

haps in the manner of an infinite chain.²² The significant parameters reported were $2J = -9.6 \text{ cm}^{-1}$ and $g = 2.22$.

Thus, although the magnitude of the interaction in Cu_2LCl_3 could only be of the order of two wave numbers, it appears that there are two possible and reasonable bridging routes over which such a coupling could occur. Unhappily, it appears impossible in this case to distinguish which or possibly if both are operable. Studies on similar complexes are continuing in an effort to resolve this difficulty.²³

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Registry No. Cu_2LCl_3 , 50859-34-2.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1042.

(23) This work was supported by a Grant from the NSF.

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Structure of a Stable π -Arene-Chromium Dicarboxyl Complex with Bis(diphenylarsino)methane

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Received August 24, 1973

AIC30629*

The crystal and molecular structure of a stable π -arene-chromium dicarbonyl complex of bis(diphenylarsino)methane (DAM) $\{[(\pi\text{-C}_6\text{H}_5)_2(\text{C}_6\text{H}_5)_2\text{AsCH}_2\text{As}(\text{C}_6\text{H}_5)_2]\text{Cr}(\text{CO})_2\}$ has been determined by three-dimensional X-ray structural analysis, using data collected by counter methods. The complex crystallizes in the space group $P\bar{1}$ (C_i^1 , No. 2), $a = 7.609$ (3), $b = 8.563$ (3), $c = 18.677$ (5) Å, $\alpha = 83.16$ (2), $\beta = 82.52$ (2), $\gamma = 81.66$ (2)°, $Z = 2$. The measured and calculated densities of 1.62 (1) and 1.622 g cm^{-3} , respectively, are in excellent agreement. The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares methods to final weighted and unweighted reliability indices of 0.042 and 0.032, respectively, for the 3208 independent reflections for which $I/\sigma(I) \geq 3.0$. One As atom is disordered, and the populations of the two possible positions have been successfully refined to 0.9510 (9) and 0.0582 (9). The coordination at the central chromium atom is essentially octahedral, with the two carbonyl groups and one σ -bonded As atom of the DAM ligand occupying three mutually cis coordination sites. The remaining sites at the chromium atom are occupied by a delocalized π -arene ring which is also bonded to the second As atom of the DAM ligand. Although the Cr-C(arene) distances vary from 2.165 (4) to 2.194 (4) Å, the Cr- π -arene bonding appears to be essentially symmetric. The shortest distances are approximately trans to the σ -bonded arsenic atom. The π -arene ring is planar within experimental error, and there is no systematic alternation of C-C bond distances within this ring.

Introduction

π -Arene-chromium tricarbonyl complexes of the form $[(\pi\text{-arene})\text{Cr}(\text{CO})_3]$ are readily formed by the reaction of $\text{Cr}(\text{CO})_6$ with benzenoid compounds. The preparative and structural aspects of much of this chemistry have been reviewed in recent years.¹⁻³ Without doubt, the best known and most widely studied of the π -arene-chromium complexes is dibenzenechromium. Early structural data for this molecule⁴ suggested a marked threefold distortion of the arene groups, with alternating carbon-carbon distances of 1.353 and 1.439 Å. However, later work cast some doubt on this result⁵⁻⁷ with, in particular, gas-phase electron diffraction studies indicating that the carbon-carbon bond length differences could not exceed 0.02 Å.⁷ The situation regarding the solid state was resolved only by a careful reinvestigation of the structure at low temperature (100°K) which indicated that the carbon-carbon distances are, in fact, all equal to within

0.001 Å.⁸ A systematic investigation of the supposed threefold distortion was also carried out by Dahl and Bailey who determined the structure of (π -hexamethylbenzene)chromium tricarbonyl⁹ and reinvestigated the structure of (π -benzene)chromium tricarbonyl.¹⁰⁻¹³ No systematic distortion was observed. However, a recent and very precise investigation of the structure of (π - C_6H_6) $\text{Cr}(\text{CO})_3$ at 78°K,¹⁴ using both X-ray and neutron diffraction methods, has unequivocally established the presence of the expected threefold distortion. The bond length alternation is small ($\Delta_{\text{av}} = 0.018$ (2) Å) but is statistically highly significant ($\Delta/\sigma \approx 9$). In each of these derivatives, the Cr-CO bonds are directed toward the mid-points of the C-C bonds of the π -arene ring, giving the staggered configuration I.

