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Structures of a series of $[4\text{-R–C}_6\text{H}_4\text{–CH(OR}')_2]\text{Cr(CO)}_3$ complexes: evidence against a favored carbonyl orientation in (*para*-disubstituted arene)chromium tricarbonyl compounds

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Abstract

The structures of eight (*para*-substituted benzaldehyde dialkylacetal)chromium tricarbonyl complexes $[4\text{-R–C}_6\text{H}_4\text{–CH(OR}')_2]\text{Cr(CO)}_3$ (R = Me_2N, Cl, Me_3Si, CF_3; R′ = Me, Et) have been determined by single-crystal X-ray diffraction. For $[4\text{-Me}_2\text{N–C}_6\text{H}_4\text{–CH(OMe)}_2]\text{Cr(CO)}_3$ (**1**), triclinic, $P\bar{1}$, $T = 291$ K, $a = 6.725$ (2) Å, $b = 7.228$ (3) Å, $c = 16.021$ (8) Å, $\alpha = 81.38$ (4)°, $\beta = 87.86$ (3)°, $\gamma = 87.77$ (3)°, $Z = 2$; for $[4\text{-Me}_2\text{N–C}_6\text{H}_4\text{–CH(OEt)}_2]\text{Cr(CO)}_3$ (**2**), monoclinic, $P2_1/n$, $T = 123$ K, $a = 10.905$ (7) Å, $b = 15.670$ (9) Å, $c = 11.158$ (9) Å, $\beta = 116.61$ (7)°, $Z = 4$; for $[4\text{-Cl–C}_6\text{H}_4\text{–CH(OMe)}_2]\text{Cr(CO)}_3$ (**3**), monoclinic, $P2_1/n$, $T = 293$ K, $a = 9.896$ (3) Å, $b = 12.872$ (4) Å, $c = 11.336$ (4) Å, $\beta = 108.21$ (3)°, $Z = 4$; for $[4\text{-Cl–C}_6\text{H}_4\text{–CH(OEt)}_2]\text{Cr(CO)}_3$ (**4**), triclinic, $P\bar{1}$, $T = 293$ K, $a = 8.305$ (3) Å, $b = 9.999$ (2) Å, $c = 11.313$ (4) Å, $\alpha = 106.71$ (2)°, $\beta = 101.66$ (3)°, $\gamma = 110.27$ (3)°, $Z = 2$; for $[4\text{-Me}_3\text{Si–C}_6\text{H}_4\text{–CH(OMe)}_2]\text{Cr(CO)}_3$ (**5**), triclinic, $P\bar{1}$, $T = 293$ K, $a = 6.933$ (2) Å, $b = 11.709$ (3) Å, $c = 12.071$ (5) Å, $\alpha = 112.57$ (3)°, $\beta = 94.32$ (3)°, $\gamma = 100.52$ (2)°, $Z = 2$; for $[4\text{-Me}_3\text{Si–C}_6\text{H}_4\text{–CH(OEt)}_2]\text{Cr(CO)}_3$ (**6**), monoclinic, $P2_1/c$, $T = 292$ K, $a = 11.823$ (3) Å, $b = 12.926$ (4) Å, $c = 14.608$ (9) Å, $\beta = 113.03$ (3)°, $Z = 4$; for $[4\text{-F}_3\text{C–C}_6\text{H}_4\text{–CH(OMe)}_2]\text{Cr(CO)}_3$ (**7**), monoclinic, $P2_1/n$, $T = 293$ K, $a = 6.756$ (3) Å, $b = 10.300$ (3) Å, $c = 21.112$ (6) Å, $\beta = 95.18$ (3)°, $Z = 4$; for $[4\text{-F}_3\text{C–C}_6\text{H}_4\text{–CH(OEt)}_2]\text{Cr(CO)}_3$ (**8**), monoclinic, $C2/c$, $T = 123$ K, $a = 18.992$ (5) Å, $b = 14.065$ (4) Å, $c = 13.232$ (4) Å, $\beta = 110.53$ (3)°, $Z = 8$. Compounds **1/2** exhibit an eclipsed carbonyl orientation, presumably owing to the presence of the strongly donating dimethylamino substituent. Compounds **3/4** exhibit a staggered arrangement, possibly reflecting electronic similarity between the chloro and acetal groups, or dominance of steric effects in conformation determination. Intriguingly, compounds **5/6** exhibit different geometries, as do **7/8**, which by their nature do not appear to relate either to steric or electronic effects. It is proposed that more subtle factors, such as crystal packing forces, dictate the carbonyl orientation in these cases, suggesting that *a priori* prediction of the conformation is often unjustified.

Key words: Chromium; Carbonyl; X-ray diffraction; Arene; Crystal structure; Nuclear magnetic resonance

1. Introduction

In 1977, Albright, Hofmann and Hoffman (AHH) examined the conformational preferences of carbonyl ligands in (η^6-arene)chromium tricarbonyl compounds through EHMO theory [1]. They concluded that the potential surface for the parent $(\text{C}_6\text{H}_6)\text{Cr(CO)}_3$ was rather flat, although the staggered carbonyl arrangement was very slightly favored by *ca.* 0.3 kcal mol^{-1}. However, substitution of a donor group onto the arene ring resulted in a detectable preference [1.3 kcal mol^{-1} rotational barrier for $(\eta^6\text{-H}_2\text{NC}_6\text{H}_5)\text{Cr(CO)}_3$] for the *syn*-eclipsed (*EE*) carbonyl orientation [2], where a carbonyl lies directly under the donor substituent. Conversely, substitution of an acceptor group onto the ring led to a preference [1.7 kcal mol^{-1} rotational barrier for $(\eta^6\text{-H}_2\text{BC}_6\text{H}_5)\text{Cr(CO)}_3$] for the *anti*-eclipsed (*E*) orientation, where all three carbonyls remain eclipsed but now a carbonyl lies directly under the hydrogen *para* to the acceptor substituent. Experimental effort has largely confirmed these suggestions for a variety of substituents; the only exceptions were ascribed to steric/packing effects [3].

AHH pointed out the concept of considering the arene ring as interpenetrating trios, and showed computationally that the carbonyl rotational barrier in

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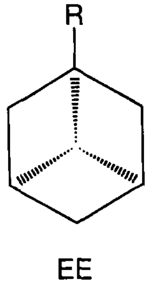
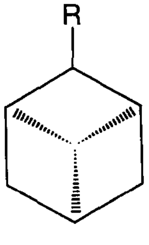
(substituted arene)chromium tricarbonyl compounds depends significantly upon the positional relationships between substituents; the barrier is higher if they relate by a three-fold rotation (*i.e.* if they occupy *meta* sites) and is lower if they do not (*ortho* or *para* sites). Thus the model predicts that (*meta*-disubstituted arene) chromium tricarbonyls should exhibit carbonyl arrangements dictated by the same electronic effects affecting the monosubstituted cases, while *ortho*- and *para*-disubstituted compounds will more likely display structures dependent upon both electronic and steric effects. Diffraction studies of such molecules reported to date typically bear out this view. The largest body of data exists for (*ortho*-disubstituted arene)chromium tricarbonyl complexes; about half of these mimic the monosubstituted cases in which the more electron-donating substituent eclipses a carbonyl, forcing the less donating group to a position staggered with respect to the carbonyls (*E*) [2], while half adopt a staggered orientation (*S*) where the arene carbon–carbon bond between the *ortho* substituents does not project onto a metal–carbonyl bond. This partitioning of structural types suggests a small barrier to carbonyl rotation. Considerably fewer (*meta*-disubstituted arene)chromium tricarbonyls have been crystallographically characterized, hampering the ability to draw conclusions, but these appear to prefer a staggered orientation.

All but one of the (*para*-disubstituted arene)chromium tricarbonyl compounds reported to date, for which the substituents are neither organometallic nor cyclized, exhibit a staggered arrangement [4–10]. At first glance, this observation belies the concept that steric and electronic effects should both contribute to the chosen orientation; to some extent, however, the observation is an artifact of those compounds selected for characterization. Several were symmetrically substituted, as in [1,4-$(Me_2N)_2C_6H_4$]Cr(CO)$_3$ and [1,4-$(MeO_2C)_2C_6H_4$]Cr(CO)$_3$ [9], where the staggered conformation represents the best electronic compromise for the system. The same situation holds for most of the asymmetrically substituted compounds: in nearly every case [for example, (*p*-F–C_6H_4–OMe)Cr(CO)$_3$] [6], the π-donating or accepting characteristics of the substituents are rather close, such that a staggered conformation again acts as an energetic compromise. The compound (*p*-Me_3C–C_6H_4–CO_2H)Cr(CO)$_3$ [4] presents a situation where the substituents clearly should dictate an electronic preference for a particular conformation (in this case, that where the t-butyl group eclipses a carbonyl and the carboxylic acid group is staggered between carbonyls; see the *E*1 structure below), and here apparently the steric demands of the t-butyl group override the electronic considerations such that the molecule is again staggered. Only one example exists where the electronic preference of a strong donor outweighs other molecular demands: a recently reported *meso*-hexestrol derivative adopts a conformation eclipsing a carbonyl with a hydroxypropoxo substituent [10].

