

Structure of Tricarbonyl[1-6- η -(2-ethylanisole)]chromium

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Abstract. $[\text{Cr}(\text{CO})_3(\text{C}_9\text{H}_{12}\text{O})]$, $M_r = 272.22$, monoclinic, $P2_1/a$, $a = 13.593$ (4), $b = 8.999$ (3), $c = 10.546$ (3) Å, $\beta = 106.48$ (5)°, $V = 1237.03$ (4) Å³, $Z = 4$, $D_x = 1.46$ g cm⁻³, $\text{Mo K}\alpha$ ($\lambda = 0.7109$ Å), $\mu = 0.87$ cm⁻¹, $T = 293$ K, $F(000) = 560$. The structure was refined from 2253 reflections with $I > 2\sigma(I)$ to $R = 0.042$. The 2-ethylanisole part of the molecule is approximately planar; the maximum deviation from the least-squares plane is 0.378 (1) Å (C8). The conformation of the molecule in the crystal is the favoured one in which the methyl group of the ethyl is located away from the methoxy group.

Introduction. The 80 MHz ¹H NMR spectrum of the title compound exhibits an ABX_3 system: $\delta \text{CH}_A\text{B}_B\text{CHX}_3$: $\delta\text{H}_X = 1.19$, $\delta\text{H}_A = 2.34$, $\delta\text{H}_B = 2.67$, $J_{AX} = J_{BX} = 7.5$ Hz, $J_{AB} = 14.8$ Hz. The effects of the intrinsic metallocenic asymmetry are small for proton spectra and the non-equivalence arises mainly from an unequal conformer population and close proximity of diastereotopic protons to the anisotropic $\text{Cr}(\text{CO})_3\text{Ar}$ group (Whitesides, Holtz & Roberts, 1964; Gracey, Jackson, McMullen & Thompson, 1969; McGlinchey, Burns, Hofer, Top & Jaouen, 1986). The striking chemical shift difference between benzylic protons (0.33 p.p.m.), similar to that observed in a cyclic arene tricarbonyl chromium complex (McGlinchey *et al.*, 1986), suggests that one conformer is highly preferred. In the favoured conformer, in which the methyl group of the ethyl should be located away from the methoxy group, the proton proximal to the metal carbonyl group is 'deshielded' relative to the resonance position of the proton distal to the tripod (McGlinchey *et al.*, 1986). We report the results of an X-ray diffraction study to compare the conformation observed in the crystal with the preferred conformation shown by the NMR study.

Experimental. Single yellow crystal $0.3 \times 0.5 \times 0.4$ mm, Phillips PW 1100 four-circle diffractometer, room temperature, $\text{Mo K}\alpha$ radiation ($\lambda = 0.7109$ Å),

lattice parameters from 25 reflections ($20 < \theta < 27^\circ$); 3234 intensities with $(\sin\theta)/\lambda \leq 0.4951$ Å⁻¹ in the ω - 2θ scan (width of scan fixed at 2.0° and $-14 \leq h \leq 14$, $k \leq 12$, $l \leq 12$), from which 2253 with $I > 2\sigma(I)$ used for structure refinement. Lp correction, absorption and extinction ignored; *MULTAN* (Germain, Main & Woolfson, 1971) and Fourier methods, anisotropic full matrix on F (Sheldrick, 1976), H from $\Delta\rho$ synthesis, isotropic not refined; atomic scattering factors from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965); final $R = 0.042$, unit weight, $S = 2.59$; $\Delta\rho$ in final map = $0.47, -0.46$ e Å⁻³, $(\Delta/\sigma)_{\text{max}} = 0.14$.

Discussion. Fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are given in Table 1, selected interatomic distances and angles in Table 2.* The conformation of the complex and the atomic numbering are depicted in Fig. 1. Fig. 2 shows the crystal packing along [010].

The configuration of the tricarbonyl group, with respect to the benzene ring, is found to be approximately eclipsed with the carbonyl group located near the C1, C3 and C5 atoms. This result is in agreement with those obtained by NMR studies on substituted arene chromium tricarbonyl complexes in solution that show that the privileged group eclipses the more electron-donating group of the substituted ring (Solladie-Cavallo & Suffert, 1980; Brocard, Laconi & Couturier, 1984).

The Cr–C (arene) distances are in the range 2.204 (2) to 2.302 (2) Å, with maxima for the substituted atoms: C1 [2.262 (2)] and C2 [2.302 (2) Å].

The least-squares plane of the ring shows that the largest deviation from the plane is 0.022 (1) Å for the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44950 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters

Fractional positional parameters are $\times 10^4$.

