

Syntheses and structures of bis(tricarbonylchromium)-substituted α, ω -diphenylhexatriene complexes

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Abstract

Treatment of several (4-substituted benzaldehyde)chromium tricarbonyl complexes with bisphosphoranes provides the first examples of (4,4'-substituted α, ω -diphenylhexatriene)bis(chromium tricarbonyl) complexes in good yield. Systems containing both donor and acceptor substituents may be prepared. The structures of three examples, [*E,E,E*- η^6 -4-R-C₆H₄-(CH=CH)₃- η^6 -C₆H₄-4'-R][Cr(CO)₃]₂, (R = Me₂N, **1**; R = Me₃Si, **3**; R = F₃C, **4**) have been determined by single crystal X-ray diffraction. The results demonstrate that the olefinic portions of the molecules adopt the all *trans E,E,E* conformation, and that the tricarbonylchromium groups adopt *anti* orientations on each face of the organic plane. Compounds **3** and **4** are soluble enough to allow acquisition of ¹H NMR spectra of sufficient quality to allow the accurate simulation of the resonances corresponding to the olefinic protons. The simulations suggest that the hexatriene moiety behaves as three independent double bonds, in accord with the structural results.

Keywords: Chromium; Arene complexes; Wittig reaction; Diphenylhexatriene; Polyene

1. Introduction

The design of soluble, processible inorganic/organometallic molecules capable of useful photonic behavior is a rapidly expanding field. In particular, the last two years have seen an explosion in the number of inorganics/organometallics exhibiting third harmonic generation [$\chi(3)$ behavior] [1–7]. The practical reason for this is obvious: in contrast with materials for second harmonic generation, $\chi(3)$ materials may contain a molecular and/or crystallographic inversion center. Thus the number of potentially useful molecules is greatly increased.

Spangler and coworkers have shown that 4, 4'-substituted α, ω -diphenylpolyenes form particularly stable polarons and bipolarons when oxidized, and that these materials exhibit the delocalization necessary for enhanced $\chi(3)$ behavior [8]. We felt it of interest to prepare organometallic α, ω -diphenylpolyene compounds in order to examine the effect of metal coordina-

tion on the physical characteristics of the diphenylpolyene chain. We report here our successes in synthesizing the first (4,4'-substituted diphenylhexatriene)bis(chromium tricarbonyl) compounds [*E,E,E*- η^6 -4-R-C₆H₄-(CH=CH)₃- η^6 -C₆H₄-4'-R][Cr(CO)₃]₂, (R = Me₂N, **1**; R = Et₂N, **2**; R = Me₃Si, **3**; R = F₃C, **4**), the structures of **1**, **3** and **4** as determined by single crystal X-ray diffraction, and our insights into the delocalization of the triene double bonds as examined by solid state and solution studies.

2. Experimental

Unless otherwise noted, all reactions and manipulations were carried out under inert atmosphere either through Schlenk or glovebox techniques. Evaporations of solvent were performed in vacuo. The complexes (4-R-C₆H₄-CHO)Cr(CO)₃ (R = Me₂N, Me₃Si, F₃C) were prepared as reported [9]. (4-Et₂N-C₆H₄-CHO)Cr(CO)₃ was prepared analogously. The bisphosphonium salt [Bu₃PCH₂CH=CHCH₂PBu₃]₂Cl₂ and the bisdiphosphonate (EtO)₂(O)PCH₂CH=CHCH₂P(O)(OEt)₂ were prepared by methods analogous to those described previously [10].

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2.1. $[E,E,E-\eta^6-4-Me_2N-C_6H_4-(CH=CH)_3-\eta^6-C_6H_4-4'-NMe_2][Cr(CO)_3]_2$, 1

A stirring ethanol solution (75 ml) of $[Bu_3P-CH_2CH=CHCH_2PBu_3]Cl_2$ (0.61 g, 1.15 mmol) and $(\eta^6-4-Me_2N-C_6H_4-CHO)Cr(CO)_3$ (0.632 g, 2.22 mmol) was treated dropwise with an ethanol solution of NaOEt (3.0 ml of 1 M solution, 3.0 mmol). During the addition, the solution darkened from orange to red, and soon after complete addition an orange solid precipitated. The reaction mixture was stirred for 24 h at room temperature, then for 24 h at 50 °C. It was then cooled to 0 °C. The solid was filtered out, washed with cold ethanol, and dried under vacuum, giving 0.390 g (0.661 mmol, 60%) of analytically pure product. Crystals suitable for diffraction studies were grown by slow cooling of a hot, saturated THF solution to room temperature. The compound has only sparing solubility in all solvents examined. 1H NMR ($CDCl_3$): δ 6.7–5.8 (m, 6H, olefinic H); 5.73 (br, 4H, phenyl H); 4.83 (br, 4H, phenyl H); 2.90 (br m, 12H, NMe_2). 1H NMR (acetone- d_6): δ 6.8–6.0 (m, 6H, olefinic H); 6.07 (br d, $J_{HH} = 7.3$ Hz, 4H, phenyl H); 5.20 (br d, $J_{HH} = 7.3$ Hz, 4H, phenyl H); 2.95 (br m, 12H, NMe_2). The compound is too sparingly soluble for ^{13}C NMR spectroscopy. IR ($CDCl_3$): ν_{CO} 1949, 1867 cm^{-1} . Anal. Calc. for $C_{28}H_{26}Cr_2N_2O_6$: C, 56.95; H, 4.44; N, 4.74%. Found: C, 56.32; H, 4.85; N, 4.45%.