It is therefore apparent that, while the extension of the theoretical constructs pertaining to the electronic preferences of monosubstituted arene systems to *para*-disubstituted arene systems appears logical, few data actually bear out the conceptual leap. To address this lack, we have examined the structures of a series of (*p*-substituted benzaldehyde dialkylacetal)chromium tricarbonyl complexes [1,4-R–C_6H_4–CH(OR')$_2$]Cr(CO)$_3$ (R = Me_2N, Cl, Me_3Si, F_3C; R' = Me, Et), which we prepared as part of our effort to synthesize (α, ω-diphenyl polyene)metal tricarbonyl species. We felt that these molecules, which incorporate a range of donor and acceptor substituents and are asymmetrically substituted, could help reveal whether the conformational preferences of the carbonyl in *para*-disubstituted arene systems are indeed determined by the electronic characteristics of the substituents, and possibly assist evaluation of the AHH model. We therefore report the structures of eight molecules of this type, and the surprising result that the conformations chosen



EE



E

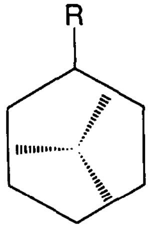


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TABLE 1. Data collection and refinement parameters for compounds **1**–**8**

	1	**2**	**2b**	**3**	**4**	**5**	**6**	**7**	**8**	**8b**
Formula	$C_{14}H_{17}CrNO_5$	$C_{16}H_{21}CrNO_5$	$C_{16}H_{21}CrNO_5$	$C_{12}H_{11}ClCrO_5$	$C_{14}H_{15}ClCrO_5$	$C_{15}H_{20}CrO_5Si$	$C_{17}H_{24}CrO_5Si$	$C_{13}H_{11}CrF_3O_5$	$C_{15}H_{15}CrF_3O_5$	$C_{15}H_{15}CrF_3O_5$
Formula weight (g mol^{-1})	331.29	359.34	359.34	322.67	350.72	360.40	388.46	356.22	384.27	384.27
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$C2/c$	$C2/c$
T(K)	291	123	293	293	293	293	292	293	123	293
a (Å) [a]	6.725(2)	10.905(7)	11.080(4)	9.896(3)	8.305(3)	6.933(2)	11.823(3)	6.756(3)	18.992(5)	19.307(9)
b (Å)	7.228(3)	15.670(9)	15.902(9)	12.872(4)	9.999(2)	11.709(3)	12.926(4)	10.300(3)	14.065(4)	14.093(4)
c (Å)	16.021(8)	11.158(9)	11.229(8)	11.336(4)	11.313(4)	12.071(5)	14.608(9)	21.112(6)	13.232(4)	13.477(8)
α (°)	81.38(4)				106.71(2)	112.57(3)				
β (°)	87.86(3)	116.61(7)	116.42(5)	108.21(3)	101.66(3)	94.32(3)	113.03(3)	95.18(3)	110.53(3)	110.28(5)
γ (°)	87.77(3)				110.27(3)	100.52(2)				
V (Å^3)	769.0	1704.7	1771.8	1372	795.0	878.2	2054.5	1463	3310.1	3439.7
Z	2	4	4	4	2	2	4	4	8	8
D_{calc} (g cm^{-3})	1.43	1.40	1.35	1.56	1.47	1.36	1.26	1.62	1.54	1.48
μ_{calc} (cm^{-1})	7.97	7.26	6.98	10.7	9.34	7.65	6.59	8.74	7.80	7.50
Maximum crystal dimensions (mm)	0.15×0.25 ×0.48	0.30×0.35 ×0.38	0.25×0.30 ×0.40	0.10×0.20 ×0.40	0.25×0.30 ×0.40	0.18×0.25 ×0.41	0.25×0.35 ×0.40	0.30×0.40 ×0.40	0.23×0.35 ×0.35	0.23×0.35 ×0.45
Decay of standard reflections	±2%	±1.5%	±3%	−4.1%	±3%	±2.5%	±1.5%	±2%	±1%	±2%
2θ Range (°)	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$
hkl Range	+8, ±8, ±19	+13, +18, ±13	+13, +18, ±13	+11, +15, ±13	+9, ±11, ±13	+8, ±13, ±14	+14, +15, ±17	+8, +12, ±25	+22, +16, ±15 (except $h+k \neq 2n$)	+23, +16, ±16 (except $h+k \neq 2n$)
Reflections measured	2690	3281	3415	2679	2794	3092	3973	2941	3114	3257
Reflections observed [b]	1807	1859	1092	1365	1837	2012	2358	1376	2506	1063
Parameters	202	215	220	178	196	214	232	205	223	223
Weights	$[\sigma(F_o)^2 + 0.0001F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.004F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0008F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0012F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0009F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0004F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0009F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.004F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0004F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.00032F_o^2]^{-1}$
R [c]	0.041	0.059	0.064	0.056	0.044	0.044	0.043	0.052	0.029	0.047
R_w	0.041	0.076	0.072	0.075	0.053	0.051	0.059	0.069	0.034	0.047
GOF [d]	0.78	0.52	0.93	2.58	0.60	0.69	1.01	0.52	1.11	0.67

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections, typically with $\theta > 15°$. [b] Corrected for Lorentz/polarization effects: $F_o > 5\sigma(F_o)$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2\}^{1/2}$. [d] GOF $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$; N_o = number of observations, N_v = number of variables.

may reflect more than simple electronic or steric effects, and thus the potential surface which determines carbonyl orientation in many cases must be quite flat.

2. Experimental details

General synthetic procedures for the preparations of compounds of **1**, **2**, and **5–8** have been reported [11].

2.1. Preparation of [4-Cl-C_6H_4-$CH(OMe)_2$]$Cr(CO)_3$ (3)

A variation of the reported method was used [12]. A mixture of 4-Cl–C_6H_4–$CH(OMe)_2$ (6.53 g, 35.0 mmol) and $Cr(CO)_6$ (6.75 g, 30.7 mmol) in a 250 ml Schlenk flask was treated with 200 ml of a 5% dioxan/5% THF/Bu_2O solution. The flask was capped with a 25 cm air-cooled condenser which, in turn, was capped with a gas inlet adapter. The reaction mixture was brought to 140°C and allowed to stir overnight. It was then warmed to gentle reflux, and maintained at this temperature for 72 h. The solution was cooled to room temperature and then filtered to remove a small amount of insoluble material. Evaporation of the solvent at 50°C and pumping at this temperature for 0.5 h left the product as an orange oil. The material was extracted with CH_2Cl_2, and the solution filtered through Celite. The solvent was then evaporated, giving the product as a yellow-orange solid. This was triturated with pentane, filtered out, and dried to give analytically pure product (3.73 g). The mother liquor was evaporated to half its volume, and the precipitated solid filtered out of the cold solution, giving a second crop (0.73 g) which was spectroscopically indistinguishable from the first. Total yield: 4.46 g (13.8 mmol, 45%). ^1H NMR (200 MHz, $CDCl_3$) δ: 5.64 (d, J_{HH} = 6.6 Hz, 2H, Ph); 5.43 (d, J_{HH} = 6.6 Hz, 2H, Ph); 4.99 (s, 1H, CH); 3.35 (s, 6H, OCH_3) ppm. Analysis: Calc. for $C_{12}H_{11}ClCrO_5$: C, 44.67; H, 3.44%. Found: C, 45.16; H, 3.44%.

2.2. Preparation of [4-Cl-C_6H_4-$CH(OEt)_2$]$Cr(CO)_3$, (4)

This was prepared similarly in 40% yield. ^1H NMR (200 Hz, $CDCl_3$) δ: 5.67 (d, J_{HH} = 6.6 Hz, 2H, Ph); 5.41 (d, J_{HH} = 6.6 Hz, 2H, Ph); 5.07 (s, 1H, CH); 3.60 (m, 4H, OCH_2); 1.22 (t, J_{HH} = 7.0 Hz, CH_3) ppm. Analysis: Calc. for $C_{14}H_{15}ClCrO_5$: C, 47.95; H, 4.31%. Found: C, 48.06; H, 4.34%.