A series of related structures, with mono- and disubstituted benzenoids, has been reported by Sim, *et al.*,¹⁵⁻¹⁸ who found

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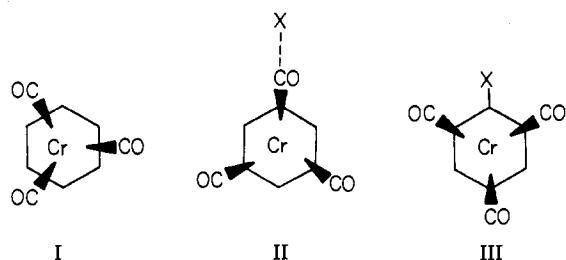
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that those derivatives containing an electron-releasing group, e.g., $-\text{OCH}_3$ or $-\text{NH}_2$,^{15,16} adopt an eclipsed configuration II, while those containing electron-withdrawing groups, such as $-\text{CO}_2\text{CH}_3$,¹⁷ adopt the alternative eclipsed configuration III. No evidence for bond length alternation was observed.



The reaction of bis(diphenylarsino)methane, $(\text{C}_6\text{H}_5)_2\text{AsCH}_2\text{As}(\text{C}_6\text{H}_5)_2$ (DAM), with $\text{Cr}(\text{CO})_6$, at elevated temperatures,¹⁹ gives a novel complex $\{[(\pi\text{-C}_6\text{H}_5)(\text{C}_6\text{H}_5)\text{AsCH}_2\text{As}(\text{C}_6\text{H}_5)_2]\text{Cr}(\text{CO})_2\}$ in which the chelated DAM ligand is bonded to the chromium atom *via* a σ bond from one As atom and *via* a delocalized π -arene ring attached to the second As atom. We now present a detailed account of the crystal and molecular structure of this unusual π -arene complex. A preliminary account of this work has been published elsewhere.²⁰

Experimental Section

Crystal Data. Orange crystals of bis(diphenylarsino)methane-chromium dicarbonyl, of suitable size and quality for X-ray structural analysis, were kindly supplied by Drs. R. Colton and C. J. Rix (University of Melbourne). *Anal.* Calcd for $\text{C}_{22}\text{H}_{22}\text{As}_2\text{CrO}_2$: C, 55.9; H, 3.8; CO, 9.7. Found: C, 55.8; H, 3.9; CO, 10.3.¹⁹

Crystals were mounted on quartz fibers, and preliminary Weissenberg ($0kl$, $1kl$) data and precession ($h0l$, $h1l$, $hk0$, hkl) data photographs showed no evidence of diffraction symmetry higher than $C_i(1)$, implying a triclinic space group (either $P1$ or $P\bar{1}$). The choice of the centrosymmetric space group $P\bar{1}$ (C_i^1 , No. 2) has been confirmed by the successful solution and refinement of the structure.

The crystal chosen for data collection, of dimension $0.025 \times 0.019 \times 0.015$ cm (elongated along the arbitrarily assigned a axis), was transferred to a computer-controlled Picker FACS-I fully automatic four-circle diffractometer and aligned with the crystal a axis and the instrumental ϕ axis approximately coincidental. The unit cell dimensions and crystal orientation matrix were obtained from least-squares refinement²¹ of the instrumental 2θ , ω , χ , and ϕ values found for 12 carefully centered high angle reflections using crystal monochromated $\text{Cu K}\alpha_1$ radiation (graphite crystal monochromator; λ 1.5405 Å; take-off angle = 3.0° ; temperature = $20 \pm 1^\circ$). The unit cell parameters are $a = 7.609$ (3), $b = 8.563$ (3), $c = 18.677$ (5) Å, $\alpha = 83.16$ (2), $\beta = 82.52$ (2), $\gamma = 81.66$ (2) $^\circ$. The estimated standard errors, given in parentheses, derive from the least-squares procedure discussed above. The reduced cell, obtained from a Delaunay reduction,²² is $a' = 8.563$, $b' = 7.609$, $c' = 19.588$ Å, $\alpha' = 93.48$, $\beta' = 108.88$, $\gamma' = 98.34^\circ$, volume of reduced cell = 1186.9 Å³. The observed density ($\rho_{\text{obsd}} = 1.62 \pm 0.01$ g cm⁻³, by flotation) is in excellent agreement with the value calculated for a formula weight of 580.31, a unit cell volume of 1187.5 Å³, and $Z = 2$ ($\rho_{\text{calcd}} = 1.622$ g cm⁻³). With $Z = 2$, no crystallographic symmetry constraints are placed upon the molecule.