2.2. $[E,E,E-\eta^6-4-Et_2N-C_6H_4-(CH=CH)_3-\eta^6-C_6H_4-4'-NEt_2][Cr(CO)_3]_2$, 2

A stirring THF solution of $(\eta^6-4-Et_2N-C_6H_4-CHO)Cr(CO)_3$ (3.00 g, 9.58 mmol) was treated with an ethanol solution of $[Bu_3PCH_2CH=CHCH_2PBu_3]Cl_2$ (46 ml, 5.04 mmol). The resulting mixture was treated dropwise with $NaN(SiMe_3)_2$ (2.46 g, 13.4 mmol) dissolved in 50 ml THF. During the addition, orange solid precipitated. The reaction mixture was stirred for 72 h at room temperature, then for 48 h at 50 °C. It was then transferred through a Teflon cannula into 1400 ml argon-sparged water. The mixture was stirred overnight, whereupon the orange solid was allowed to settle. The solid was filtered out, then pumped on in a vacuum oven for several hours. It was then dissolved in hot THF and filtered. The THF was evaporated, and the resulting solid triturated with ether. It was then filtered out and dried, giving 1.03 g (1.59 mmol, 33%) of analytically pure product. The compound has only sparing solubility in all solvents examined. 1H NMR ($CDCl_3$): δ 6.7–5.8 (m, 6H, olefinic H); 5.76 (d, $J_{HH} = 6.9$ Hz, 4H, phenyl H); 4.80 (d, $J_{HH} = 6.9$ Hz, 4H, phenyl H); 3.24 (br m, 8H, CH_2); 1.21 (br t, $J_{HH} = 7.2$ Hz, 12H, CH_3). 1H NMR (acetone- d_6): δ 6.5–5.8 (m, 6H, olefinic H); 6.07 (d, $J_{HH} = 7.0$ Hz, 4H, phenyl H); 5.17 (d, $J_{HH} = 7.0$ Hz, 4H, phenyl H); 3.35 (br m, 8H, CH_2); 1.21 (br t,

$J_{HH} = 7.0$ Hz, 12H, CH_3). The compound is too sparingly soluble for ^{13}C NMR spectroscopy. IR ($CDCl_3$): ν_{CO} 1933, 1828 cm^{-1} . Anal. Calc. for $C_{32}H_{34}Cr_2N_2O_6$: C, 59.44; H, 5.30; N, 4.33%. Found: C, 59.41; H, 5.24; N, 4.24%.

2.3. $E,E,E-4-Me_3Si-C_6H_4-(CH=CH)_3-C_6H_4-4'-SiMe_3$

This compound was prepared from $4-Me_3Si-C_6H_4-CHO$ by the Horner–Emmons–Wadsworth procedure described in Ref. [10]. It was recrystallized from CH_3CN as pale yellow needles. 1H NMR ($CDCl_3$): δ 7.50 (d, $J_{HH} = 7.8$ Hz, 4H, phenyl H); 7.40 (d, $J_{HH} = 7.8$ Hz, 4H, phenyl H); 7.0–6.5 (m (see Section 3.2), 6H, olefinic H); 0.28 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.0, 137.8 (olefinic C's); 132.8, 129.4 (*ipso* phenyl C's); 133.7, 125.7 (*ortho*, *meta* phenyl C's); –1.14 ($SiMe_3$). The missing olefinic carbon resonance appears to lie under the phenyl carbon resonance at δ 133.7.

2.4. $[E,E,E-\eta^6-4-Me_3Si-C_6H_4-(CH=CH)_3-\eta^6-C_6H_4-4'-SiMe_3][Cr(CO)_3]_2$, 3

$(\eta^6-4-Me_3Si-C_6H_4-CHO)Cr(CO)_3$ (0.912 g, 2.90 mmol) and $(EtO)_2(O)PCH_2CH=CHCH_2P(O)(OEt)_2$ (0.476 g, 1.45 mmol) were dissolved in 1,2-dimethoxyethane (dme, 30 ml). The resulting mixture was treated dropwise with a dme solution (40 ml) of $KOBu^t$ (0.393 g, 3.5 mmol). The reaction mixture darkened from orange to deep burgundy, and turbidity was evident. The reaction mixture was stirred for 16 h at room temperature, then for 24 h at 85 °C. It was then transferred through a Teflon cannula into 400 ml argon-sparged water. The mixture was stirred for 4 h then saturated with NaCl. The resulting heterogeneous system was extracted in air with 4×75 ml CH_2Cl_2 . The combined organic layers were dried over $MgSO_4$ then filtered, giving a dark orange solution. The volatiles were evaporated, giving a red solid. This was recrystallized by dissolving it in minimum boiling heptane (ca. 150 ml), filtering the hot solution, and cooling it to –10 °C. The orange powder which precipitated was filtered out and dried, giving 0.421 g (0.649 mmol, 45%) of product. Crystals suitable for diffraction studies were grown from CH_2Cl_2 /ether at –30 °C. 1H NMR ($CDCl_3$): δ 7.16–6.18 (m, 6H, olefinic H); 5.51 (d, $J_{HH} = 6.7$ Hz, 4H, phenyl H); 5.32 (d, $J_{HH} = 6.7$ Hz, 4H, phenyl H); 0.29 (s, 18H, $SiMe_3$). 1H NMR (acetone- d_6): δ 7.15–6.41 (m (see Section 3.2), 6H, olefinic H); 5.87 (d, $J_{HH} = 6.6$ Hz, 4H, phenyl H); 5.75 (d, $J_{HH} = 6.6$ Hz, 4H, phenyl H); 0.35 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (acetone- d_6): δ 237.6 (CO); 138.1, 135.7, 133.8 (olefinic C's); 112.3, 102.8 (*ipso* phenyl C's); 103.9, 94.0 (*ortho*, *meta* phenyl C's); 1.43 ($SiMe_3$). IR ($CDCl_3$): ν_{CO} 1970, 1898 cm^{-1} .

2.5. *E,E,E*-4- $F_3C-C_6H_4-(CH=CH)_3-C_6H_4-4'-CF_3$

This compound was provided by the C.W. Spangler research group. 1H NMR (acetone- d_6): δ 7.70 (AB q, $J_{HH} = 8.9$ Hz, 8H, phenyl H); 7.35–6.65 (m (see Section 3.2), 6H, olefinic H).

2.6. [*E,E,E*- η^6 -4- $F_3C-C_6H_4-(CH=CH)_3-\eta^6-C_6H_4-4'-CF_3$] $[Cr(CO)_3]_2$, **4**

