for 60 h. After being left sitting in a hot water bath for 1 h, the mixture was filtered. The crystals were washed with 0.6 N NaOH, and the combined wash and filtrate were extracted with ether and then acidified with 10 mL of 6 N HCl to precipitate the dicarboxylic acid, crude yield 55.7 mg.

A 2 M solution of CH_2N_2 in 4 mL of ether (8 mmol) was added to a solution of the dicarboxylic acid in 250 mL of ether, and the mixture was kept in a refrigerator at 0 °C for 3 days. Excess CH_2N_2 was destroyed by adding 10 mL of glacial acetic acid, and the mixture was then extracted with 5% NaOH. The ether layer was washed with H_2O, dried over Na_2SO_4, and evaporated to dryness to give the crude diester VII. The crude diester was chromatographed on a 1 cm × 20 cm silica gel column with benzene. Four bands developed. The third and major band was eluted with 1:99 ethyl acetate–benzene mixture to give 44.5 mg of crude VII. Recrystallization from hexane at −20 °C gave a yellow-orange solid: mp 93–93.5 °C; ^1H NMR δ 4.61, 4.63, 4.64 (2 H, dd, J = 1.3, 1.3 Hz, 2,5′), 4.50, 4.52, 4.53, 4.55 (2 H, dd, J = 1.3, 2.6 Hz, 3,4), 4.39, 4.41, 4.42, 4.44 (2 H, dd, J = 1.3, 2.7 Hz, 2′,5), 3.73 (6 H, s, CH_3), 1.97 (6 H, s, CH_2). Anal. $C_{17}H_{18}O_4Fe$: C, H.

Acknowledgment. We wish to thank Mr. Donald Lawler for the ^{13}C NMR and the 360-MHz ^1H NMR spectra and Drs. J. J. Eisch and T. E. Bitterwolf for valuable discussions. The NSF financed the time that U.J. spent at Brookhaven National Laboratory. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under Contract No. DE-AC02-76CH00016.

Registry No. I, 12302-04-4; IIa, 56800-49-8; IIb, 82522-08-5; IIc, 82522-09-6; II (X = Li), 82522-13-2; IIIa, 82544-14-7; IIIb, 82544-15-8; IIIc, 82544-16-9; III (X = Li), 82544-23-8; IVa, 82522-10-9; IVb, 82522-11-0; IVc, 82522-12-1; IV (X = Li), 82522-14-3; Va, 82544-17-0; Vb, 82544-18-1; Vc, 82544-19-2; V (X = Li), 82544-24-9; VI, 41558-92-3; VIIIa, 82544-20-5; VIIIb, 82544-21-6; VIIIc, 82544-22-7; VIII (X = Li), 82544-25-0.

Substituent Effects in Cationic Bis(arene)chromium Compounds. Electronic and Electron Spin Resonance Spectra and an X-ray Structure of Bis(1,3,5-triisopropylbenzene)chromium(I) Iodide

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For a series of monosubstituted bis(arene)chromium cations, the UV ligand–metal charge-transfer (LMCT) bands and electron spin resonance (ESR) parameters do not depend on the nature or ring substituents. However, as the number of electron-donating groups on the arene ring are increased inductive effects become more significant. X-ray crystallography has been applied to determine the molecular structure of bis-(1,3,5-triisopropylbenzene)chromium(I) iodide. The staggered conformation was found to be stabilized by steric factors. Crystal data for bis-(1,3,5-triisopropylbenzene)chromium(I) iodide are as follows: space group $P\bar{1}$ (triclinic), unit-cell dimensions a = 9.988 (3) Å, b = 16.199 (3) Å, c = 9.479 (2) Å, α = 91.08 (2)°, β = 106.92 (2)°, and γ = 96.33 (2)°, and ρ_{calcd} = 1.340 g cm^{-3} for Z = 2. The final R factor is 0.037 for 5358 observed independent reflections. The ring angle at the substituted carbon has an average value of 118.6°, consistent with the electron-donating nature of isopropyl groups as predicted by Domenicano[28] for uncomplexed benzene rings.

Introduction

Charge-transfer spectra have been measured for $Cr(C_6H_6)_2$ and $Cr(C_6H_6)_2^+$ and assignments are clearly tentative.[1,2] The effects on the shifts of charge-transfer spectra induced by substitution in the bis(arene)chromium cations are investigated here in order to examine the assignment of the ligand to metal ($e_{1u} \rightarrow a_{1g}$) charge-transfer bands.

Substituent effects on the ESR data in cationic bis(arene)chromium complexes have been the subject of several reports,[3-5] dealing primarily with alkyl-substituted bis(benzene)chromium compounds.[4,5] It is instructive to examine these results in the light of ESR data and the nature of the substituents in the arene ring.

To avoid the impurities formed in the synthesis by the Friedel–Crafts method, bis(1,3,5-triisopropylbenzene)chromium has been prepared by using the cocondensation of chromium vapor with 1,3,5-triisopropylbenzene at −196 °C. Oxidation of the complex in air in presence of an aqueous KI solution gives the iodide of bis(1,3,5-triisopropylbenzene)chromium(I) which was obtained in the crystalline state and used for the X-ray structure study. The structure of bis(benzene)chromium(I) iodide,[7] bis(toluene)chromium(I) iodide,[8] bis(ethylbenzene)chromium iodide,[9] η^{12}-[3,3](paracyclophane)chromium(I) triiodide,[10]

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and (1,1′-tetramethylenedibenzene)chromium(I) iodide[11] have been studied. Studies of effects of the substituents on structures, stereochemistry and bonding of bis(arene)chromium complexes have been reported recently by Eyring, Zuerner, and Radonovich.[12] There has been only one conformational study in the bis(arene)chromium complexes by means of dynamic NMR spectroscopy.[13] Here, X-ray crystallography has been applied to determine the molecular structure of bis(1,3,5-triisopropylbenzene)chromium iodide.

