplet or broad.

was concentrated under reduced pressure, the oily residue being solidified by hexane.\* The solid product was purified by column chromatography [twice from silica gel and hexane-dichloromethane (5:1 v/v for cone- $\text{I}_4\text{Pr}$ , 1:1 v/v for 1,2-alternate- $\text{I}_4\text{Pr}$  and 2:1 v/v for 1,3-alternate- $\text{I}_4\text{Pr}$ ) and once from silica gel and benzene]. These operations were all carried out under the anaerobic ( $\text{N}_2$ ) conditions. The solvents used herein were purified as follows: dibutyl ether, benzene and dichloromethane were dried over  $\text{CaH}_2$  and THF and dibutyl ether were dried by sodium benzophenone ketyl. They were distilled under a nitrogen stream.

Cone- $\text{I}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3$ : m.p. 171.6–173.0 °C, yield 76%;  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1868 and 1951 (CO) (Found: C, 71.05; H, 6.6.  $\text{C}_{43}\text{H}_{48}\text{CrO}_7$  requires C, 70.86; H, 6.64%).

1,2-Alternate- $\text{I}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3$ : m.p. (decomp.) 144 °C, yield 61%;  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1869 and 1952 (CO) (Found: C, 70.8; H, 6.75.  $\text{C}_{43}\text{H}_{48}\text{CrO}_7$  requires C, 70.86; H, 6.64%).

1,3-Alternate- $\text{I}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3$ : m.p. 248.7–250.2 °C, yield 48%;  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1868 and 1952 (CO) (Found: C, 70.6; H, 6.7.  $\text{C}_{43}\text{H}_{48}\text{CrO}_7$  requires C, 70.86; H, 6.64%).

We also synthesized a  $\text{Cr}(\text{CO})_3$  complex with partial-cone- $\text{I}_4\text{Pr}$  as a 1:1 complex. The  $^1\text{H}$  NMR spectrum showed that the product consisted of three isomers. This complexity stems from three inequivalent benzene rings present in partial-cone- $\text{I}_4\text{Pr}$ . We attempted the isolation of each isomer but failed. Hence, partial-cone- $\text{I}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3$  was analysed as a mixture of three isomers. The  $^1\text{H}$  NMR spectral data are recorded in the Results and Discussion section.

(2,6-Dimethyl-1-propoxybenzene)tricarbonylchromium [ $2\cdot\text{Cr}(\text{CO})_3$ ].—2,6-Dimethyl-1-propoxybenzene (1.0 g, 6.1 mmol) and  $\text{Cr}(\text{CO})_6$  (1.4 g, 6.4 mmol) were dissolved in a mixed solvent

\* The synthetic method for  $\text{I}_4\text{Pr}\cdot 2\text{Cr}(\text{CO})_3$  is a little different from this. Hexane was added to the oily residue. The precipitate [containing cone- $\text{I}_4\text{Pr}$  and cone- $\text{I}_4\text{Pr}\cdot 2\text{Cr}(\text{CO})_3$ ] was removed by filtration, the filtrate being concentrated to dryness. The solid residue was subjected to purification by column chromatography.

of dibutyl ether (45  $\text{cm}^3$ ) and THF (5  $\text{cm}^3$ ) and the solution was heated at 110 °C for 4 days under a nitrogen stream. After cooling the insoluble material was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was recrystallized under a nitrogen stream from hexane: m.p. 48 °C, yield 65%;  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1880 and 1961 (CO);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.05 (3 H, t,  $\text{CCH}_3$ ), 1.80 (2 H, m,  $\text{CCH}_2\text{C}$ ), 2.24 (6 H, s,  $\text{ArCH}_3$ ), 3.76 (2 H, t,  $\text{OCH}_2$ ) and 5.05 and 5.20 (2 H, and 1 H, d and t, *m*-H and *p*-H respectively) (Found: C, 55.85; H, 5.3.  $\text{C}_{14}\text{H}_{16}\text{CrO}_4$  requires C, 56.00; H, 5.37%).

*General Procedure for the Synthesis of  $\text{I}_4\text{Pr}\cdot x\text{Cr}(\text{CO})_3$  Complexes.*—Cone- $\text{I}_4\text{Pr}$  (0.30 g, 0.51 mmol) and  $\text{Cr}(\text{CO})_6$  (0.84 g, 4.05 mmol) were treated in a manner similar to that described above for  $\text{I}_4\text{Pr}\cdot\text{Cr}(\text{CO})_3$  complexes. The reaction was stopped after 27 h, and the solution was concentrated to dryness. The residue was dissolved in dichloromethane and the insoluble material was removed by filtration. The filtrate was subjected to the separation by column chromatography [silica gel, hexane-dichloromethane (1:1 v/v)]. Each eluent was concentrated to dryness and the residue was recrystallized. These operations were all carried out under the anaerobic ( $\text{N}_2$ ) conditions. We thus isolated cone- $\text{I}_4\text{Pr}\cdot\text{distal-}2\text{Cr}(\text{CO})_3$ , cone- $\text{I}_4\text{Pr}\cdot 3\text{Cr}(\text{CO})_3$  and cone- $\text{I}_4\text{Pr}\cdot 4\text{Cr}(\text{CO})_4$ .