2.3. Single-crystal X-ray diffraction studies of compounds 1–8

Yellow or yellow–orange crystals of **1–8** were grown from cooled CH_2Cl_2/pentane mixtures. They were handled in air during optical inspection, but were sealed in argon-flushed capillaries for the experiments. Data collection and refinement parameters appear in Table 1. All reflection data were measured on an Enraf-Nonius CAD-4 diffractometer in ω–2θ scan mode using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). During the two low-temperature experiments, the crystals were cooled in a stream of cold nitrogen gas. Cell constants were determined from least-squares refinement of $((\sin\theta)/\lambda)^2$ values of 25 well-centered reflections, typically with $\theta > 15°$, occasionally this limit was lowered slightly. The raw data were corrected for Lorentz and polarization effects. The atoms were located using SHELXS [13] and the model refined employing the SHELX suite of computer programs [14], which provided neutral scattering factors and anomalous dispersion corrections drawn from standard sources. All nonhydrogen atoms were refined anisotropically, except as noted in Table 3 below. Only the data for **2** were corrected for absorption, through a ψ-scan correction; inspection of the data for the other molecules indicated either that no correction was necessary or that correction led to a poorer agreement factor. The range of relative transmission factors was 75/100 for **2** and 80/100 for **2b** (see below). Arene and methylene hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. Methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom.

TABLE 2. Final fractional coordinates for compound 1

Atom	x/a	y/b	z/c	B_{eq} [a]
Cr	0.3817(1)	0.29900(9)	0.71627(4)	2.97
O(1)	0.6371(5)	−0.0297(5)	0.6852(3)	7.95
O(2)	0.1533(6)	0.2771(6)	0.5627(2)	7.71
O(3)	0.1085(5)	0.0255(5)	0.8155(2)	5.89
O(4)	0.8616(4)	0.4310(5)	0.8891(2)	5.08
O(5)	0.5897(5)	0.2580(5)	0.9471(2)	5.21
N	0.2509(5)	0.7430(5)	0.6147(2)	3.67
C(1)	0.5379(7)	0.0983(6)	0.6962(3)	4.73
C(2)	0.2427(7)	0.2831(6)	0.6224(3)	4.47
C(3)	0.2135(6)	0.1336(6)	0.7780(3)	4.01
C(4)	0.5742(6)	0.4104(5)	0.8063(3)	3.41
C(5)	0.6528(6)	0.4529(5)	0.7234(3)	3.55
C(6)	0.5443(6)	0.5545(5)	0.6585(3)	3.51
C(7)	0.3498(6)	0.6290(5)	0.6746(3)	3.19
C(8)	0.2636(6)	0.5682(5)	0.7560(2)	3.37
C(9)	0.3749(6)	0.4659(6)	0.8206(3)	3.44
C(10)	0.7067(6)	0.3129(6)	0.8748(3)	4.49
C(11)	0.7938(8)	0.6027(7)	0.9138(4)	6.53
C(12)	0.6965(8)	0.1471(8)	1.0130(4)	7.13
C(13)	0.3289(8)	0.7768(8)	0.5280(3)	5.49
C(14)	0.0432(6)	0.7964(7)	0.6271(3)	4.91

[a] In Tables 2–9, $B_{eq} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + b(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

TABLE 3. Final fractional coordinates for compound **2**

Atom	x/a	y/b	z/c	B_{eq}
Cr	0.73914(8)	0.62499(5)	0.81329(7)	1.23
O(1)	0.5973(5)	0.6032(3)	0.9874(4)	3.47
O(2)	1.0100(4)	0.6066(3)	1.0538(4)	3.01
O(3)	0.7624(5)	0.8113(3)	0.8715(4)	3.13
O(4)	1.0335(4)	0.6143(2)	0.7062(4)	2.13
O(5)	0.8761(4)	0.6342(2)	0.4879(3)	1.97
N	0.4492(4)	0.4985(3)	0.6608(4)	1.71
C(1)	0.6542(6)	0.6114(3)	0.9214(5)	1.97
C(2)	0.9049(5)	0.6121(3)	0.9599(5)	1.85
C(3)	0.7541(5)	0.7385(4)	0.8501(5)	1.75
C(4)	0.7912(5)	0.6132(3)	0.6433(5)	1.61
C(5)	0.6665(5)	0.6568(3)	0.6010(5)	1.44
C(6)	0.5526(5)	0.6209(3)	0.6117(5)	1.63
C(7)	0.5613(5)	0.5359(3)	0.6607(5)	1.50(9) [a]
C(8)	0.6928(6)	0.4961(3)	0.7156(5)	1.85
C(9)	0.8026(5)	0.5327(3)	0.7028(5)	1.52
C(10)	0.9065(5)	0.6516(4)	0.6208(5)	1.80
C(11)	1.1191(6)	0.6682(4)	0.8154(6)	2.77
C(12)	1.2296(6)	0.6137(5)	0.9174(6)	3.19
C(13)	0.9669(6)	0.6743(4)	0.4441(5)	2.77
C(14)	0.9141(7)	0.6561(6)	0.2964(6)	4.15
C(15)	0.4638(6)	0.4180(4)	0.7318(6)	2.52
C(16)	0.3268(5)	0.5485(4)	0.6310(6)	2.24

[a] Isotropic refinement.

TABLE 5. Final fractional coordinates for compound **4**

Atom	x/a	y/b	z/c	B_{eq}
Cr	0.4782(1)	0.24584(8)	0.27953(7)	3.81
Cl	0.8708(2)	0.2267(2)	0.4582(2)	8.61
O(1)	0.3513(7)	0.0750(5)	0.4453(4)	9.29
O(2)	0.1206(5)	0.2615(5)	0.2137(5)	
O(3)	0.3048(6)	−0.0598(4)	0.0541(4)	7.68
O(4)	0.6336(5)	0.6431(4)	0.1438(3)	5.87
O(5)	0.4289(5)	0.6034(5)	0.2580(4)	7.93
C(1)	0.4016(7)	0.1410(6)	0.3825(5)	5.51
C(2)	0.2587(7)	0.2577(6)	0.2410(6)	5.76
C(3)	0.3701(7)	0.0575(6)	0.1401(5)	5.16
C(4)	0.6046(6)	0.4634(5)	0.2526(4)	4.12
C(5)	0.6592(6)	0.3563(5)	0.1840(5)	4.95
C(6)	0.7419(6)	0.2830(5)	0.2467(5)	5.37
C(7)	0.7688(6)	0.3160(5)	0.3788(5)	5.11
C(8)	0.7153(6)	0.4251(5)	0.4516(4)	4.45
C(9)	0.6362(6)	0.4976(5)	0.3885(4)	4.15
C(10)	0.5137(7)	0.5373(6)	0.1810(5)	5.44
C(11)	0.7806(8)	0.7745(6)	0.2485(6)	6.87
C(12)	0.873(1)	0.8824(8)	0.1922(8)	9.93
C(13)	0.315(1)	0.657(1)	0.190(1)	18.57
C(14)	0.159(1)	0.617(2)	0.179(1)	31.93

Positional parameters and equivalent isotropic thermal parameters for **1**–**8** are given in Tables 2–9, respectively; selected bond distances and angles for **1**–**8** appear in Table 10.

To assess the effect of temperature on the carbonyl orientation, both room- and low-temperature data were collected for compounds **2** and **8**. As anticipated, the unit cells contracted slightly, but refinement of the data established that the room- and low-temperature molecular structures of each species were identical. The data collection parameters and bond distances and angles for **2** and **8** at both temperatures (room-temperature molecules are denoted **2b** and **8b**) appear in the appropriate tables for completeness and to demon-

TABLE 4. Final fractional coordinates for compound **3**

Atom	x/a	y/b	z/c	B_{eq}
Cr	0.6208(1)	0.28207(8)	0.7469(1)	2.91
Cl	0.8309(3)	0.4116(2)	0.5862(2)	6.79
O(1)	0.5769(8)	0.1720(5)	0.9655(6)	7.41
O(2)	0.4702(7)	0.1113(5)	0.5789(6)	6.31
O(3)	0.8922(6)	0.1662(5)	0.7845(6)	6.01
O(4)	0.2719(6)	0.3619(5)	0.7910(6)	5.93
O(5)	0.3554(5)	0.5224(4)	0.8714(5)	4.41
C(1)	0.5949(8)	0.2146(6)	0.8837(7)	4.55
C(2)	0.5253(8)	0.1773(5)	0.6439(7)	3.68
C(3)	0.7866(8)	0.2110(5)	0.7707(7)	3.89
C(4)	0.7021(8)	0.4122(5)	0.6602(7)	4.00
C(5)	0.7422(8)	0.4293(5)	0.7883(6)	3.59
C(6)	0.6390(8)	0.4320(5)	0.8462(6)	3.59
C(7)	0.4931(7)	0.4141(5)	0.7786(6)	3.43
C(8)	0.4556(8)	0.3951(5)	0.6521(7)	3.77
C(9)	0.5622(8)	0.3927(5)	0.5915(6)	3.83
C(10)	0.3886(8)	0.4186(6)	0.8513(7)	4.09
C(11)	0.175(1)	0.3482(8)	0.860(1)	8.01
C(12)	0.287(1)	0.5803(7)	0.7632(9)	6.43