A stirring THF solution of (η^6 -4- $F_3C-C_6H_4-CHO$) $Cr(CO)_3$ (3.00 g, 9.67 mmol) was treated with an ethanol solution of $[Bu_3PCH_2CH=CHCH_2PBu_3]Cl_2$ (46 ml, 5.1 mmol). The resulting mixture was treated dropwise with a THF solution of $NaN(SiMe_3)_2$ (2.48 g, 13.5 mmol). The murky, dark red reaction mixture was stirred 24 h at room temperature, 48 h at 50 °C, and 6 d at room temperature. It was then transferred by cannula into 1400 ml argon-sparged water. The mixture was

stirred overnight, whereupon the red solid was allowed to settle. The water was removed by cannula. The flask and product contained therein were pumped on in a vacuum oven for several hours. Heptane was then added to loosen the material from the walls of the flask; the red solid was filtered out and dried to give 2.18 g (3.40 mmol, 70%) of analytically pure product. Crystals suitable for diffraction studies were grown from CH_2Cl_2 /pentane at -30 °C. 1H NMR ($CDCl_3$): δ 6.9–6.1 (m, 6H, olefinic H); 5.72 (d, $J_{HH} = 6.7$ Hz, 4H, phenyl H); 5.37 (d, $J_{HH} = 6.7$ Hz, 4H, phenyl H). 1H NMR (acetone- d_6): δ 7.25–6.35 [m (see Section 3.2), 6H, olefinic H]; 6.13 (d, $J_{HH} = 6.9$ Hz, 4H, phenyl H); 5.86 (d, $J_{HH} = 6.9$ Hz, 4H, phenyl H). $^{13}C\{^1H\}$ NMR (acetone- d_6): δ 231.9 (CO); 135.7, 133.8, 130.1 (olefinic C's); 124.4 (q, $J_{CF} = 272$ Hz, CF_3); 109.0 (*ipso* Ph C); 92.0, 89.0 (*ortho*, *meta* C). The other *ipso* Ph C resonance was not located. IR ($CDCl_3$): ν_{CO} 1990, 1925 cm^{-1} . Anal. Calc. for $C_{26}H_{14}Cr_2F_6O_6$: C, 48.77; H, 2.20%. Found: C, 48.89; H, 2.31%.

Table 1
Data collection and refinement parameters for **1**, **3** and **4**

	1	3	4
Formula	$C_{28}H_{26}Cr_2N_2O_6$	$C_{30}H_{32}Cr_2O_6Si_2$	$C_{26}H_{14}Cr_2F_6O_6$
Formula weight	590.52	648.75	640.37
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
Cell constants:			
<i>a</i> (Å)	9.009 (3) ^a	9.623 (3) ^a	7.432 (5) ^b
<i>b</i> (Å)	13.060 (4)	12.861 (3)	17.215 (12)
<i>c</i> (Å)	13.164 (4)	13.420 (4)	10.387 (7)
α (deg)	117.56 (3)		
β (deg)	95.77 (3)	99.70 (2)	101.355 (14)
γ (deg)	97.58 (3)		
Volume (Å ³)	1338	1637	1303 (2)
Formula units/cell	2	2	2
D_{calc} (g cm ⁻³)	1.47	1.32	1.63
μ_{calc} (cm ⁻¹)	8.95	8.03	9.17
Decay of standard reflections	$\pm 1\%$	$\pm 1\%$	
2θ range (deg)	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 47$
Reflections measured	4708	3201	4500
Reflections observed	2340 ^c	942 ^d	1019 ^e
Number of parameters	355	190	181
Weights	0.001 ^f	0.004 ^f	0.0439, 2.2239 ^g
<i>R</i>	0.055 ^h	0.049 ^h	0.081 ⁱ
<i>R_w</i>	0.068	0.059	0.137 (wR^2)
Goodness of fit ^j	1.0	0.30	1.073

^a Cell parameters were determined by least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 reflections, typically with $\theta > 14^\circ$.

^b Cell parameters were determined by least-squares refinement of $((\sin \theta)/\lambda)^2$ for 125 reflections over the full θ range.

^c Corrected for Lorentz/polarization effects and empirically corrected for absorption (Ψ -scans); $F_o > 5\sigma(F_o)$.

^d Corrected for Lorentz/polarization effects; $F_o > 5\sigma(F_o)$.

^e Corrected for Lorentz/polarization effects; $I_o > 2\sigma(I_o)$.

^f SHELX-76 weighting scheme; $w = [\sigma(F_o)^2 + a(F_o)^2]^{-1}$, where w is the weight and a is the value given.

^g SHELXTL weighting scheme; $w = [\sigma^2(F_o)^2 + (a \times P)^2 + b \times P]^{-1}$, where w is the weight, $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$, and a and b are the values given.

^h $R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$; $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2\}^{1/2}$.

ⁱ $R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$; $wR^2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$.

^j Goodness of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$; N_o = number of observations, N_v = number of variables.

2.7. Diffraction studies

Crystals of the three compounds studied proved quite air-stable and were therefore inspected and selected in air. They were then wedged into glass capillaries which were in turn flushed with argon, flame sealed and attached to the goniometer head. Data collection and reduction parameters appear in Table 1. Data for **1** and **3** were collected on an Enraf-Nonius CAD-4 diffractometer employing ω - 2θ scans, while data for **4** were collected on a Siemens SMART diffractometer equipped with a CCD area detector. In each case, graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) was used, and data were collected at ambient temperature. The structures were solved and the data refined using either SHELXS [11] and SHELX, [12] or SHELXTL [13]. For **1** and **3**, the geometrically constrained hydrogen atoms were placed in calculated positions 0.95 \AA from the bonded carbon atom and allowed to ride on that atom with a fixed $B_{\text{eq}} = 5.5 \text{ \AA}^2$. Methyl hydrogen atoms were given the same distance/thermal parameters and were included as a rigid group with rotational freedom at the bonded carbon. For **4**, hydrogen atom thermal parameters were fixed as $B_{\text{eq}} = 1.2 \times U_{\text{eq}}$ of the attached carbon atom. Positional parameters for the anisotropically refined atoms appear in Tables 2–4. Averaged bond distances and angles appear in Table 5.

3. Results and discussion

Coupling of the organochromium benzaldehydes (4-R-C₆H₄-CHO)Cr(CO)₃ (R = Me₂N, Et₂N, Me₃Si, F₃C) with the Wittig reagent Bu₃P=CH-CH=CH-CH=PBu₃ occurs smoothly to give the bis(tricarbonylchromium)-coordinated α, ω -diphenylhexatriene complexes [*E,E,E*- η^6 -4-R-C₆H₄-(CH=CH)₃- η^6 -C₆H₄-4'-R][Cr(CO)₃]₂ (R = Me₂N, **1**; Et₂N, **2**; Me₃Si, **3**; F₃C, **4**) in fair-to-good yields. The reactions proceed somewhat more slowly than the analogous reactions of organic benzaldehydes, as indicated by the reaction times indicated in Section 2. In one preparation of **3**, quenching the reaction after 24 h at room temperature provided the desired product contaminated with a sizable amount of a material which ¹H NMR spectroscopy indicated was probably the intermediate [*E,E*- η^6 -4-Me₃Si-C₆H₄-(CH=CH)₂-CH=PBu₃][Cr(CO)₃]. Therefore we generally opted for long reaction periods. The spectroscopic characteristics of the compounds **1**–**4** are unexceptional, save that the olefinic regions of the ¹H NMR spectra of **3** and **4** are sufficiently well-resolved to allow spectral simulation (see below).