Cone- $\text{I}_4\text{Pr}\cdot\text{distal-}2\text{Cr}(\text{CO})_3$ : recrystallized from methanol-dichloromethane, m.p. (decomp.) 184 °C, yield 23%;  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1876 and 1951 (CO) (Found: C, 63.3; H, 5.58.  $\text{C}_{46}\text{H}_{48}\text{Cr}_2\text{O}_{10}$  requires C, 63.88; H, 5.59%).

Cone- $\text{I}_4\text{Pr}\cdot 3\text{Cr}(\text{CO})_3$ : recrystallized from hexane-dichloromethane, m.p. (decomp.) 209 °C, yield 4%;  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1890, 1957 and 1972 (CO) (Found: C, 57.1; H, 4.85.  $\text{C}_{49}\text{H}_{48}\text{Cr}_3\text{O}_{13}\cdot 0.5\text{CH}_2\text{Cl}_2$  requires C, 56.98; H, 4.73%).

Cone- $\text{I}_4\text{Pr}\cdot 4\text{Cr}(\text{CO})_3$ : recrystallized from dichloromethane, m.p. (decomp.) 178 °C, yield 14%;  $\nu_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1963 and 1895 (CO) (Found: C, 51.25; H, 4.1.  $\text{C}_{52}\text{H}_{48}\text{Cr}_4\text{O}_{16}$  requires C, 50.82; H, 4.07%). The  $^1\text{H}$  NMR spectral data are summarized in Table 2.

Cone- $\text{I}_4\text{Pr}\cdot\text{proximal-}2\text{Cr}(\text{CO})_3$ ,  $\text{Cr}(\text{CO})_6$  (0.08 g, 0.37 mmol)

was dissolved in anhydrous acetonitrile (5 cm<sup>3</sup>) and the solution was heated at reflux for 48 h under a nitrogen stream. The concentration of the solution resulted in the yellow powder of (MeCN)<sub>3</sub>Cr(CO)<sub>3</sub>. The powder and cone-1<sub>4</sub>Pr were dissolved in THF (20 cm<sup>3</sup>) and the solution was heated at reflux for 6 h under a nitrogen stream. After cooling the solution was concentrated to dryness, the residue being subjected to column chromatography [silica gel, benzene-hexane (1:2 v/v)]. We thus isolated cone-1<sub>4</sub>Pr-distal-2Cr(CO)<sub>3</sub> (in 30% yield) and cone-1<sub>4</sub>Pr-proximal-2Cr(CO)<sub>3</sub>: m.p. 90 °C followed by gradual recrystallization, which gives second m.p. (decomp.) 175 °C, yield 32%;  $\nu_{\max}(\text{CH}_2\text{Cl}_2)/\text{cm}^{-1}$  1880, 1953 and 1964 (CO) (Found: C, 64.25; H, 5.6. C<sub>46</sub>H<sub>48</sub>Cr<sub>2</sub>O<sub>10</sub> requires 63.88; H, 5.59%). The <sup>1</sup>H NMR spectral data are summarized in Table 2.

**Kinetic Measurements.**—To a DMF solution (3 cm<sup>3</sup>) containing unhydrated CuCl<sub>2</sub> (4.43 × 10<sup>-3</sup> mol dm<sup>-3</sup>) in a UV cell was injected a THF solution (0.03 cm<sup>3</sup>) containing 1<sub>4</sub>Pr-Cr(CO)<sub>3</sub> or 2-Cr(CO)<sub>3</sub> (1.51 × 10<sup>-3</sup> mol dm<sup>-3</sup>) at 25 °C under the anaerobic conditions. The progress of the reaction was followed at 315 nm (CT band of arene-tricarbonylchromium complexes). The reaction obeyed the first-order kinetics for up to three half-lives. The same experiments were repeated at least three times. The pseudo-first-order rate constants described in Results and Discussion section are the average of these values. The correlation coefficients were always higher than 0.99. The colour of the CuCl<sub>2</sub> stock solution changed because of its hygroscopic nature, so a new solution was prepared immediately before the measurement.

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