Data Collection. Graphite crystal monochromated $\text{Cu K}\alpha$ radiation was used to collect 4342 reflections (including "standards," *vide*

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infra) of the types $+h\neq k\neq l$ within the range $3^\circ < 2\theta \leq 125^\circ$, using the θ - 2θ scan technique (takeoff angle, 3.0° ; crystal-counter distance, 28.5 cm; 2θ velocity, $2^\circ/\text{min}$). Peaks were scanned in 2θ from 1.2° below the $\text{Cu K}\alpha_1$ peak to 1.2° above the $\text{Cu K}\alpha_2$ peak. The pulse-height analyzer was set to admit 95% of the $\text{Cu K}\alpha$ peak. Back-grounds, which were assumed to be linear, were measured for 20 sec on either side of each reflection at the scan range limits. The intensities of three reflections, widely separated in reciprocal space, were monitored after each 40 measurements and none showed any significant variation during data collection. Intensity data were reduced to values of $|F_o|$,²³ and were assigned individual estimated standard deviations

$$\sigma(F_o) = \{[\sigma(I)/LP]^2 + (\rho|F_o|^2)^2\}^{1/2}/|F_o|$$

where $\sigma(I) = [CT + (t_p/t_b)^2(B_1 + B_2)]^{1/2}$; LP is the Lorentz polarization factor; CT is the integrated peak intensity counted for t_p sec; B_1 and B_2 are the individual background counts, counted for $t_b/2$ sec each; ρ $[(0.001)^{1/2}]$ is the instrumental "uncertainty factor."^{24,25} Reflections for which the individual background measurements differed significantly (*i.e.*, if $(|B_1 - B_2|)/(B_1 + B_2)^{1/2} \geq 4.0$) were discarded as were those for which $I/\sigma(I) < 3.0$ (where $I = [CT - (t_p/t_b)(B_1 + B_2)]$). The data were sorted, and equivalent zero-level data (*i.e.*, $0kl$, $0k\bar{l}$, $0\bar{k}l$, $0\bar{k}\bar{l}$ data) were averaged. The statistical R factor, R_s , for the 3208 reflections comprising the terminal data set is 0.014. ($R_s = \Sigma\sigma_s(F_o)/\Sigma|F_o|$, where $\sigma_s(F_o) = \sigma(I)/(2LP)(|F_o|)$.)

Solution and Refinement of the Structure. The positions of the two As atoms and the Cr atom were readily obtained from a three-dimensional Patterson map; the remaining nonhydrogen atoms were obtained from successive difference Fourier syntheses. Four cycles of full-matrix least-squares refinement, varying the overall scale factor, individual isotropic temperature factors for all atoms, rigid body positional parameters for the three "free" phenyl rings, and individual positional parameters for the remaining atoms, converged with $R = 0.091$ and R_w (unit weights) = 0.095.²⁶ Atomic scattering factors were taken from ref 27, with those for As and Cr being corrected for the real and imaginary parts of anomalous scattering.^{28,29}

The intensity data were corrected for absorption effects ($\mu = 77.85$ cm⁻¹), using a grid of $8 \times 6 \times 4$ points parallel to a , b^* , and c^* , respectively. Refinement was continued using block-diagonal least-squares methods. Three cycles of refinement, varying the scale factor and individual positional and isotropic thermal parameters for all nonhydrogen atoms, converged with $R = 0.082$ and $R_w = 0.110$ (individual weights ($w = 1/\sigma^2(F_o)$) were used in these and all subsequent refinement cycles). Anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were introduced for all nonhydrogen atoms, and refinement converged after five further cycles with $R = 0.051$ and $R_w = 0.073$.