TABLE 6. Final fractional coordinates for compound **5**

Atom	x/a	y/b	z/c	B_{eq}
Cr	−0.7569(1)	0.68611(7)	0.79049(6)	2.49
Si	−0.4243(2)	0.8948(1)	0.6820(1)	3.24
O(1)	−0.9880(6)	0.6356(4)	0.9727(4)	6.89
O(2)	−1.1346(5)	0.5821(4)	0.6121(3)	5.75
O(3)	−0.8549(6)	0.9412(4)	0.8797(4)	6.25
O(4)	−0.4567(5)	0.4023(3)	0.8632(3)	4.39
O(5)	−0.7577(5)	0.3299(3)	0.7278(3)	4.12
C(1)	−0.8976(7)	0.6547(5)	0.9029(4)	3.93
C(2)	−0.9890(7)	0.6231(5)	0.6820(4)	3.60
C(3)	−0.8162(7)	0.8430(5)	0.8453(4)	3.81
C(4)	−0.5829(6)	0.6357(4)	0.6400(4)	2.64
C(5)	−0.6331(6)	0.5301(4)	0.6692(4)	2.71
C(6)	−0.5850(6)	0.5425(4)	0.7889(4)	2.77
C(7)	−0.4823(6)	0.6634(4)	0.8784(4)	2.92
C(8)	−0.4326(6)	0.7669(4)	0.8481(4)	2.91
C(9)	−0.4837(6)	0.7567(4)	0.7275(4)	2.73
C(10)	−0.6468(8)	0.8926(6)	0.5837(5)	5.55
C(11)	−0.351(1)	1.0460(5)	0.8209(5)	5.72
C(12)	−0.2158(8)	0.8747(6)	0.5947(5)	5.17
C(13)	−0.6335(7)	0.4329(4)	0.8262(4)	3.40
C(14)	−0.3347(9)	0.3667(6)	0.7724(6)	6.00
C(15)	−0.834(1)	0.2252(5)	0.7556(6)	5.63

TABLE 7. Final fractional coordinates for compound **6**

Atom	x/a	y/b	z/c	B_{eq}
Cr	0.14911(5)	0.24844(4)	0.70151(4)	4.60
Si	0.3331(1)	0.44640(9)	0.63151(9)	5.57
O(1)	0.3812(3)	0.1331(3)	0.8118(3)	10.76
O(2)	0.2129(5)	0.3852(3)	0.8778(3)	13.01
O(3)	0.0174(4)	0.1170(3)	0.7964(3)	9.23
O(4)	−0.1288(3)	0.0909(2)	0.4323(2)	5.88
O(5)	−0.2086(3)	0.1869(2)	0.5291(2)	6.32
C(1)	0.2899(5)	0.1769(4)	0.7701(4)	6.95
C(2)	0.1877(5)	0.3338(3)	0.8086(3)	7.91
C(3)	0.0683(4)	0.1677(3)	0.7598(3)	5.84
C(4)	−0.0010(4)	0.2122(3)	0.5548(3)	4.68
C(5)	−0.0131(4)	0.3161(3)	0.5796(3)	5.01
C(6)	0.0861(3)	0.3837(3)	0.6037(3)	4.76
C(7)	0.2003(3)	0.3541(3)	0.6023(3)	4.65
C(8)	0.2088(4)	0.2488(3)	0.5770(3)	5.32
C(9)	0.1112(4)	0.1790(3)	0.5538(3)	5.25
C(10)	−0.1064(4)	0.1352(3)	0.5255(3)	5.60
C(11)	−0.1642(5)	0.1626(3)	0.3522(3)	6.71
C(12)	−0.1687(5)	0.1098(4)	0.2614(4)	8.21
C(13)	−0.3091(5)	0.1203(4)	0.5178(5)	8.99
C(14)	−0.4118(6)	0.1783(5)	0.5190(6)	11.77
C(15)	0.4770(5)	0.3806(5)	0.7000(6)	13.11
C(16)	0.3294(6)	0.4968(6)	0.5140(4)	10.72
C(17)	0.3198(7)	0.5513(5)	0.7096(7)	16.64

TABLE 8. Final fractional coordinates for compound **7**

Atom	x/a	y/b	z/c	B_{eq}
Cr	0.0618(2)	0.20636(9)	0.86782(5)	2.80
F(1)	−0.156(1)	0.1950(6)	1.0274(2)	11.24
F(2)	−0.051(1)	0.3757(7)	1.0138(2)	12.24
F(3)	−0.357(1)	0.346(1)	1.0027(3)	15.12
O(1)	0.3833(9)	0.4057(6)	0.8612(3)	6.80
O(2)	0.291(1)	0.0909(6)	0.9818(3)	7.92
O(3)	0.2822(9)	0.0251(6)	0.7884(3)	6.40
O(4)	−0.1105(7)	0.2897(5)	0.6894(2)	3.73
O(5)	−0.3789(7)	0.1502(4)	0.6954(2)	3.56
C(1)	0.264(1)	0.3282(7)	0.8643(4)	4.12
C(2)	0.200(1)	0.1343(8)	0.9381(3)	4.99
C(3)	0.197(1)	0.0958(7)	0.8199(3)	4.11
C(4)	−0.1836(8)	0.2192(5)	0.7909(2)	2.41
C(5)	−0.2297(9)	0.1184(6)	0.8338(3)	3.01
C(6)	−0.229(1)	0.1437(7)	0.8980(3)	3.71
C(7)	−0.183(1)	0.2713(6)	0.9217(3)	3.72
C(8)	−0.139(1)	0.3692(6)	0.8797(3)	3.27
C(9)	−0.1405(9)	0.3429(6)	0.8140(3)	2.81
C(10)	−0.1857(9)	0.1850(6)	0.7204(3)	2.87
C(11)	−0.079(1)	0.2632(8)	0.6251(3)	5.07
C(12)	−0.522(1)	0.2516(8)	0.6952(4)	4.79
C(13)	−0.188(2)	0.3005(9)	0.9912(4)	6.23

strate how similar the models proved; however, the discussion focuses on the low-temperature structures, since these exhibit slightly lower esds and slightly improved agreement factors. The ORTEP drawings are of the low-temperature structures. The positional parameters for **2b** and **8b** are available as supplementary material.

3. Results and discussion

Top view ORTEP drawings of the eight molecules discussed here appear in Figs. 1–8. We examined both the dimethylacetal and diethylacetal complexes of each arene type to assess the effect of substituent steric interactions on carbonyl orientation. If these are important, it seems likely that the more demanding diethylacetal group should orient so as to attain the most space. As noted above, steric considerations were invoked to explain the staggered orientation adopted by the carbonyl ligands in [p-Me_3C-C_6H_4-CO_2H]$Cr(CO)_3$ [4], where consideration of the donating properties of the t-butyl group and the accepting properties of the carboxylic acid group might lead one to suspect an electronic preference for an eclipsed conformation.

Despite the variation in donor/acceptor properties from pair to pair, the bond lengths observed in **1**–**8** are nearly identical across the series; we discuss the only obvious anomalies, the Cr–carbonyl and Cr–arene distances of compounds **1** and **2**, below. In each case, the chromium atom lies *ca.* 1.7 Å below the centroid of the

TABLE 9. Final fractional coordinates for compound **8**

Atom	x/a	y/b	z/c	B_{eq}
Cr	0.31017(2)	0.50101(2)	0.19278(3)	1.48
F(1)	0.39760(9)	0.7236(1)	0.1619(1)	3.91
F(2)	0.38819(9)	0.7064(1)	−0.0030(1)	3.76
F(3)	0.46937(8)	0.6253(1)	0.1205(1)	3.87
O(1)	0.2306(1)	0.3803(1)	0.3063(1)	3.27
O(2)	0.4550(1)	0.4233(2)	0.3479(2)	4.31
O(3)	0.3194(2)	0.6589(1)	0.3475(2)	6.24
O(4)	0.10929(8)	0.4090(1)	0.0457(1)	1.85
O(5)	0.15121(8)	0.3208(1)	−0.0729(1)	1.87
C(1)	0.2609(1)	0.4272(2)	0.2629(2)	2.05
C(2)	0.3996(1)	0.4531(2)	0.2876(2)	2.59
C(3)	0.3161(2)	0.5973(2)	0.2887(2)	3.32
C(4)	0.2292(1)	0.4433(1)	0.0415(2)	1.45
C(5)	0.3024(1)	0.4166(2)	0.0485(2)	1.69
C(6)	0.3584(1)	0.4860(2)	0.0650(2)	1.88
C(7)	0.3419(1)	0.5826(2)	0.0740(2)	1.80
C(8)	0.2685(1)	0.6092(2)	0.0664(2)	1.87
C(9)	0.2120(1)	0.5409(2)	0.0485(2)	1.76
C(10)	0.1707(1)	0.3666(2)	0.0284(2)	1.68
C(11)	0.0594(1)	0.3439(2)	0.0707(2)	2.43
C(12)	0.0095(1)	0.4018(2)	0.1124(2)	3.20
C(13)	0.1205(1)	0.3822(2)	−0.1647(2)	2.35
C(14)	0.1046(2)	0.3221(2)	−0.2645(2)	3.56
C(15)	0.3997(1)	0.6586(2)	0.0894(2)	2.52