Experimental Section

(1) Syntheses of Bis(arene)chromium(0) and Bis(arene)chromium(I) Compounds. The bis(η^6-arene)chromium(0) complexes containing the functional groups CH_3, H, $COOC_2H_5$, Cl, i-C_3H_7, and OCH_3 were synthesized by metal–ligand cocondensation techniques.[14,15] The compounds prepared by Friedel–Crafts syntheses[16] contained H, CH_3, and Ph. The CHO compound was prepared by metalation of bis(benzene)chromium.[17]

A new bis(arene)chromium compound, $[1,3,5\text{-}(C_6H_3)(i\text{-}C_3H_7)_3]_2Cr^0$, was prepared by the following procedure, which is typical of the vapor synthesis of the chromarenes.

A 0.7-g sample of chromium was condensed with 30 mL of 1,3,5-triisopropylbenzene at −196 °C and $\leq 10^{-4}$ torr as described previously.[15] The mixture was allowed to warm to room temperature. The excess 1,3,5-triisopropylbenzene was removed in a vacuum ($<10^{-4}$ torr) at 100 °C, and a cold finger was placed in the flask. The bis(1,3,5-triisopropylbenzene)chromium was sublimed at 130 °C and 10^{-4} torr (5% yield). The orange-brown solid was scraped from the cold finger and stored in the argon-filled glovebox: mass spectrum (70 eV), m/e (relative intensity) 460 (M^+, 41.8), 250 (CrL, 72.5), 204 (L, 48.5), 189 (L − CH_3, 100), 52 (Cr, 19.9); ^1H NMR (toluene-d_8, 23 °C) δ 1.32 (d, 36 H), 3.23 (m, 6 H, isopropyl CH protons), 4.32 (br s, 6 H, ring protons); ^{13}C NMR (toluene-d_8, 23 °C) δ 25.09 (q, $^1J_{CH}$ = 123 Hz, methyl carbons), 33.19 (d, $^1J_{CH}$ = 122 Hz, isopropyl CH carbons), 73.48 (d, $^1J_{CH}$ = 157 Hz, unsubstituted ring carbons), 99.08 (s, substituted ring carbons).

The bis(η^6-arene)chromium(I) cations were obtained by oxidizing these chromium(0) compounds in the air in the presence of water to give the hydroxide of bis(η^6-arene)chromium(I). When sodium tetraphenylborate or potassium iodide was added to these aqueous solutions, the precipitate of the yellow tetraphenylborate or iodide salt of bis(η^6-arene)chromium(I) was collected, filtered, washed with water and then ether, and dried in a vacuum at room temperature. The purity of the compounds was verified by IR and UV–visible spectra and microanalyses. The IR bands in the 300–500-cm^{-1} region are characteristic of bis(arene)metal sandwich compounds.[18,19] The functional groups CH_3, Ph, i-C_3H_7, H, OCH_3, $COOC_2H_5$, Cl, and CHO were confirmed by IR spectroscopy.

Table I. ESR Parameters[a] for $Cr(\eta^6\text{-arene})_2^+$ in Me_2SO solution 25 °C

arene	$A(H_{Ar})$	$A(^{53}Cr)$	g	UV[b] L–M charge-transfer, nm
C_6H_6	3.42	18.1	1.9860	340
$C_6H_5CH_3$	3.46	18.0	1.9865	341
$C_6H_5OCH_3$	3.72	17.7	1.9872	346
$C_6H_5C_6H_5$	3.44	18.3	1.9853	346
$C_6H_5COOC_2H_5$	3.30	18.3	1.9858	345
C_6H_5CHO	3.25	17.3	1.9863	339
1,3,5-C_6H_3-$(CH_3)_3$	3.54	18.0	1.9860	356
C_6H_5CHO, C_6H_6	3.23	18.1	1.9856	342
C_6H_5Cl	3.58	18.1	1.9867	342
1,3,5-C_6H_3-$(i\text{-}C_3H_7)_3$	3.50	18.0	1.9866	359
$C_6(CH_3)_6$		18.2	1.9867	366

[a] The experimental error of A, ±0.02 G, and g, ±0.005. [b] Measured in methanol, error in ±1 nm; log ϵ 3.7–4.1 for the absorption coefficient.

(2) Physical Measurements. NMR spectra were obtained by use of a Varian T-60 or a Bruker WM 250 spectrometer. Benzene-d_6 and toluene-d_8 were used as solvents for all the bis(arene)chromium(0) compounds in the measurements. Chemical shifts are relative to internal Me_4Si. Variable-temperature ^{13}C and ^1H NMR spectra were obtained by use of the Bruker WM 250 spectrometer with Me_4Si as an internal standard. ESR spectra were recorded on a E-4 ESR spectrophotometer with a variable-temperature controller, and DPPH was used as an external standard. Infrared spectra of KBr pellet samples were obtained by use of a Perkin-Elmer 457 spectrophotometer at room temperature. Mass spectra were recorded by use of a Finnigan 4000 mass spectrometer (70 eV) with an Incos data system. UV–visible spectra were recorded by use of a Cary Model 17 spectrophotometer. Microanalyses were carried out by Schwarzkopf Laboratory, Woodside, NY.

(3) Crystallographic Data and X-ray Structure Analysis. A single-crystal was prepared by the slow evaporation in a mixed solvent of methanol/chloroform at 25 °C. Crystal data: crystals of $C_{30}H_{48}CrI$ are triclinic; space group $P\bar{1}$; a = 9.988 (3) Å, b = 16.199 (3) Å, c = 9.479 (2) Å, α = 91.08 (2)°, β = 106.92 (2)°, γ = 96.33 (2)°, Z = 2, M_r = 587.61, ρ_{calcd} = 1.340 g cm^{-3}, ρ_{obsd} = 1.330 g m^{-3}. Lattice dimensions were determined by using a Picker FACS-I automatic diffractometer and Mo $K\alpha_1$ (λ = 0.70926 Å) radiation.

Intensity data were measured by using Mo $K\alpha$ radiation ($2\theta_{max}$ = 60°), yielding 8422 total unique data and, based on $I > 3\sigma(I)$, 5358 observed data. The data were reduced.[20] Atomic scattering factors, including real and imaginary dispersion corrections, for Cr, C, and H were calculated from the coefficients in ref 21. The structure was solved by Patterson methods.[22] The final refinement by full-matrix least squares[23] reduced $R_w = [\sum w(\Delta F)^2/\sum wF_o^2]$, the quantity minimized, to 0.037. In the last cycle no parameters shifted more than 0.21σ (non-hydrogen) or 0.37σ (hydrogen). Secondary extinction effects were investigated and found to be insignificant.