Once isolated, the compounds display surprising stability to oxygen and water; for example, solutions of trimethylsilyl-substituted **3** in acetone show no signs of decomposition after several weeks in air. However, **3**

Table 2
Final fractional coordinates for **1**

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> _{eq} ^a
Cr(1)	0.0982(1)	0.7259(1)	0.4429(1)	2.49
Cr(2)	-0.6792(1)	1.2913(1)	1.0801(1)	2.66
O(1)	0.2141(8)	0.6216(6)	0.2177(5)	5.03
O(2)	-0.1216(7)	0.8177(6)	0.3388(5)	4.80
O(3)	-0.1387(7)	0.5082(6)	0.3551(6)	5.00
O(4)	-0.8056(7)	1.3910(6)	1.3006(5)	4.81
O(5)	-0.4403(8)	1.5106(6)	1.1816(6)	5.68
O(6)	-0.4686(7)	1.1861(7)	1.1762(6)	6.58
N(1)	0.4847(8)	0.7451(7)	0.5021(6)	2.42
N(2)	-1.0696(8)	1.2541(7)	1.0231(7)	2.75
C(1)	0.1709(9)	0.6599(7)	0.3051(7)	3.12
C(2)	-0.0367(9)	0.7815(7)	0.3789(7)	3.15
C(3)	-0.0459(9)	0.5923(8)	0.3891(7)	3.18
C(4)	-0.7555(9)	1.3519(7)	1.2154(7)	3.20
C(5)	-0.532(1)	1.4268(8)	1.1436(7)	3.61
C(6)	-0.5484(9)	1.2293(8)	1.1402(7)	3.65
C(7)	0.1247(9)	0.7309(7)	0.6125(6)	3.04
C(8)	0.2571(9)	0.6982(7)	0.5670(6)	2.98
C(9)	0.3524(9)	0.7729(7)	0.5406(7)	2.80
C(10)	0.3015(9)	0.8736(7)	0.5456(7)	3.26
C(11)	0.1712(8)	0.9040(7)	0.5916(7)	2.96
C(12)	0.0785(9)	0.8348(7)	0.6277(7)	2.79
C(13)	-0.0623(9)	0.8631(7)	0.6720(6)	3.01
C(14)	-0.1134(9)	0.9620(8)	0.6991(7)	3.43
C(15)	-0.2545(9)	0.9786(8)	0.7397(7)	3.50
C(16)	-0.3155(9)	1.0755(8)	0.7678(6)	3.22
C(17)	-0.4588(9)	1.0883(7)	0.8101(7)	3.17
C(18)	-0.5164(9)	1.1845(8)	0.8455(6)	3.14
C(19)	-0.6587(9)	1.2014(7)	0.8933(7)	2.81
C(20)	-0.7378(9)	1.1193(7)	0.9195(7)	3.23
C(21)	-0.8725(9)	1.1396(7)	0.9672(7)	3.06
C(22)	-0.939(1)	1.2381(8)	0.9844(7)	3.45
C(23)	-0.846(1)	1.3243(8)	0.9657(7)	3.62
C(24)	-0.7143(9)	1.3040(7)	0.9189(6)	3.17
C(25)	0.530(1)	0.6391(8)	0.4897(9)	5.12
C(26)	0.561(1)	0.8029(9)	0.4453(9)	4.84
C(27)	-1.120(1)	1.360(1)	1.0525(9)	6.07
C(28)	-1.138(1)	1.179(1)	1.0620(9)	5.72

$$^a B_{\text{eq}} = (8\pi^2/3)[a^2 U_{11}(a^*)^2 + b^2 U_{22}(b^*)^2 + c^2 U_{33}(c^*)^2 + ab(\cos \gamma)U_{12}(a^* b^*) + ac(\cos \beta)U_{13}(a^* c^*) + bc(\cos \alpha)U_{23}(b^* c^*)].$$

and **4** decompose nearly completely over the course of a few days when dissolved in chloroform in the air and left in normal room light. Radical reactions initiated by decomposition of the chloroform are the likely cause here.

Compounds **1**–**4** exhibit solubilities equivalent to or only slightly greater than those of the corresponding free 4,4'-disubstituted diphenylhexatrienes. As is true for the free organics, the dialkylamino systems **1** and **2** are the least soluble, while **3** and **4** form solutions at least an order of magnitude more concentrated. This observation correlates with our previous observations regarding (nitrostilbene)chromium tricarbonyl complexes [9] but continues to surprise us. Solubility, or the lack thereof, in conjugated organic systems is normally ascribed to the ability of highly planar, "two-dimen-

Table 3
Final fractional coordinates for 2

Atom	<i>x/z</i>	<i>y/b</i>	<i>z/c</i>	<i>B_{eq}^a</i>
Cr	0.5360(2)	0.2523(1)	0.1699(1)	3.79
Si	0.8707(4)	0.1419(3)	0.3267(2)	5.35
O(1)	0.752(1)	0.4204(7)	0.1924(8)	9.47
O(3)	0.378(1)	0.3718(7)	−0.0037(7)	10.37
O(2)	0.378(1)	0.3693(6)	0.3052(6)	7.59
C(1)	0.669(1)	0.3547(9)	0.1834(9)	6.12
C(2)	0.439(1)	0.3243(8)	0.2531(8)	4.94
C(3)	0.442(1)	0.3276(9)	0.0656(9)	5.76
C(4)	0.557(1)	0.1209(8)	0.0684(7)	4.27
C(5)	0.683(1)	0.1346(7)	0.1334(7)	3.91
C(6)	0.695(1)	0.1335(7)	0.2393(7)	3.94
C(7)	0.569(1)	0.1211(7)	0.2776(7)	3.80
C(8)	0.439(1)	0.1067(7)	0.2137(8)	4.07
C(9)	0.430(1)	0.1056(7)	0.1086(8)	3.85
C(10)	0.298(1)	0.0900(8)	0.0391(8)	4.34
C(11)	0.183(1)	0.0450(8)	0.0605(7)	4.40
C(12)	0.056(1)	0.0253(7)	−0.0100(8)	4.37
C(13)	0.852(2)	0.214(1)	0.4427(8)	7.34
C(14)	1.004(1)	0.208(1)	0.262(1)	8.72
C(15)	0.923(2)	0.008(1)	0.355(1)	9.27