At this point, a difference Fourier synthesis showed not only the phenyl and methylene hydrogen atoms in stereochemically reasonable positions but also one peak of density *ca.* 4.5 e/Å³. As accurate map coordinates could not be obtained, calculated phenyl and methylene hydrogen atom coordinates were included, as fixed contributions to F_o , in all subsequent cycles of least-squares refinement (phenyl C-H = 1.087 Å; methylene C-H = 1.09 Å). The hydrogen atom positional parameters and fixed isotropic temperature factors (assuming $B_H = B_C + 1.0$ Å²) were recalculated prior to each subsequent refinement cycle. Hydrogen atom scattering factors were taken from the compilation of Stewart, *et al.*³⁰

The spurious peak (of density 4.5 e/Å³) was found to be within bonding distance of the methylene carbon atom C(12) and the phenyl carbon atoms C(212) and C(221). This peak was assigned as As(2),

(23) The Lorentz polarization factor takes the form $LP = (\cos^2 2\theta + \cos^2 2\theta_m)/[\sin 2\theta(1 + \cos^2 2\theta_m)]$. θ and θ_m (13.25°) are the reflection and monochromator Bragg angles, respectively.

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(26) Throughout the refinement, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is the weight. The agreement indices R and R_w are defined as $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$.

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Table I. Fractional Atomic Positional and Thermal Parameters for $[(\eta^6\text{-C}_6\text{H}_5)_2(\text{C}_6\text{H}_5)_2\text{AsCH}_2\text{As}(\text{C}_6\text{H}_5)_2]\text{Cr}(\text{CO})_2$ ^a