Results and Discussion

Characterization and Identification. A. Electronic Spectra. A characteristic UV absorption band at 340 nm

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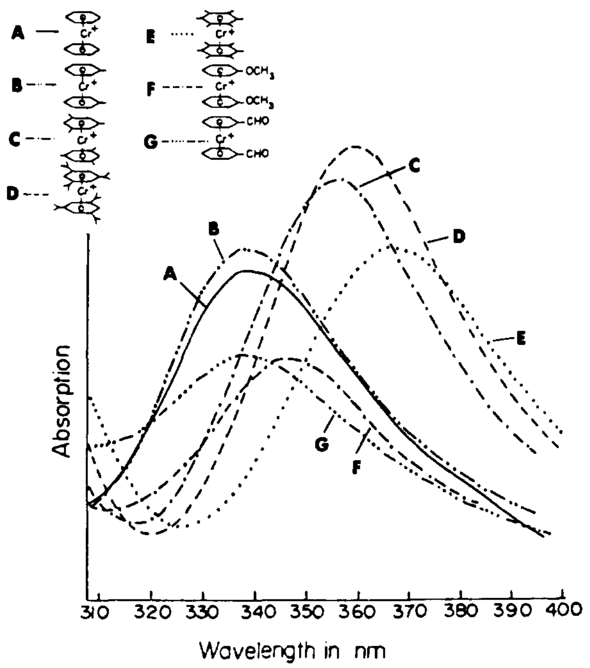

Figure 1. UV L–M charge-transfer bands for bis(arene)chromium(1+) in methanol.

for bis(benzene)chromium(I) has been associated with the ligand to metal ($e_{1u} \rightarrow a_{1g}$) charge transfer.[1,2] The analogous bands, assigned by analogy, are listed in Table I for a series of substituted bis(arene)chromium cations. The results show that variation of monosubstituents in the ring has little effect on the UV ligand to metal bands. It is of interest to note, however, that those bands in bis(1,3,5-trimethylbenzene)chromium(1+), bis(1,3,5-triisopropylbenzene)chromium(1+), and bis(hexamethylbenzene)chromium(1+) are a red-shifted by 16–26 nm compared with the bis(benzene)chromium cation (Figure 1). These shifts might be due to significant inductive effects from the increase in the number of electron-donating groups in the arene ring, since the electronic and resonance effects differ only slightly in monosubstituted bis(arene)chromium cations. The evidence of the red-shifts induced by three or more alkyl substituents in the bis(arene)chromium(I) compounds can provide a satisfactory interpretation of the assignment of L–M ($e_{1u} \rightarrow a_{1g}$) charge-transfer bands.

B. ESR Spectra. (a) Measured in Me_2SO at 25 °C. The cationic bis(arene)chromium compounds show a decrease in the number of hyperfine components with an increase in the number of substituents, due to the smaller number of ring protons ($I = {}^1/_2$) coupled with the unpaired electron[3-5] (Figure 2). The results in Table I indicate that the ESR parameters for a series of monosubstituted bis(η^6-arene)chromium(1+) in Me_2SO are not sensitive to the nature of substituents. These results are consistent with the UV bands that show no significant substituent effects on L–M charge transfer in monosubstituted cationic bis(arene)chromium complexes. In view of the ESR spectra

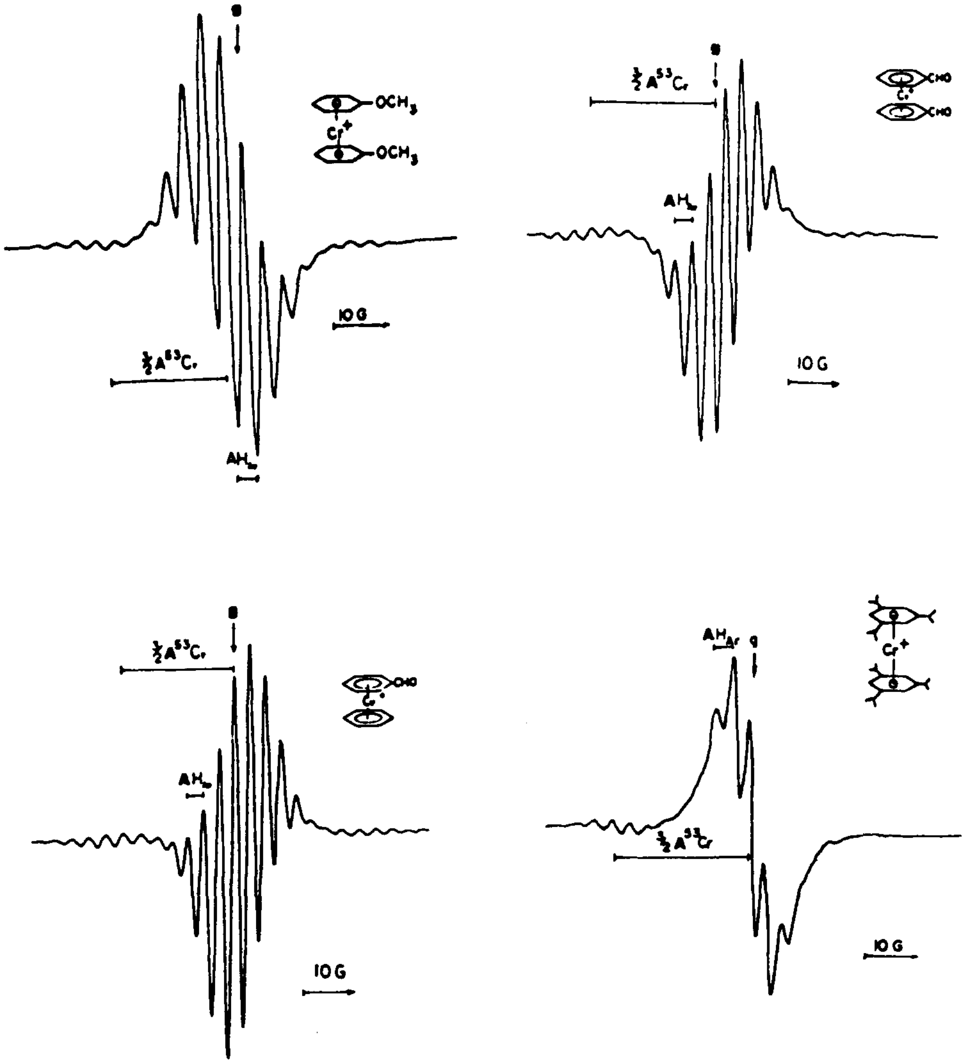

Figure 2. Isotropic ESR spectra for bis(arene)chromium(1+) in Me_2SO at 25 °C.