TABLE 10. Selected bond distances (Å) and angles (°) for compounds **1**–**8** [a]

	1	**2**	**2b**	**3**	**4**
Cr–C (carbonyl) (avg.)	1.823(5, 7)	1.825(6, 8)	1.81(1, 3)	1.842(8, 20)	1.841(5, 3)
Cr–C (ring) (avg.)	2.248(4, 70)	2.249(5, 67)	2.25(1, 8)	2.210(7, 8)	2.206(4, 6)
Cr–Cent	1.75	1.75	1.76	1.71	1.70
C–C (ring) (avg.)	1.408(5, 13)	1.411(7, 14)	1.41(1, 3)	1.400(10, 24)	1.402(6, 18)
C–O (carbonyl) (avg.)	1.155(5, 4)	1.161(7, 3)	1.17(1, 3)	1.148(8, 11)	1.144(6, 2)
C (ring)–substituent atom X	1.345(5) (N)	1.356(7) (N)	1.33(1) (N)	1.730(7) (Cl)	1.733(5) (Cl)
C (ring)–C (acetal)	1.513(5)	1.512(7)	1.47(1)	1.511(9)	1.502(6)
C (carbonyl)–Cr–C (carbonyl) (avg.)	89.0(2, 12)	88.6(2, 11)	88.2(5, 9)	89.8(3, 7)	88.1(2, 3)
Cr–C–O (carbonyl) (avg.)	178.4(4, 3)	178.4(5, 5)	177.8(9, 18)	178.5(7, 8)	178.7(5, 6)
Cent–Cr–C (carbonyl) (avg.)	126(–, 3)	126(–, 4)	126(–, 3)	125.4(–, 9)	126.5(–, 4)

	5	**6**	**7**	**8**	**8b**
Cr–C (carbonyl) (avg.)	1.835(5, 3)	1.826(5, 7)	1.839(8, 20)	1.843(3, 9)	1.82(1, 3)
Cr–C (ring) (avg.)	2.220(4, 8)	2.217 (4, 19)	2.208(6, 15)	2.204(2, 11)	2.202(9, 14)
Cr–Cent	1.72	1.71	1.70	1.69	1.70
C–C (ring) (avg.)	1.408(6, 14)	1.406(5, 12)	1.405(9, 23)	1.410(3, 9)	1.41(1, 1)
C–O (carbonyl) (avg.)	1.155(5, 5)	1.153(5, 6)	1.156(8, 16)	1.153(3, 2)	1.15(1, 1)
C (ring)–substituent atom X	1.886(4) (Si)	1.884(4) (Si)	1.499(9) (CF_3)	1.495(3) (CF_3)	1.49(1) (CF_3)
C (ring)–C (acetal)	1.506(6)	1.520(5)	1.528(8)	1.514(3)	1.51(1)
C (carbonyl)–Cr–C (carbonyl) (avg.)	88.2(2, 7)	88.1(2, 11)	88.7(3, 12)	88.6(1, 7)	88.6(4, 6)
Cr–C–O (carbonyl) (avg.)	179.2(4, 3)	178.6(4, 12)	178.3(7, 8)	179.0(2, 2)	179(1, 1)
Cent–Cr–C (carbonyl) (avg.)	127(–, 2)	127(–, 2)	126(–, 3)	126.2(–, 8)	126.3(–, 3)

[a] Esds of averaged values are given in the form (a, b), where a is the average of the individual esds, and b is the standard deviation of the values from the average.

arene ring, and 1.84 Å from the carbonyl carbons in a 'three-legged piano stool' arrangement. All the distances associated with the arene ring, substituent group, acetal function and carbonyl ligands lie within the expected ranges [15].

Before examining the carbonyl arrangements in detail, we provide a shorthand for referring to the available conformations, based on that employed by Muetterties *et al.* [2]. For (*para*-substituted arene dialkylacetal)chromium tricarbonyl compounds, five possible limiting carbonyl orientations exist. In one, the substituent group of interest eclipses a carbonyl, the other two carbonyls are eclipsed by hydrogen atoms *meta* to this group and the acetal groups is staggered; we term this *E*1. If electronic effects dictate the carbonyl arrangement, one expects the *E*1 conformation to occur when the substituent group is a π donor; since the acetal group is an acceptor (albeit a weak one; see

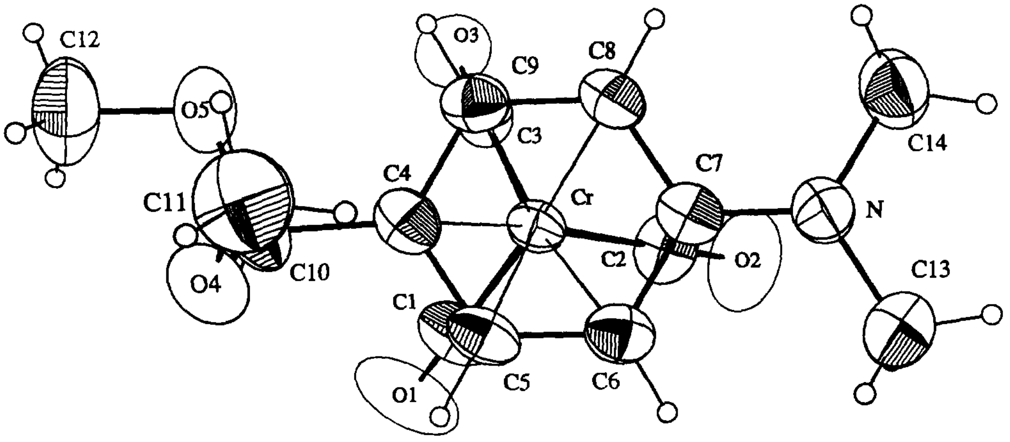


Fig. 1. Top-down ORTEP drawing of compound 1, showing the atomic labeling.

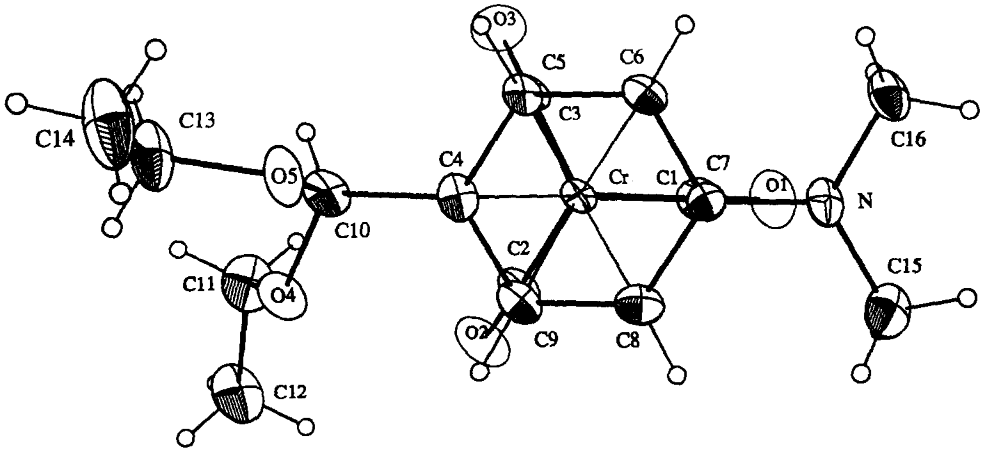


Fig. 2. Top-down ORTEP drawing of compound **2**, showing the atomic labeling.

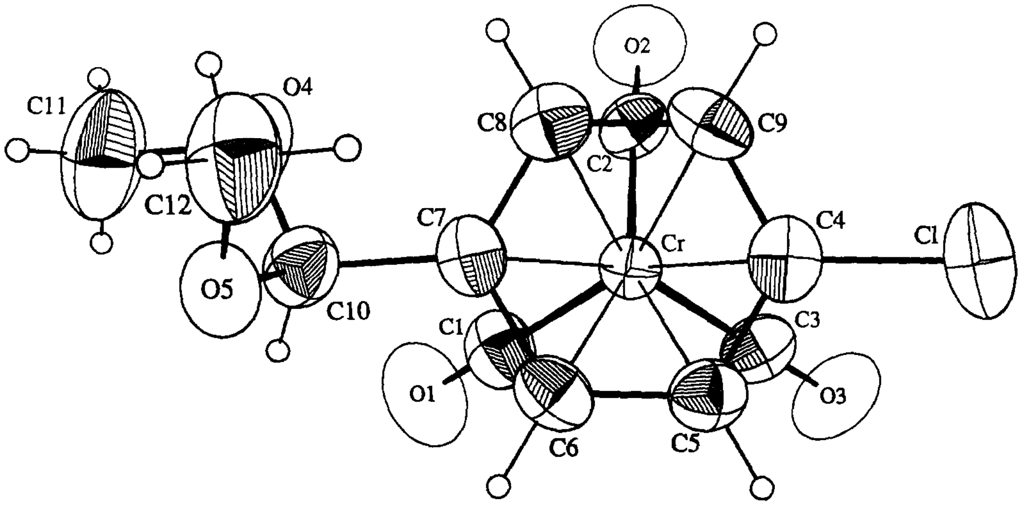


Fig. 3. Top-down ORTEP drawing of compound **3**, showing the atomic labeling.