(a) Refined Positional and Anisotropic Thermal Parameters												
Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}			
As(1)	0.02706 (5)	0.17616 (4)	0.19616 (2)	0.01308 (7)	0.01071 (5)	0.00205 (1)	-0.00151 (5)	0.00013 (2)	-0.00040 (2)			
As(2)	-0.07321 (5)	-0.07890 (5)	0.32428 (2)	0.01635 (8)	0.01147 (6)	0.00252 (1)	-0.00082 (6)	-0.00050 (3)	0.00041 (2)			
As(2)	-0.32253 (92)	0.11046 (89)	0.29662 (42)	0.01331 (132)	0.01484 (118)	0.00352 (26)	-0.00251 (99)	0.00181 (46)	0.00112 (45)			
Cr	0.02963 (9)	0.33118 (7)	0.29525 (3)	0.02061 (13)	0.01255 (9)	0.00245 (2)	-0.00128 (9)	-0.00082 (4)	-0.00092 (3)			
C(1)	0.2654 (6)	0.3517 (7)	0.2692 (3)	0.0215 (10)	0.0353 (13)	0.0054 (2)	-0.0045 (9)	-0.0019 (4)	-0.00067 (4)			
O(1)	0.4126 (5)	0.3742 (7)	0.2525 (3)	0.0224 (9)	0.0673 (16)	0.0107 (3)	-0.0142 (10)	-0.0013 (4)	-0.0128 (5)			
C(2)	-0.0179 (6)	0.5180 (5)	0.2384 (2)	0.0293 (10)	0.0238 (1)	0.0026 (1)	-0.0065 (6)	0.0003 (3)	-0.0014 (2)			
O(2)	-0.1279 (4)	0.6372 (3)	0.2039 (2)	0.0566 (12)	0.0127 (5)	0.0035 (1)	-0.0081 (6)	-0.0021 (3)	0.0008 (2)			
C(11)	-0.0666 (4)	0.0119 (4)	0.2270 (2)	0.0138 (7)	0.0137 (6)	0.0022 (1)	-0.0026 (5)	0.0004 (2)	-0.0002 (2)			
C(12)	-0.0033 (5)	0.2652 (4)	0.1055 (2)	0.0130 (6)	0.0114 (5)	0.0023 (1)	-0.0035 (4)	0.0002 (2)	0.0001 (2)			
C(13)	-0.0743 (5)	0.2027 (5)	0.0401 (2)	0.0159 (7)	0.0171 (7)	0.0024 (1)	-0.0012 (5)	0.0005 (2)	-0.0006 (2)			
C(14)	-0.2081 (5)	0.2680 (5)	-0.0229 (2)	0.0183 (8)	0.0221 (8)	0.0026 (1)	-0.0032 (6)	-0.0007 (2)	0.0000 (2)			
C(15)	-0.2725 (6)	0.3935 (5)	-0.0212 (2)	0.0216 (9)	0.0179 (7)	0.0033 (1)	-0.0043 (6)	-0.0027 (3)	0.0013 (3)			
C(16)	-0.2039 (5)	0.4535 (5)	0.0428 (2)	0.0219 (9)	0.0141 (6)	0.0047 (2)	0.0017 (6)	-0.0038 (3)	0.0006 (3)			
C(17)	0.2484 (4)	0.3906 (4)	0.1068 (2)	0.0175 (8)	0.0130 (6)	0.0035 (1)	-0.0003 (5)	-0.0011 (3)	-0.0007 (2)			
C(18)	0.3825 (5)	0.0542 (4)	0.1588 (2)	0.0128 (6)	0.0126 (5)	0.0022 (1)	-0.0020 (5)	0.0000 (2)	-0.0003 (2)			
C(19)	0.5433 (5)	0.1353 (5)	0.1191 (2)	0.0154 (7)	0.0161 (7)	0.0038 (1)	-0.0049 (6)	0.0004 (3)	-0.0007 (2)			
C(20)	0.5724 (5)	0.0516 (5)	0.0918 (2)	0.0125 (7)	0.0229 (8)	0.0042 (2)	-0.0056 (6)	0.0008 (3)	-0.0018 (3)			
C(21)	0.4423 (5)	-0.1102 (5)	0.1042 (2)	0.0139 (7)	0.0222 (8)	0.0040 (2)	-0.0009 (6)	0.0001 (3)	-0.0033 (3)			
C(22)	0.2809 (5)	-0.1927 (5)	0.1443 (2)	0.0187 (8)	0.0152 (7)	0.0041 (2)	0.0021 (6)	-0.0004 (3)	-0.0022 (3)			
C(23)	-0.0780 (6)	0.1302 (4)	0.1710 (2)	0.0154 (7)	0.0143 (6)	0.0030 (1)	-0.0017 (5)	0.0007 (2)	-0.0009 (2)			
C(24)	-0.2209 (6)	0.2522 (5)	0.3600 (2)	0.0299 (10)	0.0133 (6)	0.0020 (1)	-0.0024 (6)	0.0004 (3)	0.0002 (2)			
C(25)	0.2107 (7)	0.4049 (5)	0.3485 (2)	0.0255 (10)	0.0162 (7)	0.0029 (1)	-0.0018 (6)	0.0031 (3)	0.0002 (2)			
C(26)	-0.0596 (8)	0.4355 (5)	0.3961 (2)	0.0387 (14)	0.0159 (7)	0.0034 (2)	0.0015 (8)	0.0051 (4)	0.0002 (3)			
C(27)	0.0779 (8)	0.3190 (6)	0.4076 (2)	0.0594 (19)	0.0152 (7)	0.0024 (1)	-0.0054 (9)	0.0013 (4)	-0.0016 (3)			
C(28)	0.0694 (7)	0.1601 (5)	0.3909 (2)	0.0580 (19)	0.0178 (8)	0.0031 (2)	-0.0067 (10)	-0.0055 (4)	-0.0007 (3)			
C(29)	-0.3088 (5)	-0.1319 (4)	0.3673 (2)	0.0426 (15)	0.0161 (7)	0.0032 (1)	-0.0002 (8)	-0.0054 (4)	0.0006 (3)			
C(30)	-0.4304 (6)	-0.1731 (6)	0.3265 (2)	0.0204 (9)	0.0141 (6)	0.0027 (1)	-0.0016 (6)	0.0007 (3)	0.0012 (2)			
C(31)	-0.5823 (6)	-0.2351 (6)	0.3597 (3)	0.0163 (9)	0.0239 (9)	0.0036 (2)	-0.0036 (7)	-0.0003 (3)	0.0020 (3)			
C(32)	-0.6142 (7)	-0.2536 (7)	0.4341 (3)	0.0250 (12)	0.0299 (11)	0.0057 (2)	-0.0029 (8)	-0.0006 (4)	0.0008 (4)			
C(33)	-0.4953 (8)	-0.2121 (8)	0.4742 (3)	0.0401 (16)	0.0306 (12)	0.0053 (2)	-0.0052 (9)	0.0038 (4)	0.0026 (4)			
C(34)	-0.3450 (7)	-0.1487 (7)	0.4411 (2)	0.0305 (12)	0.0394 (15)	0.0033 (2)	-0.0086 (12)	0.0032 (4)	0.0021 (4)			
C(35)					0.0310 (11)	0.0031 (2)	-0.0094 (9)	0.0012 (3)	0.0008 (3)			