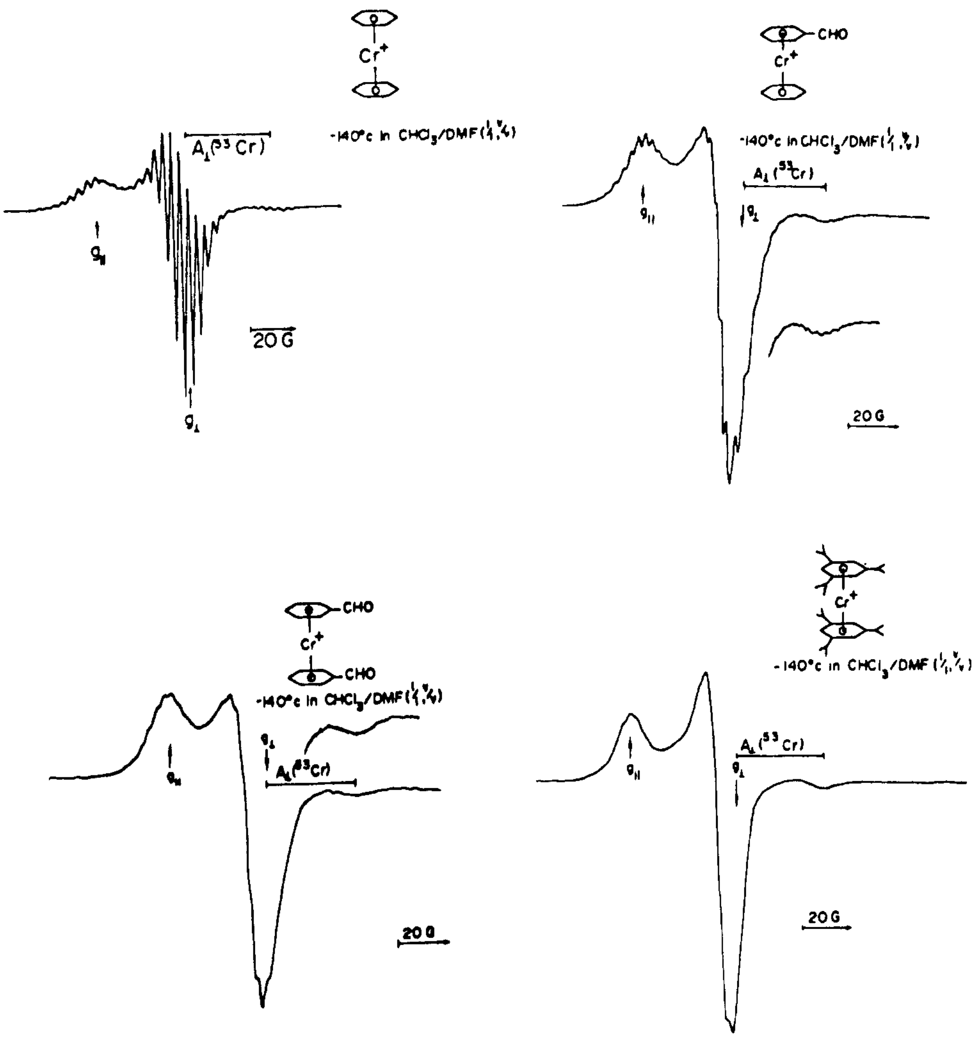

Figure 3. Anisotropic ESR spectra for bis(arene)chromium(1+) in $CHCl_3$/DMF (1:1, v/v) at -140 °C.

one finds that a substituent attached to a complexed arene induced little change in the electron density distribution in the ring in contrast to the uncomplexed arene radical.

In the ESR spectra, the proton hyperfine constants, $A(H_{Ar})$ increase with increasing number of alkyl substituents on the arene ring.[4,5] A possible rationalization for this observation can be made by considering that the electronic effect is greater when more electron-donating groups are transmitted to fewer ring protons in contrast to the effects on five ring protons in monosubstituted bis(arene)chromium cations. The satellites in the spectra of bis(arene)chromium cations arise from the ^{53}Cr isotope with a spin $I = {}^3/_2$ (Figure 2). The hyperfine splittings are calculated from the observed satellites and are about 18 G for all the bis(arene)chromium cations (Table I). All the g values are close to 1.986 which is less than g values ($\sim$2.003) of uncomplexes substituted benzene radicals.[25]

It is generally recognized from several MO calculations[2,4,24] that overlap of the metal($3d_{z^2}$) with arene(σ, a_{1g}) results in the delocalization of the unpaired spin over the ring protons. This lack of sensitivity of ESR $A(H_{Ar})$, $A(^{53}Cr)$, and g values to the substituents in the monosubstituted bis(arene)chromium(I) cations leads to the conclusion that the spin delocalization from Cr($3d_{z^2}$) to arene(σ, a_{1g}) is approximately equal and is less effective than the delocalization of the unpaired C_{2p_z} electron in the uncomplexed free arene.[25] The substituent merely effects a redistribution of magnetization among these arene protons.