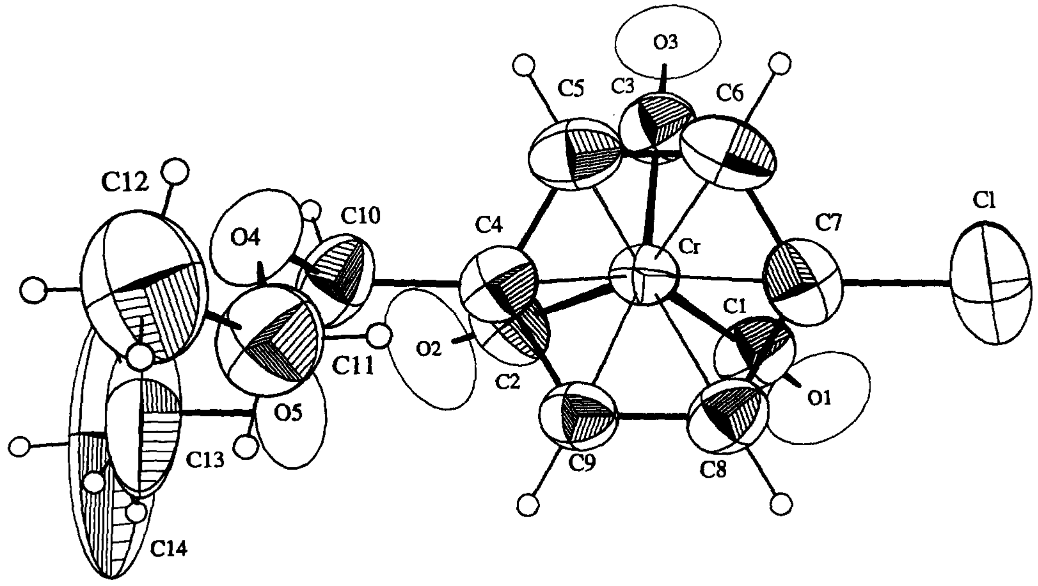


Fig. 4. Top-down ORTEP drawing of compound **4**, showing the atomic labeling.

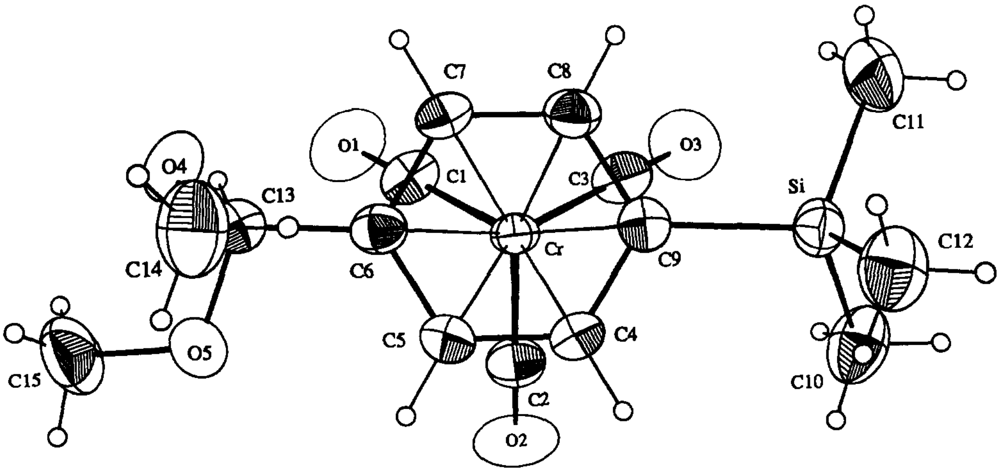


Fig. 5. Top-down ORTEP drawing of compound 5, showing the atomic labeling.

below), this situation accords with the predictions based on AHH's work. The opposite case, where the acetal group eclipses a carbonyl and the substituent group is staggered, we term *E*1′; this structure is unlikely to be observed if electronic effects dictate the carbonyl orientation, since the acceptor group is eclipsed and the donor group is staggered.

The next two possibilities, which represent those cases where the substituent group of interest is a π acceptor, we term *E*2 and *E*2′. The *E*2 conformation presents the electronically motivated carbonyl orientation: the substituent is staggered, while the more weakly accepting acetal group eclipses a carbonyl. Note that *E*2 differs from the *E*1′ conformation only by the donating/accepting characteristics of the substituent; structurally they are identical. Conformation *E*2′ is the inverse of *E*2, with the acceptor group eclipsing a carbonyl, while the acetal group is staggered. Structurally, *E*2′ is identical to *E*1, differing from it only in the electronic nature of the substituent; as with *E*1′, one would predict that *E*2′ would rarely be observed. Finally, the gauche-like form, which staggers all the ring groups and carbonyl ligands, we term *S*. This conformation, as noted above, prevails when the donating/accepting characteristics of the substituents are similar.

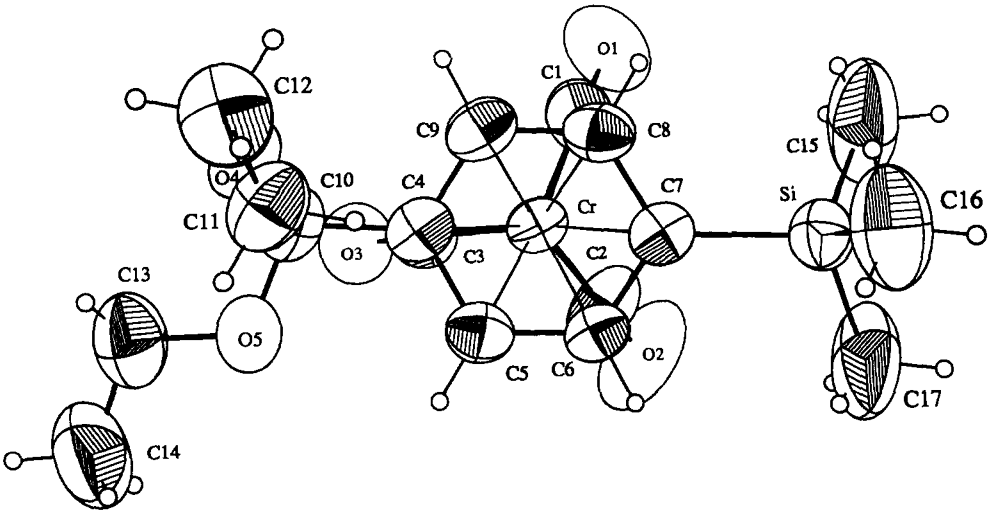


Fig. 6. Top-down ORTEP drawing of compound 6, showing the atomic labeling.

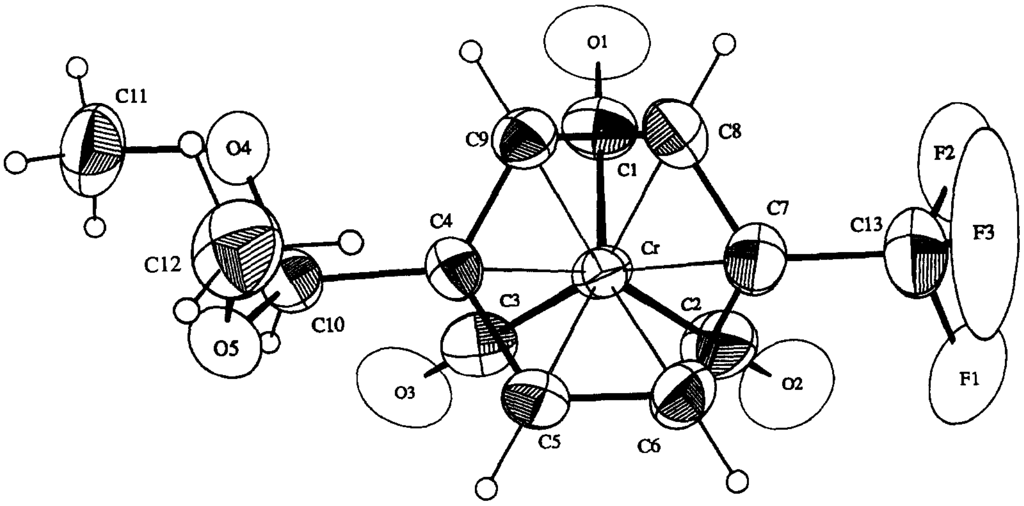
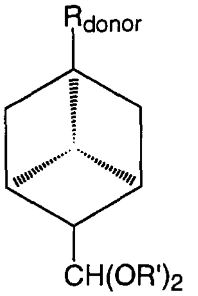
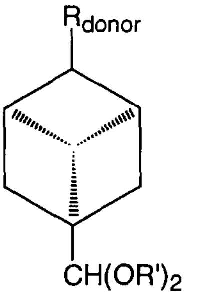


Fig. 7. Top-down ORTEP drawing of compound **7**, showing the atomic labeling.