(b) Calculated Hydrogen Atom Coordinates and Isotropic Thermal Parameters ^b												
Atom	x	y	z	B_x , Å ²	Atom	x	y	z	B_x , Å ²			
H(12A)	-0.268	0.063	0.229	4.37	H(126)	0.178	-0.173	0.202	4.93			
H(12B)	-0.101	-0.079	0.190	4.37	H(212)	-0.337	0.226	0.326	6.02			
H(112)	0.103	0.103	0.039	4.98	H(213)	-0.319	0.500	0.358	7.41			
H(113)	-0.023	0.220	-0.074	5.67	H(214)	-0.053	0.554	0.410	8.03			
H(114)	-0.264	0.444	-0.071	5.78	H(215)	0.194	0.345	0.431	8.18			
H(115)	-0.379	0.553	0.044	6.07	H(216)	0.178	0.065	0.400	7.10			
H(116)	-0.255	0.439	0.158	5.10	H(222)	-0.404	-0.158	0.268	6.58			
H(122)	0.359	0.264	0.109	5.39	H(223)	-0.677	-0.269	0.327	7.78			
H(123)	0.646	0.115	0.061	5.96	H(224)	-0.734	-0.302	0.460	8.56			
H(124)	0.699	-0.174	0.083	5.96	H(225)	-0.521	-0.228	0.533	9.52			
H(125)	0.466	-0.321	0.154	5.76	H(226)	-0.251	-0.114	0.473	7.68			

^a Estimated standard deviations (in parentheses) in this and the following tables, and also in the text, refer to the last significant digit(s) in each case. ^b The hydrogen atoms are numbered according to the carbon atoms to which they are bonded.

Table II. Principal Bond Distances and Interbond Angles

(a) Bond Distances, Å			
Atoms	Distance	Atoms	Distance
Cr-C(1)	1.825 (5)	Cr-C(2)	1.829 (4)
Cr-As(1)	2.406 (1)	Cr-C(211)	2.180 (4)
Cr-C(212)	2.192 (4)	Cr-C(213)	2.187 (5)
Cr-C(214)	2.168 (4)	Cr-C(215)	2.165 (5)
Cr-C(216)	2.194 (4)	Cr-CofG ^a	1.670
As(1)-C(12)	1.953 (3)	As(1)-C(111)	1.950 (3)
As(1)-C(121)	1.941 (3)	As(2)-C(12)	1.960 (3)
As(2)-C(211)	1.978 (4)	As(2)-C(221)	1.959 (4)
As(2)-C(12)	1.998 (8)	As(2)-C(211)	2.368 (8)
As(2)-C(212)	1.939 (8)	As(2)-C(221)	2.320 (8)
C(1)-O(1)	1.160 (6)	C(2)-O(2)	1.152 (5)
C(211)-C(212)	1.413 (6)	C(212)-C(213)	1.409 (6)
C(213)-C(214)	1.401 (8)	C(214)-C(215)	1.357 (8)
C(215)-C(216)	1.443 (6)	C(211)-C(216)	1.394 (6)