The substituent effects on the ESR hyperfine constants are not large in the bis(arene)chromium(I) cations. However, these data might be related to paramagnetic NMR measurements which might yield much more useful information.[26]

(b) ESR Measured in $CHCl_3$/DMF (1:1, v/v) at -140 °C. The anisotropic ESR spectra of all the substituted bis(arene)chromium cations studied in a glassy dimethylformamide/chloroform (1:1) solution consist of two lines attributed to coupling of the unpaired electron with the nuclear spin of the protons ($I = {}^1/_2$) and with anisotropic g tensors ($g_\parallel$ and $g_\perp$) (see Table II). However, the observed hyperfine structure was well resolved only for the bis(benzene)chromium cation and increasingly less well resolved on passing from (benzene)(benzaldehyde)chromium to the bis(benzaldehyde)chromium to bis(1,3,5-triisopropylbenzene)chromium cations (Figure 3) and implies that, in the glassy solution, the increase in the number of substituents prevents molecular rotation from averaging out the anisotropy. Such hindered rotation has previously been suggested by the observed lack of resolution in the ESR spectra of alkyl-substituted bis(arene)chromium complexes.[5,24]

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Table II. Anisotropic ESR Data[a] for $Cr(\eta^6\text{-arene})_2^+$ in $DMF/CHCl_3$ (1:1, v/v) Glassy Solution -140 °C

arene	$A_{\parallel}(H_{Ar})$	$A_{\perp}(H_{Ar})$	$A_{\parallel}{}^b(^{53}Cr)$	$A_{\perp}(^{53}Cr)$	$g_{\parallel}$	$g_{\perp}$
C_6H_6	3.1	3.6	2.9	25.6	2.0031	1.9786
$C_6H_5CH_3$	3.0^b	3.7	2.6	25.7	2.0051	1.9785
$C_6H_5OCH_3$	3.5	3.9^b	4.8	24.6	2.0055	1.9800
$C_6H_5C_6H_5$			4.7	25.1	2.0025	1.9768
$C_6H_5COOC_2H_5$	2.9	3.5^b	4.1	25.4	2.0046	1.9774
C_6H_5CHO	2.9^b	3.4	1.3	25.3	2.0030	1.9793
1,3,5-$C_6H_3(CH_3)_3$			2.4	25.8	2.0018	1.9793
C_6H_5CHO, C_6H_6	3.0	3.4	2.9	25.7	2.0034	1.9783
C_6H_5Cl	3.4	3.6^b	3.9	25.2	2.0033	1.9800
1,3,5-$C_6H_3(i\text{-}C_3H_7)$			3.4	25.3	2.0014	1.9801

[a] The experimental error of A, ±0.02 G, and g, ±0.0005. [b] A values obtained from $A = {}^1/_3(A_{\parallel} + 2A_{\perp})$.

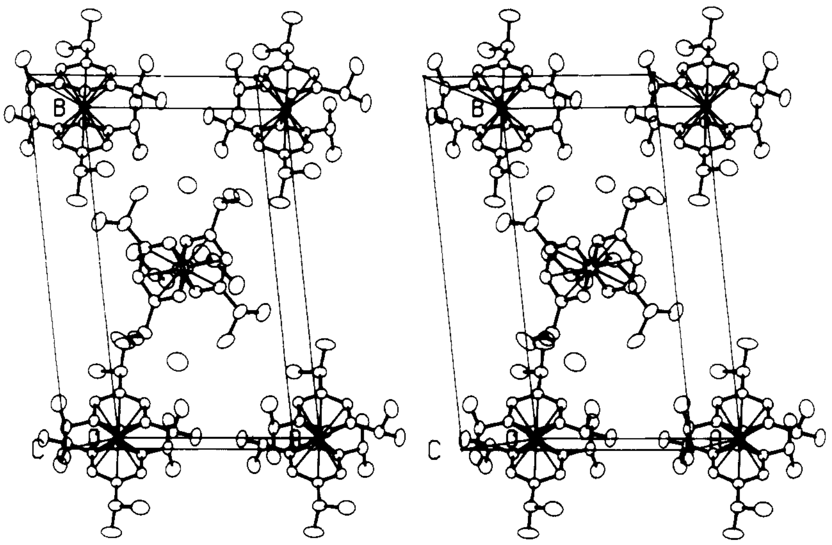

Figure 4. Stereoview of the unit cell of $[1,3,5\text{-}C_6H_3(i\text{-}C_3H_7)_3]_2CrI$.

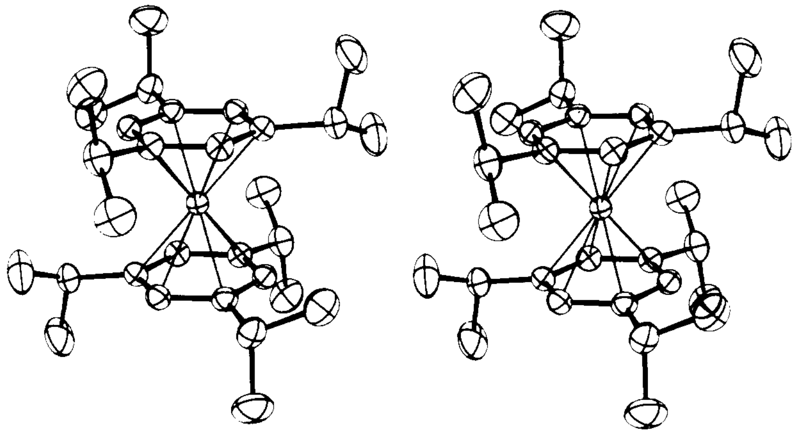

Figure 5. Stereoview of $[1,3,5\text{-}C_6H_3(i\text{-}C_3H_7)_3]_2Cr^+$ cation. Hydrogen atoms are omitted for clarity.

In the bis(arene)chromium(I) compounds with small substituent groups such as H, CHO, Cl, OCH_3, and CH_3, the values of $A_{\parallel}(H_{Ar})$ and/or $A_{\perp}(H_{Ar})$ can be observed since the rotation averages out the anisotropy around z and/or x,y axes. However, the compounds which possess bulky substituents such as Ph or $i\text{-}C_3H_7$ or have more substituents on the ring cause the hyperfine lines to be broadened and no hyperfine structure can be obtained on z and x,y peaks. All the $A_{\parallel}(H_{Ar})$ and $A_{\perp}(H_{Ar})$ are listed in Table II.