$${}^a B_{eq} = (8\pi^2/3)[a^2 U_{11}(a^*)^2 + b^2 U_{22}(b^*)^2 + c^2 U_{33}(c^*)^2 + ab(\cos \gamma)U_{12}(a^* b^*) + ac(\cos \beta)U_{13}(a^* c^*) + bc(\cos \alpha)U_{23}(b^* c^*)].$$

sional” molecules to tightly pack “face-to-face” in a crystal lattice. More three-dimensional molecules are expected to be more soluble. The three-dimensionality of the trimethylsilyl and trifluoromethyl substituents as compared with the nearly planar, two-dimensional dialkylamino groups in the free disubstituted diphenylhexatrienes likely accounts for the increased solubilities of the former. It is thus somewhat curious that coordination of the tricarbonylchromium fragments to the organics, which inherently decreases the face-to-face packing ability and makes the molecules more three-dimen-

Table 4
Final fractional coordinates for 4

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U_{eq}^a</i>
Cr(1)	0.6450(2)	0.3582(1)	0.8662(1)	0.057(1)
F(1)	1.1411(9)	0.2795(5)	0.7283(6)	0.142(3)
F(2)	0.9682(10)	0.1992(4)	0.7999(9)	0.159(4)
F(3)	1.1078(7)	0.2861(4)	0.9200(6)	0.111(2)
O(1)	0.3400(10)	0.4320(4)	0.9706(7)	0.104(3)
O(2)	0.5048(10)	0.2072(4)	0.9443(8)	0.104(3)
O(3)	0.8813(9)	0.3792(5)	1.1314(7)	0.117(3)
C(1)	0.4595(14)	0.4043(6)	0.9286(9)	0.073(3)
C(2)	0.5623(13)	0.2662(6)	0.9174(9)	0.067(3)
C(3)	0.7887(12)	0.3713(6)	1.0290(9)	0.078(3)
C(4)	0.5392(11)	0.3460(6)	0.6521(7)	0.062(2)
C(5)	0.6901(12)	0.2962(5)	0.6915(8)	0.065(3)
C(6)	0.8583(12)	0.3255(7)	0.7602(9)	0.064(3)
C(7)	0.8736(12)	0.4048(6)	0.7854(8)	0.068(3)
C(8)	0.7248(12)	0.4543(6)	0.7477(8)	0.068(3)
C(9)	0.5514(11)	0.4263(5)	0.6805(8)	0.058(2)
C(10)	0.3960(12)	0.4789(5)	0.6452(9)	0.074(3)
C(11)	0.2351(11)	0.4595(5)	0.5701(8)	0.066(3)
C(12)	0.0808(11)	0.5099(6)	0.5373(8)	0.070(3)
C(13)	1.0140(15)	0.2711(8)	0.8029(12)	0.088(3)

$${}^a U_{eq} \text{ equals one third of the trace of the orthogonalized } U_{ij} \text{ tensor.}$$

sional, has only a minimal effect on the overall molecular solubility.

3.1. Molecular structures

We were motivated to examine some of these compounds by single crystal X-ray diffraction by the variety of structural isomers which could exist. For example, an *E,Z,E* configuration for the triene moiety would be consistent with the ¹H NMR spectra (although inconsistent with the simulation results; see below). Further, the spectroscopic techniques available did not distinguish between an *anti* isomer, where the chromium tricarbonyl

Table 5
Selected bond distances (Å) and angles (deg) for 1, 3 and 4^a

	1	3	4
Cr–C (arene)	2.247 (8, 64, 12)	2.22 (1, 2, 6)	2.204 (9, 26, 6)
Cr–centroid	1.75 (–, 1, 2)	1.71	1.699 (3)
Cr–C (carbonyl)	1.829 (9, 11, 6)	1.82 (1, 1, 3)	1.820 (11, 7, 3)
C–O (carbonyl)	1.155 (9, 8, 6)	1.15 (1, 2, 3)	1.160 (9, 5, 3)
C (arene)–X	1.36 (1, 2, 2) (N)	1.89 (1) (Si)	1.488 (13) (CF ₃)
C–C (arene)	1.41 (1, 1, 12)	1.40 (1, 2, 6)	1.405 (11, 13, 6)
C–C (olefinic)	1.33 (1, 2, 3)	1.33 (1, 1, 2)	1.337 (15, 3, 2)
C–C (vinylic)	1.46 (1, 2, 4)	1.45 (1, 2, 2)	1.441 (11, 21, 2)
C (carbonyl)–Cr–C (carbonyl)	89.2 (4, 10, 6)	88.1 (5, 16, 3)	88.5 (4, 16, 3)
Centroid–Cr–C (carbonyl)	125.8 (–, 19, 6)	126.6 (–, 15, 3)	126.3 (–, 7, 3)
Cr–C (carbonyl)–O (carbonyl)	178.7 (8, 9, 6)	178.3 (7, 21, 3)	178.0 (9, 12, 3)
C–C (olefinic–vinylic)	124.6 (8, 19, 6)	126 (1, 0, 3)	124.8 (10, 3, 3)

^a E.s.d.s of averaged values are given in the form (*a*, *b*, *c*), where *a* is the average e.s.d., *b* is the standard deviation of the values from the average, and *c* is the number of trials.

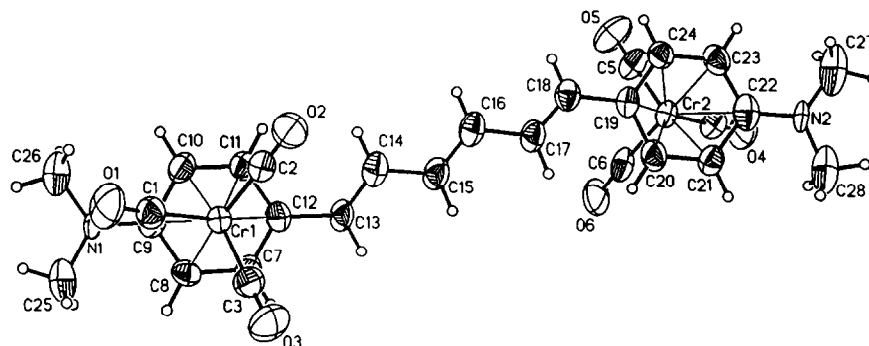


Fig. 1. ORTEP drawing of 1.

bonyl groups coordinate to opposite faces of the diphenylhexatriene, and a *syn* isomer, where coordination is to the same face. Finally, we wished to know the extent to which the electron density in the diphenylhexatriene was delocalized, as determined by the olefinic and vinylic carbon–carbon bond distances.