(b) Interbond Angles, Deg			
Atoms	Angle	Atoms	Angle
As(1)-Cr-C(1)	91.4 (2)	As(1)-Cr-C(2)	92.3 (2)
C(1)-Cr-C(2)	86.3 (2)	Cr-C(1)-O(1)	176.1 (5)
Cr-C(2)-O(2)	178.6 (3)	Cr-As(1)-C(12)	109.3 (1)
Cr-As(1)-C(111)	122.9 (1)	Cr-As(1)-C(121)	118.9 (1)
C(12)-As(1)-C(111)	99.8 (1)	C(12)-As(1)-C(121)	102.3 (1)
C(111)-As(1)-C(121)	100.4 (1)	As(1)-C(12)-As(2)	106.6 (2)
As(1)-C(12)-As(2)	104.8 (3)	C(12)-As(2)-C(211)	94.0 (1)
C(12)-As(2)-C(221)	100.3 (2)	C(211)-As(2)-C(221)	100.4 (2)
As(2)-C(211)-C(212)	120.6 (3)	As(2)-C(211)-C(216)	118.9 (3)
C(212)-C(211)-C(216)	120.3 (3)	C(211)-C(212)-C(213)	119.1 (4)
C(212)-C(213)-C(214)	120.3 (5)	C(213)-C(214)-C(215)	121.0 (5)
C(214)-C(215)-C(216)	120.1 (4)	C(211)-C(216)-C(215)	119.1 (5)

^a CofG is the center of gravity of the π -arene ring C(211)-C(216).

associated with a small percentage of a second isomer resulting from rotation about the As(1)-C(12) bond. Refinement of the (now) disordered model was continued. After six further cycles, in which the scale factor, individual nonhydrogen atom positional and anisotropic thermal parameters, and the population densities of As(2) and As(2)' were varied, refinement converged with $R = 0.032$ and $R_w = 0.042$. The population densities were 0.9510 (9) and 0.0582 (9) for As(2) and As(2)', respectively. For the fully ordered model, the terminal R factors were $R = 0.046$ and $R_w = 0.064$. The disordered model was, therefore, assumed to be correct. No attempt was made to account for any disorder in the phenyl rings C(211)-C(216) and C(221)-C(226).

On the final refinement cycle, no parameter shift was greater than 0.1 esd (estimated standard deviations were obtained from inversion of the block-diagonal matrices), and a final electron density difference map showed no positive maxima greater than 0.3 e/Å³. The standard deviation of an observation of unit weight, defined as $[\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2}$, where m is the number of observations and n (300) is the number of parameters varied, is 1.90 *cf.* an expected value of 1.0 for ideal weighting. Part of this discrepancy results from the incomplete nature of the scattering model which, together with residual systematic errors in the data set, cannot be adequately represented by the weighting scheme employed. There is no evidence of serious extinction effects, and no serious dependence of $w(|F_o| - |F_c|)^2$ on either $|F_o|$ or $\lambda^{-1} \sin \theta$ is apparent. Final atom coordinates and thermal parameters, together with their estimated standard deviations (where appropriate), are listed in Table I.

Computer Programs. The data reduction and sorting programs SETUP and SORTIE were written by Dr. B. M. Foxman. The Fourier program MUF3 was originally written by Dr. J. D. White (University of Melbourne) and was modified by Foxman. A second Fourier program ANUFOR, adapted from Zalkin's FORDAP by R. Dellaca (University of Canterbury, New Zealand), was substantially modified (Whimp) for local operation. The least-squares refinement program, BLKLSQ, was adapted from Prewitt's SFLS-5.²⁶ The full-matrix rigid-body modification was by Bennett and Foxman,³¹ while the block-diagonal approximation, using either 4 × 4 or 3 × 3 and 6 × 6 matrices, was by Foxman, who also adapted the absorption correction program ACACA³² to the geometry of the Picker four-circle

diffractometer. Figures were produced with ORTEP.³³ Calculations were carried out on the CDC3600 computer of the CSIRO Division of Computing Research, Canberra, and the IBM360/50 and Univac-1108 computers of The Australian National University Computer Centre.