In the ESR spectra of substituted bis(arene)chromium cations, the $A_{\perp}(^{53}Cr)$ can be evaluated from the observed ^{53}Cr line around the x,y peak. No axial ^{53}Cr hyperfine structure can be found because it is hidden under the z peak,[24] but $A_{\parallel}(^{53}Cr)$ still can be estimated from the formalism $A = {}^1/_3(A_{\parallel} + 2A_{\perp})$ and are listed in Table II.

In summary, the lack of any significant dependence of ESR parameters on the ring substituent is not surprising in view of the small effects of ring substituents on ligand–metal charge-transfer bands.

X-ray Structural Study of Bis(1,3,5-triisopropylbenzene)chromium(I) Iodide. In the crystal there are two independent cations ($CrC_{30}H_{48}^+$) and two symmetry related anions (I^-) in the unit cell. The stereoscopic view of two unit cells of $Cr[1,3,5\text{-}C_6H_3(i\text{-}C_3H_7)_3]_2^+\ I^-$ along c is shown in Figure 4. Two chromium atoms are situated in special positions, (0,0,0) and $(^1/_2,^1/_2,^1/_2)$, and the iodines are situated in a general position. The four Cr–I distance are 6.178, 6.266, 6.357, and 6.592 Å. Each cation consists of a chromium(I) atom situated at an inversion center. For

Table III. Anisotropic Thermal Parameters[a] and Standard Deviations in Bis(1,3,5-triisopropylbenzene)chromium Iodide

atom	*B*(11)	*B*(22)	*B*(33)	*B*(12)	*B*(13)	*B*(23)
C_1	2.6 (1)	2.04 (9)	2.4 (1)	0.31 (7)	0.69 (8)	0.14 (7)
C_2	1.9 (1)	2.6 (1)	2.7 (1)	−0.05 (8)	0.74 (8)	0.09 (8)
C_3	2.1 (1)	2.6 (1)	2.5 (1)	0.32 (8)	0.60 (8)	0.12 (8)
C_4	2.3 (1)	2.6 (1)	2.2 (1)	0.52 (8)	0.68 (8)	0.19 (8)
C_5	2.3 (1)	2.5 (1)	2.3 (1)	0.47 (8)	0.87 (8)	−0.01 (8)
C_6	2.3 (1)	2.4 (1)	2.6 (1)	0.67 (8)	0.65 (8)	0.14 (8)
C_7	3.9 (1)	2.5 (1)	2.9 (1)	0.45 (9)	1.2 (1)	0.81 (9)
C_8	7.7 (3)	2.4 (1)	5.4 (2)	−0.1 (1)	0.2 (2)	0.9 (1)
C_9	5.4 (2)	4.2 (2)	4.4 (2)	0.4 (1)	−0.5 (2)	1.9 (1)
C_{10}	2.0 (1)	3.4 (1)	3.6 (1)	0.42 (9)	0.38 (9)	0.7 (1)
C_{11}	3.2 (1)	5.9 (2)	3.9 (2)	−0.0 (1)	−0.1 (1)	−0.7 (1)
C_{12}	2.2 (1)	6.2 (2)	5.0 (2)	1.2 (1)	0.8 (1)	−0.3 (2)
C_{13}	2.3 (1)	4.2 (1)	2.7 (1)	0.86 (9)	1.07 (9)	0.5 (1)
C_{14}	4.0 (2)	4.6 (2)	4.4 (2)	0.4 (1)	2.6 (1)	0.8 (1)
C_{15}	6.3 (2)	5.0 (2)	5.8 (2)	1.2 (2)	4.2 (2)	−0.3 (2)
C_{16}	2.7 (1)	2.7 (1)	2.4 (1)	0.18 (8)	0.64 (9)	0.26 (8)
C_{17}	2.9 (1)	2.4 (1)	2.7 (1)	0.35 (9)	0.80 (9)	0.63 (8)
C_{18}	2.5 (1)	2.6 (1)	2.8 (1)	−0.05 (8)	0.79 (9)	0.28 (8)
C_{19}	2.2 (1)	3.2 (1)	3.0 (1)	0.12 (9)	0.61 (9)	0.22 (9)
C_{20}	3.0 (1)	3.0 (1)	2.7 (1)	0.60 (9)	0.88 (9)	0.15 (9)
C_{21}	3.2 (1)	2.5 (1)	2.4 (1)	0.28 (9)	0.80 (9)	−0.01 (8)
C_{22}	3.0 (1)	3.1 (1)	2.8 (1)	−0.00 (9)	0.09 (9)	0.30 (9)
C_{23}	3.7 (2)	5.6 (2)	4.9 (2)	1.4 (2)	−0.8 (1)	−0.3 (2)
C_{24}	4.5 (2)	5.9 (2)	2.9 (1)	−0.0 (2)	0.3 (1)	−0.0 (1)
C_{25}	3.0 (1)	2.8 (1)	4.0 (1)	−0.3 (1)	0.6 (1)	0.3 (1)
C_{26}	4.3 (2)	3.5 (1)	4.1 (2)	−0.6 (1)	0.8 (1)	−0.3 (1)
C_{27}	5.7 (2)	5.4 (2)	4.8 (2)	−2.2 (2)	1.3 (2)	1.2 (2)
C_{28}	3.7 (1)	3.9 (1)	3.5 (1)	1.7 (1)	0.3 (1)	−0.2 (1)
C_{29}	6.0 (2)	3.6 (1)	4.9 (2)	2.2 (1)	1.5 (2)	0.4 (1)
C_{30}	4.8 (2)	5.9 (2)	8.1 (3)	2.4 (2)	2.7 (2)	0.2 (2)
I	6.63 (2)	5.20 (1)	5.87 (2)	0.12 (2)	1.14 (1)	1.03 (1)
Cr_1	1.73 (2)	1.95 (2)	1.98 (2)	0.28 (2)	0.62 (2)	0.17 (2)
Cr_2	2.26 (2)	2.01 (2)	2.27 (2)	0.26 (2)	0.53 (2)	0.27 (2)

[a] Calculated standard deviations are indicated in parentheses. The temperature factor has the form $T = -\Sigma(H(I)H(J)B(IJ)\mathrm{ASTAR}(I)\mathrm{ASTAR}(J))/4$, where H is the miller index, ASTAR is the reciprocal cell length, and I and J are cycled 1 through 3.