ORTEP drawings of **1**, **3** and **4** appear in Figs. 1–3. All three compounds crystallize with the chromium tricarbonyl moieties in *anti* positions. This is unsurprising on steric grounds, as these fragments thereby avoid any interaction. It is intriguing to note, however, that molecular models suggest that if the tricarbonyl moieties took *syn* positions, the closest approach of any two opposing carbonyl oxygens (the most peripheral atoms of the fragment) would be $> 5 \text{ \AA}$, well outside van der Waals contact distance. Furthermore, several examples of *syn*-bis(tricarbonylchromium) molecules are known, some of which exhibit significant intramolecular interactions [14–16]. The lack of formation of detectable quantities of the *syn* product in our reactions implies that at least one of the mechanistic steps is highly stereospecific. Given our reaction procedure of adding base slowly to a mixture of phosphonium salt and (substituted benzaldehyde)chromium tricarbonyl, which probably provides an intermediate (arene phosphonium)chromium tricarbonyl such as $[\text{Bu}_3\text{P}=\text{CH}(\text{CH}=\text{CH})_2-\eta^6\text{-C}_6\text{H}_4\text{-4-R}]\text{Cr}(\text{CO})_3$ (see above), it is

plausible, though unproven, that the stereospecific step is attack of the second (substituted benzaldehyde)chromium tricarbonyl on this intermediate. Why this step should be stereospecific is unclear, but we suspect that the reason is electronic rather than steric in origin.

As is evident from Table 5, the bond distances and angles fall into the expected ranges for (arene)chromium tricarbonyl molecules. Of note is the poor agreement between the Cr–arene carbon bond distances for **1**; this arises because the amino group and its attached ring carbon bend away from the metal center. The two pertinent distances, Cr1–C9 and Cr2–C22, average 2.376 \AA (8, 18, 2), while the other ten metal–ring distances average 2.221 \AA (8, 24, 10). These differ significantly at a 99.9% confidence level [17]. The effect is further seen by determining the least squares plane containing the five carbon atoms not bound to the substituent; C9 lies 0.10 \AA above the plane containing C7, C8, C10, C11 and C12, which is planar to within 0.008 \AA , while C22 lies 0.10 \AA above its ring plane (planar to within 0.009 \AA). Correspondingly, N1 and N2, which ideally should also lie in the arene planes, in fact ride 0.18 and 0.19 \AA , respectively, above them. As discussed previously by Hunter et al. and ourselves [9,18–20], the effect arises from the sizable π -donor properties of the NMe_2 group in **1**, which allows significant contribution of an iminium-like structure to the

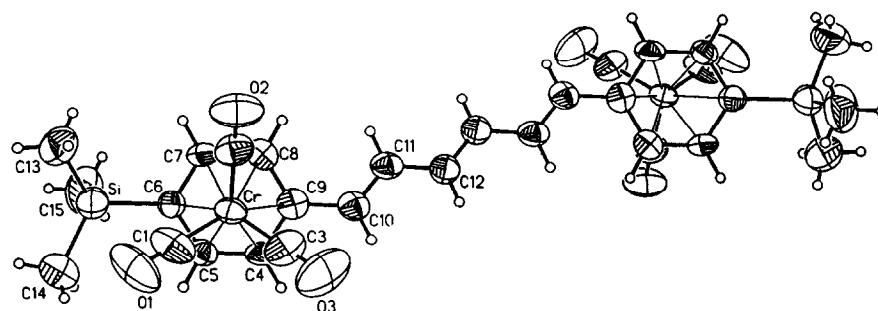
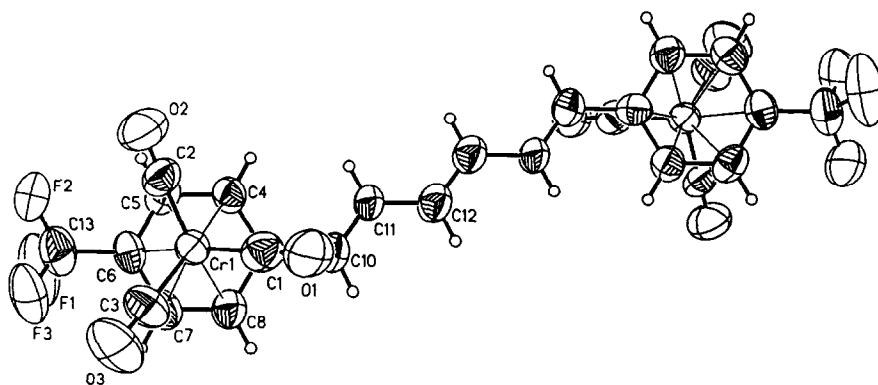


Fig. 2. ORTEP drawing of 3.

Fig. 3. ORTEP drawing of **4**.

overall molecular configuration. In **3** and **4**, containing electron-withdrawing Me₃Si and F₃C substituents, this bending is absent; all carbon atoms within the arene rings are planar to within 0.01 Å.

As anticipated, the triene fragment adopts the *E,E,E* all-*trans* conformation. We noted in our studies of (nitrostilbene)tricarbonylchromium compounds [9] that the bond distances for the olefinic moiety were inconsistent with complete ground-state delocalization of the π -electron cloud, since they alternated in a long-short-long fashion rather than being equivalent. We observe the same situation with the diphenylhexatriene compounds here (Table 5). The nominally single bonds average 1.44–1.46 Å in each case, while the double bonds average 1.33–1.34 Å, a clear indication that electron density is not spread equally over the entire π -framework.

One unusual and currently inexplicable observation is that the diphenylhexatriene fragment is surprisingly

nonplanar in **3**; the angle between the arene ring plane and the triene plane is 158°. As a result, the planes containing the two arene rings, though required by crystallographic symmetry to be parallel, are displaced by 1.52 Å. This argues for a significant loss of conjugation between the arene ring π cloud and the hexatriene π cloud in this compound. In contrast, **1** and **4** do not show this behavior; here the arene plane and triene plane intersect at an angle of 173° and 171.5°, respectively, resulting in arene ring plane displacements of only 0.30 and 0.17 Å.