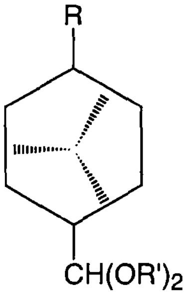
To characterize the extent to which the molecules correspond to these ideal cases, we employ the torsion angle τ [4,9]. The angle contains the ring-carbon atom (C7 for **1**/**2**, C4 for **3**, C7 for **4**, C9 for **5**, and C7 for **6**–**8**) bound to the primary substituent atom, the calculated arene ring centroid, the chromium and the car-



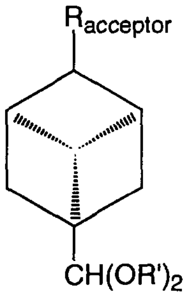
E1



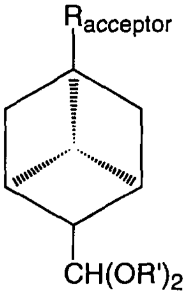
E1'



S



E2



E2'

bonyl carbon closest to the primary substituent atom. The definition provides a shorthand method of evaluating the extreme situations noted above: for a perfect *E*1 or *E*2' structure, τ is 0°; for a perfect *E*1' or *E*2 structure, τ is 60°. All other values of τ lie between these; perfectly staggered molecules (*S*) will exhibit $\tau = 30°$.

Finally, it is necessary to provide a standard by which a substituent group may be described as donating or accepting. As Hunter noted [9,16], the donating or accepting properties of an arene substituent may change once the arene coordinates to a chromium tricarbonyl moiety; thus use of, for example, σ_R values for the free arenes may prove unwarranted for the corresponding complex. He suggested instead using variations in ^{13}C NMR chemical shifts, and showed that the resulting parameter $\Delta_\pi[= \delta(\textit{para}\text{ carbon}) - \delta(\textit{meta}\text{ carbon})$ in the monosubstituted complex containing the substituent of interest] correlates well with structural parameters expected to depend on donating/accepting properties. We have no need for such quantitative relationships, but we have chosen to use the Δ_π parameter as a qualitative measure of donor/acceptor ability. This leads to conclusions consistent with chemical intuition and with most tabulations of σ_R for the free arenes: Me_2N and Cl act as π donors, with the former a much stronger one, while $SiMe_3$ and CF_3 are acceptors, with the latter stronger. We have determined that, by this measure, the dimethylacetal and diethylacetal groups function as very weak π acceptors [$\Delta_\pi = 0.3$–1.0 in $CDCl_3$, 0.4–1.6 in $(CD_3)_2SO$] [11]. This is fortunate and useful as it means these substituents can be considered as nearly 'hydrogen-like' electronically (neither donating or accepting); they are unlikely to electronically dictate the carbonyl conformation by themselves or to interfere with the electronic characteristics of the other substituent. Any orientational preference must be based on the electronic demands of the other substituent.

As can be seen in Figs. 1 and 2, the dimethylamino complexes **1** and **2a** adopt exclusively the *E*1 orientation, where the Me_2N group is eclipsed and the acetal group by constraint is staggered. For compound **1**, τ is 8.9°, and for **2a**, τ is 0.1°. As commented on above, this conformation is predicted through application of AHH concepts to (*para*-disubstituted arene)Cr(CO)$_3$ complexes, yet has only been observed once before. Evidently the dimethylamino group, unlike the t-butyl group in [*p*-Me_3C-C_6H_4-CO_2H]Cr(CO)$_3$, is sufficiently small to allow it to eclipse a carbonyl ligand. Electronic considerations in the form of the considerable donor properties of the dimethylamino group then dictate the structure. Of course, the *E*1 conformation also allows the slightly larger acetal groups to obtain

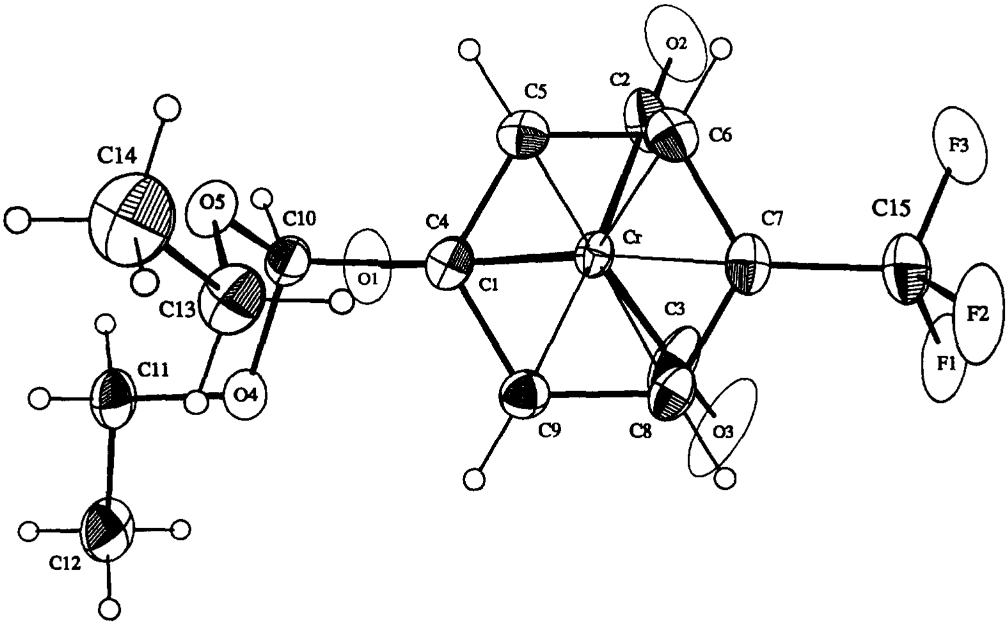


Fig. 8. Top-down ORTEP drawing of compound **8**, showing the atomic labeling.

the greatest amount of space, since they are fully staggered; therefore steric considerations cannot be totally ruled out.

When compared with compounds **3**–**8**, the chromium–carbonyl carbon lengths are somewhat short, and the chromium–arene carbon distances (equally, the chromium–ring centroid distance) in **1** and **2** appear long. The synergistic bonding model for metal carbonyls argues that a decrease in metal–carbonyl bond length largely results from increased metal → carbonyl backbonding, which in turn implies an unusually electron-rich metal center [17,18]. Undoubtedly the presence of the strong donor dimethylamino group produces an arene ring which donates strongly to the metal, fulfilling the requirements of the model.

The explanation for the increased metal–ring distance is also electronic in origin, but more subtle. Hunter and co-workers demonstrated structurally that arenes containing strong π-donor substituents such as the dimethylamino group flex into a boat conformation upon coordination to Cr(CO)$_3$ moieties, a consequence of the contribution of the iminium resonance form [9]. Their model predicts than the metal–carbon bond distance for the nitrogen-bonded carbon should be considerably longer that any other metal–ring carbon distance. This in fact holds for compounds **1** and **2**. For **1**, the Cr–C7 distance is 2.383(4) Å; the average of the other five Cr–C distances is 2.221(4, 26) Å [19]. For **2**, the analogous values are 2.377(5) Å *vs.* 2.223(5, 27) Å. It is apparent that the anomalous length accounts for a significant fraction of the difference between the normal esd values and the extraordinarily large standard deviations from the average reported in Table 10 for the average metal–ring carbon distance. Further, it is obvious that the five-carbon averages lie within the range set by compounds **3**–**8**.