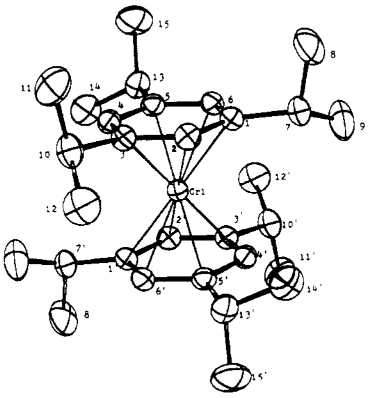

Figure 6. ORTEP drawing of bis(1,3,5-triisopropylbenzene)chromium(1+) cation.

Table IV. Bond Distance (Å)[a] of Bis(1,3,5-triisopropylbenzene)chromium(1+) in Cation 1 and Cation 2

cation 1		cation 2	
C_1-Cr_1	2.185 (0)	C_{16}-Cr_2	2.199 (1)
C_2-Cr_1	2.167 (1)	C_{17}-Cr_2	2.188 (0)
C_3-Cr_1	2.191 (1)	C_{18}-Cr_2	2.204 (1)
C_4-Cr_1	2.165 (1)	C_{19}-Cr_2	2.147 (1)
C_5-Cr_1	2.184 (0)	C_{20}-Cr_2	2.183 (1)
C_6-Cr_1	2.170 (0)	C_{21}-Cr_2	2.169 (0)
C_2-C_1	1.416 (4)	C_{17}-C_{16}	1.412 (4)
C_6-C_1	1.410 (3)	C_{21}-C_{16}	1.412 (4)
C_7-C_1	1.523 (2)	C_{22}-C_{16}	1.526 (3)
C_3-C_2	1.414 (2)	C_{18}-C_{17}	1.414 (3)
C_4-C_3	1.419 (3)	C_{19}-C_{18}	1.414 (4)
C_{10}-C_3	1.522 (3)	C_{25}-C_{18}	1.518 (4)
C_5-C_4	1.416 (4)	C_{20}-C_{19}	1.409 (4)
C_6-C_5	1.417 (2)	C_{21}-C_{20}	1.413 (4)
C_{13}-C_5	1.511 (3)	C_{28}-C_{20}	1.512 (4)
C_8-C_7	1.512 (4)	C_{23}-C_{22}	1.518 (5)
C_9-C_7	1.515 (4)	C_{24}-C_{22}	1.532 (5)
C_{11}-C_{10}	1.524 (4)	C_{26}-C_{25}	1.514 (2)
C_{12}-C_{10}	1.512 (2)	C_{27}-C_{25}	1.531 (3)
C_{14}-C_{13}	1.516 (4)	C_{29}-C_{28}	1.513 (5)
C_{15}-C_{13}	1.520 (3)	C_{30}-C_{28}	1.528 (5)

[a] Estimated standard deviations are in parentheses in the units of least significant digits.

example, cation 1 contains Cr_1, C_1 to C_{15}, and $C_{1'}$ to $C_{15'}$ and cation 2 contains Cr_2, C_{16} to C_{30}, and $C_{16'}$ to $C_{30'}$. The normal vectors of the two sets of arene rings form an angle of ~70°. The detailed conformations of the two cations are very similar. The stereoview and the ORTEP drawing of cation 1 are shown in Figures 5 and 6, respectively. Hydrogen atoms have been omitted for clarity. The anisotropic thermal parameters are listed in Table III.

Ring carbons are planar with the maximum deviation from the ring plane being 0.008 (cation 1) and 0.01 Å (cation 2) (Table VI), and the two ring planes within the cation are parallel. The average C–C bond distance in the ring is 1.416 (cation 1) and 1.413 Å (cation 2). The average Cr–C bond distance (1.655 (cation 1) and 1.664 Å (cation 2)) is close to the corresponding values of other known bis(arene)chromium(0) and bis(arene)chromium(I) complexes.[7-12] The bond distance and bond angles for both cation 1 and cation 2 are listed in Tables IV and V, respectively. Inspection of Table VI reveals that the orientation of the isopropyl groups in cation 1 is somewhat different at carbon 3 than at carbons 1 and 5. The deviation from the ring plane for the attached isopropyl group at carbon 3 is larger [C_{10} (0.17 Å), C_{11} (1.66 Å), C_{12}

Table V. Bond Angle (Deg)[a] of $[1,3,5\text{-}C_6H_3(i\text{-}C_6H_7)_3]_2Cr^+$

cation 1		cation 2	
$C_2C_1C_6$	118.8 (2)	$C_{17}C_{16}C_{21}$	118.2 (2)
$C_2C_1C_7$	119.3 (2)	$C_{17}C_{16}C_{22}$	122.5 (2)
$C_6C_1C_7$	121.6 (3)	$C_{21}C_{16}C_{22}$	119.3 (2)
$C_1C_2C_3$	121.3 (2)	$C_{16}C_{17}C_{18}$	121.7 (2)
$C_2C_3C_4$	118.2 (2)	$C_{17}C_{18}C_{19}$	117.9 (2)
$C_2C_3C_{10}$	122.2 (2)	$C_{17}C_{18}C_{25}$	119.7 (2)
$C_4C_3C_{10}$	119.3 (1)	$C_{19}C_{18}C_{25}$	122.0 (2)
$C_3C_4C_5$	122.0 (2)	$C_{18}C_{19}C_{20}$	122.4 (2)
$C_4C_5C_6$	118.0 (2)	$C_{19}C_{20}C_{21}$	117.6 (3)
$C_4C_5C_{13}$	122.1 (1)	$C_{19}C_{20}C_{28}$	119.9 (3)
$C_6C_5C_{13}$	119.6 (2)	$C_{21}C_{20}C_{28}$	122.4 (2)
$C_1C_6C_5$	121.7 (2)	$C_{16}C_{21}C_{20}$	122.1 (2)
$C_1C_7C_8$	108.0 (1)	$C_{16}C_{22}C_{23}$	114.2 (2)
$C_1C_7C_9$	115.0 (2)	$C_{16}C_{22}C_{24}$	108.8 (2)
$C_8C_7C_9$	110.4 (4)	$C_{23}C_{22}C_{24}$	109.9 (2)
$C_3C_{10}C_{11}$	107.9 (2)	$C_{18}C_{25}C_{26}$	115.7 (2)
$C_3C_{10}C_{12}$	114.8 (1)	$C_{18}C_{25}C_{27}$	107.4 (2)
$C_{11}C_{10}C_{12}$	110.5 (1)	$C_{26}C_{25}C_{27}$	110.3 (3)
$C_5C_{13}C_{14}$	115.2 (2)	$C_{20}C_{28}C_{29}$	114.3 (3)
$C_5C_{13}C_{15}$	107.8 (2)	$C_{20}C_{28}C_{30}$	108.8 (2)
$C_{14}C_{13}C_{15}$	110.9 (0)	$C_{29}C_{28}C_{30}$	110.2 (3)