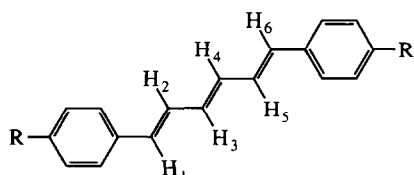
We have argued that the orientation of the carbonyl ligands with respect to the substituents on the arene ring is electronically controlled only when the substituent is highly electron-donating; when it is not, other factors such as crystal packing forces can take precedence [20]. The observed structures of **1**, **3** and **4** provide further data bearing on this point. We define τ as the torsion angle containing the carbon atom bound to the

Table 6

Calculated frequencies ω (Hz and ppm) and coupling constants J_{HH} (Hz) for the olefinic regions of the ¹H NMR spectra of **3** and **4** and the corresponding free α,ω -diphenylhexatrienes

	3	Me ₃ SiDPH ^a	4	F ₃ CDPH ^a
ω_1, ω_6 ("doublet")	1291.31 (3) (δ 6.45)	1322.26 (4) (δ 6.61)	1293.33 (1) (δ 6.46)	1363.23 (7) (δ 6.80)
ω_2, ω_5 ("octet")	1418.88 (3) (δ 7.09)	1386.80 (3) (δ 6.92)	1424.16 (1) (δ 7.12)	1447.74 (7) (δ 7.24)
ω_3, ω_4 ("quartet")	1334.64 (4) (δ 6.67)	1309.34 (4) (δ 6.54)	1332.44 (1) (δ 6.65)	1349.98 (8) (δ 6.75)
J_{12}, J_{56}	15.37 (4)	15.38 (6)	15.53 (1)	16.2 (1)
J_{13}, J_{46}	-0.12 (6)	-0.32 (7)	-0.11 (1)	-0.3 (1)
J_{14}, J_{36}	0	0	0	0
J_{15}, J_{26}	0	0	0	0
J_{16}	0	0	0	0
J_{23}, J_{45}	10.71 (6)	10.63 (7)	10.89 (1)	11.4 (1)
J_{24}, J_{35}	-1.15 (6)	-0.82 (7)	-0.93 (1)	-0.3 (1)
J_{25}	0	0	0	0
J_{34}	14.87 (8)	15.05 (9)	15.52 (3)	14.8 (2)

^a Me₃SiDPH is *E,E,E*-4-Me₃Si-C₆H₄-(CH=CH)₃-C₆H₄-4'-SiMe₃; F₃CDPH is *E,E,E*-4-F₃C-C₆H₄-(CH=CH)₃-C₆H₄-4'-CF₃.



nonolefinic substituent atom, the arene ring centroid, the chromium atom, and the carbonyl carbon atom closest to the substituent. A τ value of 0° corresponds to an orientation in which a carbonyl lies directly under the substituent (eclipsed conformation), characteristic of a strong donor group, while $\tau = 30^\circ$ corresponds to a staggered conformation, and $\tau = 60^\circ$ represents an *anti* conformation, often, but not exclusively, characteristic of a strong acceptor. In the case of *para*-disubstituted arenes such as those in **1**, **3** and **4**, it must be remembered that an eclipsed conformation with respect to one substituent is an *anti* conformation with respect to the other.

Also required is a method of evaluating whether a substituent is a donor or an acceptor. We employ the Δ_π method suggested by Hunter et al. [19], which relies on ^{13}C NMR chemical shift data for (monosubstituted arene)chromium tricarbonyls and tracks organic σ_{R}

values quite well. The method indicates that the Me_2N group is a very strong donor ($\Delta_\pi = -14.7$), that the Me_3Si group is a good acceptor ($\Delta_\pi = 4.7$), and that the F_3C group is a strong acceptor ($\Delta_\pi = 5.5$). Unfortunately, the requisite data for ω -phenylhexatriene groups have not been obtained. Bitterwolf and Dai reported the ^{13}C NMR data for the related (styrene)chromium tricarbonyl [21] and we use these data in our designation of a vinyl substituent as a weak acceptor ($\Delta_\pi = \text{ca. } 1\text{--}2$).

In **1**, containing a strong donor amine group and an acceptor vinyl group, one expects an amine-eclipsed conformation with τ angles near 0° . Indeed, we find one τ value (C9–Cent–Cr1–C1) equal to 8.8° , while the other (C22–Cent–Cr2–C4) equals 1.3° . The electronic dictates of the system overwhelm the steric advantage of a staggered orientation.

Trimethylsilyl-substituted **3** contains two π -acceptor groups on the ring. The Δ_π view suggests that, if