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j (\times 10^2) \text{ \AA}^2.$$

	x	y	z	U_{eq}
Cr	7558 (2)	1415 (1)	7759 (1)	46 (1)
C1	8994 (2)	944 (4)	7078 (4)	45 (5)
C2	8819 (3)	-257 (4)	7855 (4)	45 (5)
C3	8754 (3)	23 (5)	9135 (4)	64 (6)
C4	8826 (3)	1469 (6)	9631 (4)	67 (6)
C5	8948 (3)	2630 (5)	8854 (4)	52 (6)
C6	9029 (3)	2392 (4)	7581 (4)	56 (6)
C7	8779 (3)	-1824 (4)	7301 (4)	62 (6)
C8	8335 (4)	-2991 (5)	7976 (5)	107 (10)
C9	9176 (3)	1763 (5)	5011 (4)	86 (8)
O	9084 (2)	588 (2)	5875 (2)	65 (3)
C10	6813 (2)	919 (4)	6066 (3)	60 (5)
C20	6850 (2)	3170 (4)	7688 (3)	50 (5)
C30	6578 (3)	485 (4)	8327 (3)	72 (6)
O10	6351 (2)	569 (3)	5015 (2)	69 (4)
O20	6401 (2)	4267 (3)	7687 (3)	84 (4)
O30	5912 (2)	-115 (3)	8639 (3)	122 (5)

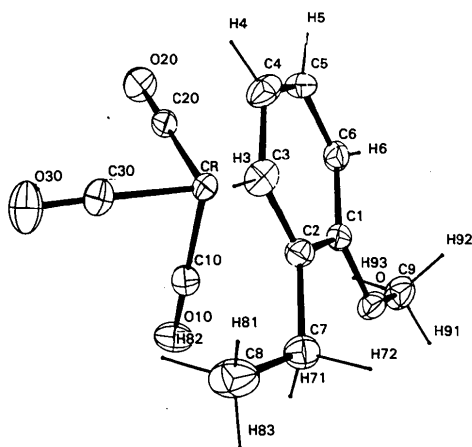


Fig. 1. Perspective view of the molecule (ORTEP; Johnson, 1976).

Table 2. Selected bond lengths (Å) and bond angles ($^\circ$) with e.s.d.'s in parentheses

C2-C3	1.401 (1)	C2-C3-C4	120.8 (1)
C3-C4	1.396 (1)	C1-C2-C3	119.1 (1)
C1-C2	1.416 (1)	C1-C2-C7	118.6 (1)
C2-C7	1.521 (1)	C2-C1-C6	118.9 (1)
C1-C6	1.401 (1)	C2-C1-O	116.0 (1)
C1-O	1.348 (2)	C1-C6-C5	120.2 (1)
C5-C4	1.367 (1)	C3-C4-C5	119.7 (1)
C7-C8	1.492 (2)	C2-C7-C8	116.4 (1)
O-C9	1.424 (1)	C3-O-C9	118.3 (1)
Cr-C3	2.231 (2)	C3-Cr-C4	36.5 (1)
Cr-C2	2.262 (2)	C3-Cr-C2	36.3 (1)
Cr-C1	2.302 (2)	Cr-Cr-C1	36.1 (1)
Cr-C6	2.240 (2)	C1-Cr-C6	35.9 (1)
Cr-C5	2.204 (2)	C6-Cr-C5	36.5 (1)
Cr-C4	2.222 (2)	C5-Cr-C4	36.0 (1)
Cr-C10	1.841 (1)	C10-Cr-C10	91.8 (1)
Cr-C20	1.841 (1)	C20-Cr-C30	89.1 (1)
Cr-C30	1.813 (2)	C10-Cr-C30	87.4 (1)
C10-O10	1.153 (1)	Cr-C10-O10	178.1 (1)
C20-O20	1.160 (1)	Cr-C20-O20	177.6 (1)
C30-O30	1.178 (2)	Cr-C30-O30	177.0 (1)
Cr-A1	2.169 (3)		
Cr-A2	2.134 (4)		
Cr-A3	2.114 (4)		
Cr-A4	2.097 (4)		
Cr-A5	2.110 (4)		
Cr-A6	2.160 (4)		

Ai: middle of each C-C ring bond.

C1 atom to which is attached the oxygen atom of the O-CH₃ group. The O, C7 and C9 atoms lie in the plane with a maximum deviation of 0.050 (1) Å for the O atom; only the C8 atom (ethyl group) is located at 0.378 (1) Å from the plane, on the same side as the Cr(CO)₃ group with respect to the plane.

The X-ray structure determination indicates that distal and proximal benzylic protons are situated on both sides of the zero shift surface between the shielding and deshielding zones (McGlinchey *et al.*, 1986) (Fig.