[a] Estimated standard deviations are in parentheses in the units of least significant digits.

Table VI. Distance[a] (Å) to the Ring Plane from the Atoms

cation 1		cation 2	
atom	dist to the plane	atom	dist to the plane
C_1	0.003 69	C_{16}	−0.003 52
C_2	−0.007 46	C_{17}	−0.003 02
C_3	0.006 22	C_{18}	0.011 80
C_4	−0.001 35	C_{19}	−0.014 15
C_5	−0.002 32	C_{20}	0.007 33
C_6	0.001 23	C_{21}	0.001 55
Cr_1	−1.653 96	Cr_2	−1.662 90
C_7	0.143 78	C_{22}	0.067 28
C_8	1.613 76	C_{24}	1.497 64
C_9	−0.465 59	C_{23}	−0.368 84
C_{10}	0.173 36	C_{25}	0.217 49
C_{11}	1.662 29	C_{27}	1.707 50
C_{12}	−0.600 26	C_{26}	−0.616 58
C_{13}	0.129 09	C_{28}	0.132 70
C_{14}	−0.467 83	C_{29}	−0.486 21
C_{15}	1.603 07	C_{30}	1.611 14

[a] Distance (Å); sign "−" means atoms under the plane; sign "+" means atoms above the plane.

(−0.60 Å)] compared with values at carbon 1 [C_7 (0.14 Å), C_8 (1.61 Å), C_9 (−0.47 Å)] and carbon 5 [C_{13} (0.13 Å), C_{15} (1.60 Å), C_{14} (−0.47 Å)]. The interplanar distance between the two rings in cation 1 is 3.31 Å larger than the corresponding value in bis(benzene)chromium iodide (3.18 Å).[7] There must be considerable steric hindrance between the isopropyl groups, taking the bond between the ring carbon and the attached isopropyl carbon ~6° out of the ring plane. There is a similar conformation for cation 2 (Table VI). Because of the steric interaction of six isopropyl groups between two rings, the orientation of cationic bis(1,3,5-triisopropylbenzene)chromium with respect to the isopropyl groups favors the staggered conformer, which is formed. The stabilization of the staggered conformer is dominated by steric factors due to the three bulky isopropyl substituents in the ring.[27]

It is of interest to note the effect of the isopropyl groups on the internal ring angles. Domenicano and co-workers[28,29] have determined the effects of various substituents on the internal ring angle of uncomplexed benzene rings. They gave a general rule in which the ring angles at the substituted carbon appears to be larger than 120° for electron-withdrawing groups and less than 120° for electron-donating groups. The X-ray determination reveals that the ring angle at the substituted carbon has the average value of 118.6°, consistent with values observed in uncomplexed aromatics and consistent with the electron-donating nature of isopropyl groups. Similar results have been found with electron-withdrawing substituents in bis(arene)chromium(0) compounds.[12]

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Registry No. $Cr(\eta^6\text{-}C_6H_6)_2^+$, 11077-47-7; $Cr(\eta^6\text{-}C_6H_5CH_3)_2^+$, 33505-50-9; $Cr(\eta^6\text{-}C_6H_5OCH_3)_2^+$, 75170-79-5; $Cr(\eta^6\text{-}C_6H_5C_6H_5)_2^+$, 33154-48-2; $Cr(\eta^6\text{-}C_6H_5COOC_2H_5)_2^+$, 57219-88-2; $Cr(\eta^6\text{-}C_6H_5CHO)_2$, 82544-76-1; $Cr[\eta^6\text{-}1,3,5\text{-}C_6H_3(CH_3)_3]_2^+$, 12243-05-9; $Cr(\eta^6\text{-}C_6H_5CHO)(\eta^6\text{-}C_6H_6)^+$, 82544-77-2; $Cr(\eta^6\text{-}C_6H_5Cl)_2^+$, 75170-75-1; $Cr[\eta^6\text{-}1,3,5\text{-}C_6H_3(i\text{-}C_3H_7)_3]_2$, 82544-78-3; $Cr(\eta^6\text{-}C_6(CH_3)_6)^+$, 12243-39-6; $Cr[\eta^6\text{-}1,3,5\text{-}C_6H_3(i\text{-}C_3H_7)_3]_2^+I^-$, 82544-80-7; Cr, 7440-47-3; isopropylbenzene, 717-74-8; bis(1,3,5-triisopropylbenzene)chromium, 82544-79-4.

Supplementary Material Available: Tables of positional parameters (Table VII), thermal parameters (Table VIII), bond lengths (Table IX), bond angles (Table X), and structure factors (Table XI) and their standard deviations (68 pages). Ordering information is given on any current masthead page.

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(27) Preliminary dynamic NMR data suggest that restricted rotation around the chromium–arene bond occurs in solution. Two unequal population sites exist between the staggered and eclipsed conformer with an approximate barrier to rotation of 10 kcal/mol for the sterically preferred staggered conformation.

(28) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr., Sect. B* **1975**, *B31*, 221.

(29) Domenicano, A.; Vaciago, A. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1382.