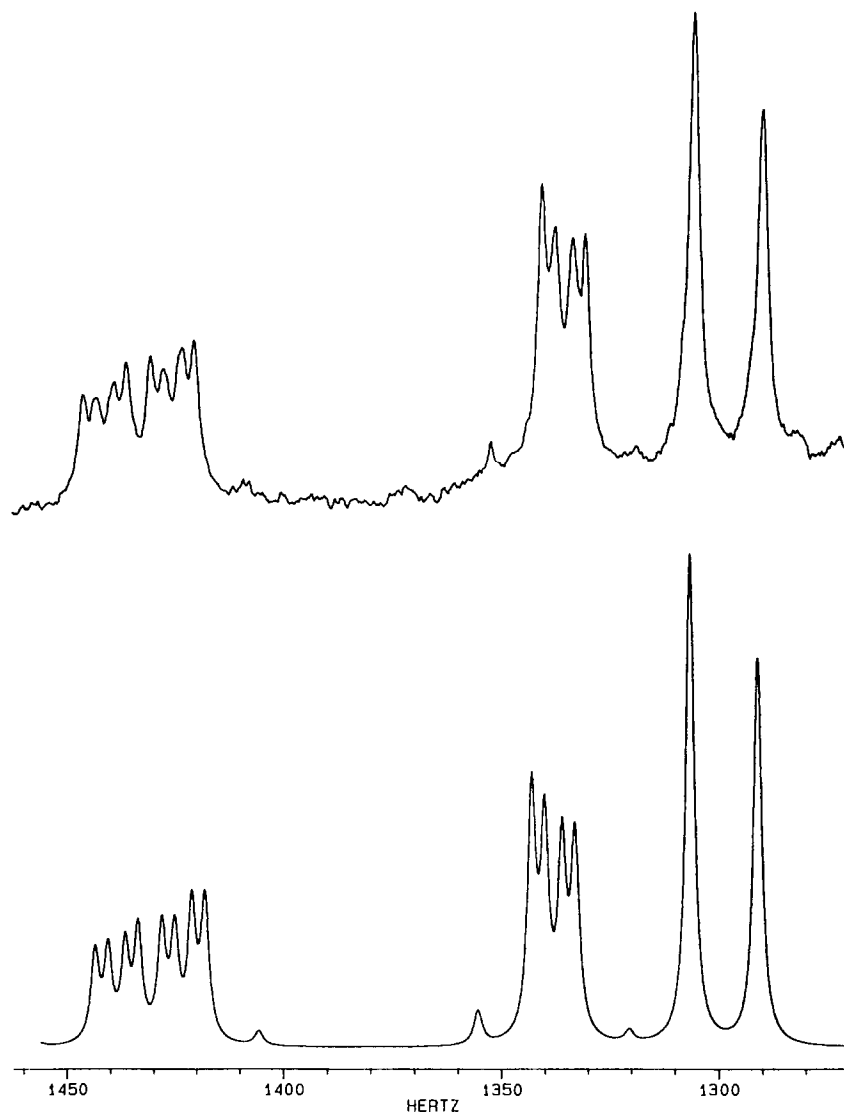


Fig. 4. Experimental (top) and calculated (bottom) ^1H NMR spectra of the olefinic region of **4**.

electronic considerations were to determine the carbonyl positions, the Me_3Si group, being the better acceptor, should dominate, resulting in an Si-*anti* conformation. In fact, the carbonyls adopt a staggered orientation, with τ (C6–Cent–Cr–C1) = 28.9° . Here it appears that steric considerations dictate the carbonyl positions in preference to electronic concerns; the staggered conformation minimizes interactions between the arene ring carbons and benzylic carbon C10 and the carbonyl groups at the minor expense of requiring a possible van der Waals contact between the trimethylsilyl methyl group of C14 and carbonyl oxygen O1 (C14–O1 = $3.68(2)$ Å; presumably the distance between O1 and a methyl hydrogen atom is shorter). However, it might be argued that the staggered choice represents the best compromise between the electron-acceptor demands of the trimethylsilyl and vinyl substituents. Since the Δ_π method distinguishes between donor/acceptor ability in a broad manner rather than in detail, we cannot distinguish between these possibilities.

Complex **4** also contains two π -acceptors, but the F_3C group, as gauged by the Δ_π value, accepts electrons rather more strongly than the Me_3Si group in **3**. The data show that **4** adopts the F_3C -*anti* conformation, with τ (C6–Cent–Cr–C3) = 54.4° . It may be that here the carbonyl orientation is dictated by the acceptor properties of the F_3C group, in contrast with the behavior of the dialkylacetal molecules we studied previously.

Overall, then, it appears that **1**, **3** and **4** adopt carbonyl orientations consistent with the donor/acceptor properties of both substituents, if the vinyl group is regarded as only slightly less good an acceptor as a trimethylsilyl group.

3.2. NMR spectroscopy

It has proven difficult to determine the ^1H NMR parameters (chemical shifts and coupling constants) for the olefinic hydrogens in α,ω -diphenyl polyenes owing to both the complex, multiple order nature of the spectra and to the low signal-to-noise ratio typically observed for these resonances, which derives from the low solubilities the compounds exhibit. This is regrettable, as such data might provide insight into the delocalization of the π -electron cloud; for example, if the delocalization is significant, one would expect relatively large four- (allyl-like) and five-bond (butadiene-like) HH coupling constants. Equally, one might anticipate smaller-than-normal three-bond (vinyl-like) couplings.

We had hoped that the greater solubilities of **1–4** compared with the free organics would allow for acquisition of NMR spectra of sufficient quality for accurate simulation and parameter determination. Unfortunately, the low solubilities of **1** and **2** did not allow this; the olefinic resonances for these are barely observable above the baseline noise. However, we were able to obtain

spectra of the more soluble **3** and **4** adequate for simulation. For comparison, we also obtained and simulated the spectra of the corresponding free 4,4'-disubstituted diphenylhexatrienes, denoted Me_3SiDPH and F_3CDPH in Table 6. The olefinic region of **4** and its simulation appear in Fig. 4. The spectra of the other three compounds examined are similar. As is evident, three major resonances are present: a downfield eight-line pattern ("octet" in Table 6), an upfield doublet and a four-line pattern ("quartet") between them. Homonuclear decoupling experiments established that the proton giving rise to the doublet couples only to the proton of the octet, and not to the proton of the quartet; given the triene pattern of the system, this can only be explained by assigning the doublet resonance to the proton on the carbon bound to the phenyl ring (H1/H6 in the graphic in Table 6), the octet to the proton adjacent to H1/H6 (H2/H5), and the quartet to the only remaining unique proton (H3/H4).

Accurate simulations of the spectra required that six nuclei with symmetry-related frequencies and coupling constants coincident be used [22]. The derived spectroscopic parameters appear in Table 6. Excellent root-mean-square agreements between calculated and experimental line frequencies (rms errors < 0.5) and intensities were obtained in each case.

The coupling constant values suggest that the hexatriene fragment behaves essentially as three independent double bonds. The three-bond vinylic couplings (J_{12} , J_{56} and J_{34}) are approximately 15 Hz, while the three-bond aliphatic couplings (J_{23} and J_{45}) are smaller, at 11 Hz. These values are typical of those observed for hydrogen atoms in molecules containing independent double and single bonds [23]. The 15 Hz values for the vinylic couplings confirm the *E,E,E* configuration observed in the diffraction studies; coupling across a Z-oriented system is typically smaller (7–11 Hz). The four-bond allylic couplings (J_{13} , J_{46} , J_{24} and J_{35}) are all very small. Longer-range couplings are nonexistent.

There are some interesting aspects to the data. For example, in each case the internal double bond exhibits a slightly smaller vinylic coupling than do the external ones. Possibly correspondingly, the internal allylic four-bond couplings (J_{24} and J_{35}) are slightly larger than the external four-bond couplings (J_{13} and J_{46}). As expected from prior data, the four-bond couplings are of opposite sign to those of the three-bond couplings. Finally, the simulations demonstrate that the very small features in the spectra, which might have been taken for electronic noise or trace impurities, are in fact real transitions of low intensity.

4. Conclusion

We have shown that tricarbonylchromium-substituted compounds containing quite long polyene chains may

be prepared, and show unusual environmental stability. Examination of the nonlinear optical behavior of these compounds is in progress.

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