The chloro substituent acts as a considerably poorer π donor than the dimethylamino group; Δ_π values suggest it to be only slightly more donating than a methyl group [16]. However, since the ring contained the weak acceptor acetal substituent in the *para* position, we anticipated that the chloro-substituted compounds **3**/**4** would adopt the eclipsed structure *E*1. In fact, the structural determinations established that both crystallize in the staggered *S* conformation, with τ values of 30.6° for **3** and 37.2° for **4** (Figs. 3 and 4). That the molecules select this arrangement argues either that electronic considerations are unimportant in determining the structure, or that the donor properties of the chloro substituent, even in tandem with the acceptor properties of the acetal, are too small to dictate the carbonyl orientation. Either argument suggests that application of AHH considerations to the system is unwarranted. Such a view contrasts with that put forth regarding the similar conformations adopted by the symmetric molecules [1,4-(Me$_2$N)$_2$C$_6$H$_4$]Cr(CO)$_3$, [1,4-(MeO)$_2$C$_6$H$_4$]Cr(CO)$_3$, and [1,4-(MeO$_2$C)$_2$C$_6$H$_4$]Cr(CO)$_3$ [9], where it was suggested that the *S* arrangement provides the best electronic compromise between the donating or accepting characteristics of the substituents.

The similarity between the τ values for **3**/**4** suggests that the steric requirements of the substituents play a minimum role in determining the carbonyl orientation; in particular, the effect of the greater τ value observed in **4** is to push the carbonyl C2–O2 *closer* to the sterically more demanding diethylacetal group. Thus no evidence exists for the possibility discussed above for compounds **1**/**2** that the steric requirements of the arene substituents might play a role in forcing a particular conformation. It appears that if any intramolecular steric interactions determine the structure, they are those between the carbonyls and the ring carbon atoms. The *S* arrangement minimizes such interactions, although one presumes they are of minor importance even in the eclipsed conformation.

The trimethylsilyl-substituted arene complexes **5**/**6** present cases where prediction of the carbonyl orientation is difficult. The trimethylsilyl group is a fairly strong π acceptor, only slightly weaker than the CO$_2$Me function as gauged by Δ_π values. Electronically, then, one might predict a preference for eclipsed structures where the acetal group (the poorer acceptor) eclipses a carbonyl (*E*2). However, the Δ_π values suggest that Me$_3$Si is about as strong an acceptor as Cl is a donor; therefore, the acceptor properties could prove too weak to determine the carbonyl orientation and an *S* conformation might obtain. Finally, the trimethylsilyl group is bulkier than either the chloro or dimethylamino groups, and thus steric interactions could dominate electronic considerations for **5**/**6**. Since the similarly bulky dialkylacetal groups did not exert an obvious steric influence on the conformations of **3**/**4**, this seems unlikely, but it remains worth considering. The *E*1′ and *E*2 conformations provide the Me$_3$Si group with the greatest space, the *S* conformation presents the best compromise between all intramolecular steric demands, and the *E*1 and *E*2′ conformations provide the acetal group with the greatest space.

Surprisingly, compounds **5** and **6** exhibit different carbonyl geometries. As is shown in Fig. 5, the dimethylacetal complex **5** crystallizes with the carbonyls staggered (*S* form), with a τ value of 29.5°. This argues that the acceptor properties of the trimethylsilyl group and of the acetal group are too small to dictate the carbonyl arrangement. However, complex **6** adopts the *E*2 orientation, with $\tau = 50.9°$ (Fig. 6). What makes the situation here intriguing, other than the fact that different conformations occur for the two molecules, is that the more sterically demanding diethylacetal group in **6** eclipses a carbonyl, presumably adding to the crowding in the molecule, while the less sterically demanding dimethylacetal group in **5** occupies the staggered orientation. This, plus the data from **3**/**4**, provides compelling evidence that substituent steric effects do not dictate the carbonyl conformation in **5**/**6**, and by extension in any of the molecules **1**–**8**.

The question then arises of why compounds **5** and **6** adopt different configurations. As noted above, one's expectation from the application of AHH concepts is that either configuration could occur. It is difficult to explain why *each* occurs. The Δ_π values for the dimethyl- and diethyl-acetal functions are essentially identical, arguing against an electronic distinction between the two molecules. The only conclusion we can draw is that electronic issues are largely irrelevant in determining the conformation here, and that the observed arrangements result from other factors. This suggests that the potential surface for carbonyl rotation for these molecules is nearly flat, in contrast to **1**/**2** and possibly **3**/**4**, where the observance of identical structures between pairs argues for the presence of a rotational barrier.

Support for this concept arises from the structures of **7** and **8**. Again these exhibit different conformations; compound **7** is staggered, with $\tau = 32.1°$, essentially identical to **5**, while compound **8** adopts the eclipsed $E2$ orientation comparable to that of **6** ($\tau = 54.3°$). Again the more sterically demanding diethylacetal in **8** eclipses a carbonyl, while the dimethylacetal in **7** sits between carbonyls. It is particularly surprising that the CF_3 group in **7** does not dictate that this molecule adopt the $E2$ conformation, as occurs in **8**; one might have anticipated that the acceptor characteristics of the CF_3 substituent would demand this conformation in the same fashion that the donor characteristics of the Me_2N substituent in **1**/**2** force the molecule into an $E1$ arrangement. One can only conclude that virtually no electronic or steric basis determines the carbonyl orientation in these molecules, that the barrier between differing conformations is small (equally, the barrier to carbonyl rotation is small) and that the resulting structures depend upon more subtle factors.

Both intramolecular van der Waals attractions and crystal packing forces represent plausible candidates for such factors. The former could in theory explain the eclipsed structures of **6** and **8** contrasted with the staggered structures of **5** and **7**, as follows: the longer chain ethyl groups in **6**/**8** extend sufficiently to allow interactions with carbonyl ligands, and the carbonyls in turn rotate to the eclipsed orientation to maximize the interaction; the shorter chain acetal methyl groups cannot interact with the carbonyls, and **5**/**7** thus adopt the staggered arrangement to minimize steric interactions between the carbonyls and the ring carbons. We investigated this hypothesis by examining the nonbonded distances (≤ 4 Å) in **5**–**8**. As one would anticipate both from the radial extent of the carbon chain and the known carbonyl orientations, more close contacts exist between the diethylacetal group and the nearest carbonyl oxygen than between the corresponding dimethylacetal group and its nearest carbonyl oxygen. However, in no case are the nonbonded distances small enough to allow certainty. The shortest nonbonded contact between a carbonyl oxygen and an acetal carbon occurs in **8**, where the O1–C11 distance is 3.666(3) Å. This distance is much greater than the sum of the van der Waals radii of the elements and therefore almost certainly does not represent an interaction. The hydrogen atoms bound to C11 must point away from the oxygen; therefore they cannot be a source of interaction either. Finally, note that C11 is the methylene carbon, not the methyl carbon; if one argues that an interaction exists, one must then also address the issue of why the dimethylacetal function cannot undertake a similar interaction, since its methyl carbon occupies the same point in the acetal group as the methylene carbon in the diethylacetal group.

To secure the argument further, we point out that no close contacts between the carbonyl oxygen and neither the methylene nor methyl carbons in **6** exist; only the methine carbon C10 lies within 4 Å of O3. We therefore conclude that intramolecular van der Waals forces do not dictate the carbonyl orientations in **5**–**8**.

Determining whether packing forces are the crucial factor in the conformation chosen is difficult, since it remains unclear precisely how to assess this. We choose simply to note that a considerable number of nonbonding intermolecular contacts of < 4 Å appear in compounds **1**–**8**, many of which involve the carbonyl ligands, and thus the possibility that such between-molecule interactions control the molecular conformation in the absence of strong electronic/steric factors exists. The structures of some (trisubstituted arene) chromium tricarbonyls, where strong cases were made for packing forces determining the carbonyl orientation, have appeared [20,21], but how these might be related to our disubstituted systems is currently uncertain.

4. Conclusions

Our results here indicate that electronic factors dictate the conformation of the carbonyl ligands with respect to the ring substituents only when the donating or accepting ability of the substituent is unusually large, as in the donor Me_2N. In less extreme cases, steric requirements play a greater role, either by a large substituent forcing the carbonyls to adopt a staggered arrangement as in [p-Me_3C-C_6H_4-CO_2H]Cr$(CO)_3$, or if no substituent is large, by the ring staggering to minimize ring–carbon carbonyl ligand interactions. The structures of compounds **3–8**, however, demonstrate that theoretical predictions often prove inadequate; only the experimentally determined structure truly defines the system. Indeed, if our suggestion that crystal packing forces can control the carbonyl arrangement is correct, it implies that prediction in many cases is pointless; the crucial factor that controls the molecular geometry in such cases is too subtle to be well-modeled. Of course, AHH made the point that the carbonyl rotational barrier in most (arene)chromium tricarbonyls is likely to be small, and certainly studies of carbonyl rotation in solution have demonstrated this [22], but it is prudent to remember that the argument applies to the solid state as well. If the barrier is small, and it often is, then the preferred geometry may be dictated by unexpected factors rather than obvious ones.

5. Supplementary material available

Calculated hydrogen atom positions, anisotropic thermal parameters, least-squares planes, complete listing of bond distances and angles and observed and calculated structure factors for compounds **1–8**. All these plus refined positional parameters for **2b** and **8b** (88 pages). Ordering information is given on any current masthead page.

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