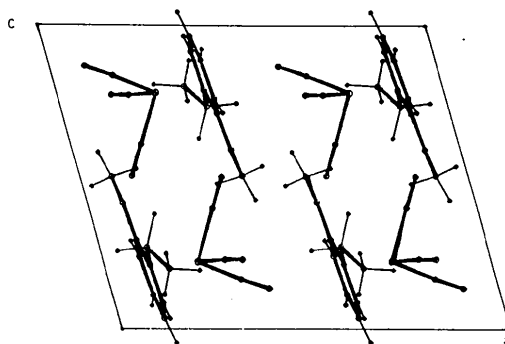
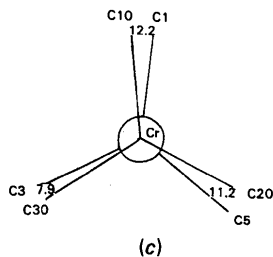
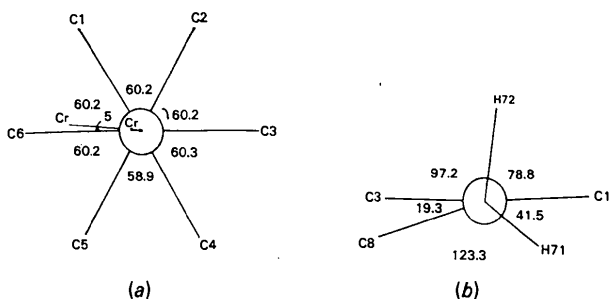


Fig. 2. Packing along the [010] axis (ORTEP; Johnson, 1976).

Fig. 3. Newman projections. (a) Along an axis perpendicular to the phenyl group. (b) Along the C7-C2 bond. (c) Along the direction from Cr to the centre of the ring. (Angles in $^\circ$.)

3). A calculation of the methylene proton chemical shift difference in the solid using the McGlinchey method is in progress to compare that difference with the NMR experimental data.

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Structures of [*N*-(*p*-Methoxyphenyl)-2-(*p*-methoxyphenylimino)propylamino-*N,N'*]-dimethylaluminium (I) and Dimethyl[*N*-(*p*-tolyl)-2-(*p*-tolylimino)propylamino-*N,N'*]aluminium (II)

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Abstract. [Al(CH₃)₂(C₁₇H₁₉N₂O₂)] (I), *M_r* = 340.40, triclinic, *P* $\bar{1}$, *a* = 9.844 (1), *b* = 10.263 (2), *c* = 11.317 (1) Å, α = 74.15 (1), β = 70.14 (1), γ = 63.70 (1)°, *V* = 953.8 (3) Å³, *Z* = 2, *D_x* = 1.185 g cm⁻³, λ (Cu *K*α) = 1.54184 Å, μ = 9.40 cm⁻¹, *F*(000) = 364, *T* = 298 K. The structure has been refined to *R* = 0.0480 for 3057 unique observed reflections with *I* ≥ 2.5σ(*I*). [Al(CH₃)₂(C₁₇H₁₉N₂)] (II), *M_r* = 308.40, triclinic, *P* $\bar{1}$, *a* = 9.593 (2), *b* = 10.135 (1), *c* = 11.274 (2) Å, α = 104.88 (5), β = 109.54 (5), γ = 102.69 (7)°, *V* = 940.5 (5) Å³, *Z* = 2, *D_x* = 1.089 g cm⁻³, λ (Cu *K*α) = 1.54184 Å, μ = 8.9 cm⁻¹, *F*(000) = 332, *T* = 298 K. The structure has been refined to *R* = 0.0735 for 1507 unique observed reflections with *I* ≥ 2.5σ(*I*). Corresponding distances, angles and conformations of (I) and (II) are very similar. The phenyl ring at N(1) is coplanar with the five-membered aluminium ring in both compounds, whereas the phenyl ring at N(2) makes an angle of 78.1 (1)° for (I) and 69.9 (3)° for (II).

Introduction. Trialkylaluminium and dialkylzinc compounds react selectively with 1,4-dihetero-1,3-butadienes (*R*-DAB with *R* = alkyl, aryl) to give, after

hydrolysis, interesting products such as 1-amino-2-iminoethanes and 1,2-diaminoethanes (Klerks, Stufkens, van Koten & Vrieze, 1979). Intermediate complexes have been obtained from the reactions of AlR₃ and ZnR₂ with *R*-N=C(*R'*)C(*R''*)=N-*R* (Klerks, Stufkens, van Koten & Vrieze, 1979; Klerks, Jastrzebski, van Koten & Vrieze, 1982; Jastrzebski, Klerks, van Koten & Vrieze, 1981; van Koten, Jastrzebski & Vrieze, 1983) and with *R*-N=C(*R'*)C(*R''*)=O (van Vliet, Jastrzebski, van Koten, Vrieze & Spek, 1983; van Vliet, van Koten, Rotteveel, Schrap, Vrieze, Kojič-Prodič, Spek & Duisenberg, 1986; van Vliet, van Koten & Buysingh, 1987; van Vliet, van Koten, de Keijser & Vrieze, 1987). In the course of our investigations with the *R*-DAB molecule as a bidentate ligand we decided to carry out crystal structure analyses on the two title compounds obtained from the reaction of *R*-DAB with trimethylaluminium.

Experimental. (I) A yellowish rod-shaped crystal (0.3 × 0.3 × 0.5 mm), mounted under nitrogen in a Lindemann-glass capillary, was used for data collection on an Enraf–Nonius CAD-4F diffractometer with