Results

Description of the Structure. The crystal structure, as defined by the unit cell parameters, symmetry operations, and atom coordinates of Table I, consists of discrete monomeric molecular units having neither crystallographic nor virtual symmetry higher than C_1 . The coordination at the central chromium atom is essentially octahedral, with two carbonyl groups and a σ -bonded As atom of the DAM ligand occupying mutually cis coordination sites. A π -bonded phenyl ring (which is also σ bonded to the second As atom) occupies the three remaining sites at the chromium atom.

Important intramolecular distances and interbond angles, together with their estimated standard deviations, as derived from the coordinates of Table I, are listed in Table II, while bond lengths and interbond angles in the three "free" phenyl rings are shown in Table III. It should be noted, at this stage, that the positional and thermal parameter estimated standard deviations derive from inversion of the block-diagonal matrices and that correlation coefficients are not available. Consequently, atom-atom correlation effects have not been considered in the calculation of bond distance and interbond angle estimated standard deviations, with the result that the quoted values in Tables II and III are most probably underestimated. The results of weighted least-squares plane calculations are collected in Table IV.³⁴ Important torsion angles are listed in Table V.

The atom numbering scheme is shown in Figure 1, while a perspective view of the molecule is shown by the stereopairs

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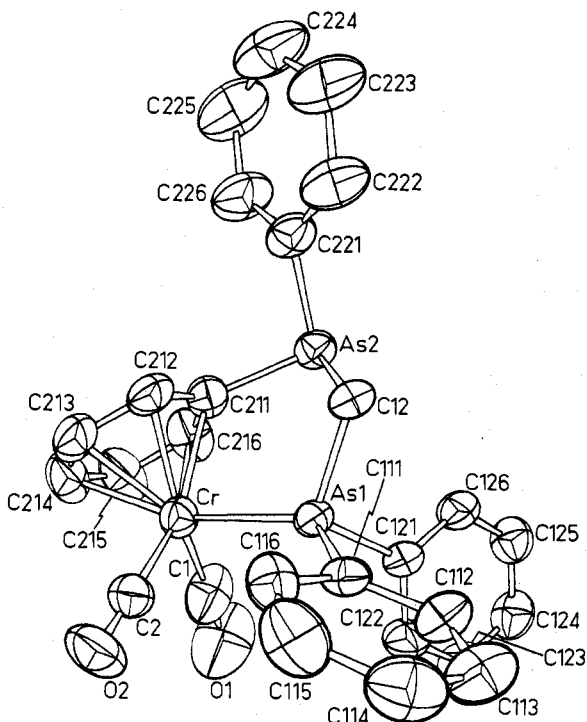
(32) B. J. Wuensch and C. T. Prewitt, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **122**, 24 (1965).

(33) C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(34) The weighting method is described in ref 27, Vol. II, p 93.

Table III. Bond Distances and Interbond Angles within the Three "Free" Phenyl Rings

(a) Bond Distances, Å			
Atoms	$m = 1, n = 1$	$m = 1, n = 2$	$m = 2, n = 2$
As(<i>m</i>)-C(<i>mn</i> 1)	1.950 (3)	1.941 (3)	1.959 (4)
C(<i>mn</i> 1)-C(<i>mn</i> 2)	1.392 (5)	1.400 (5)	1.380 (6)
C(<i>mn</i> 2)-C(<i>mn</i> 3)	1.383 (5)	1.393 (5)	1.384 (6)
C(<i>mn</i> 3)-C(<i>mn</i> 4)	1.369 (6)	1.368 (6)	1.373 (8)
C(<i>mn</i> 4)-C(<i>mn</i> 5)	1.361 (6)	1.386 (6)	1.357 (8)
C(<i>mn</i> 5)-C(<i>mn</i> 6)	1.386 (6)	1.390 (5)	1.378 (8)
C(<i>mn</i> 6)-C(<i>mn</i> 1)	1.385 (5)	1.388 (5)	1.366 (6)
(b) Interbond Angles, Deg			
Atoms	$m = 1, n = 1$	$m = 1, n = 2$	$m = 2, n = 2$
As(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 2)	121.8 (2)	118.7 (3)	122.4 (3)
As(<i>m</i>)-C(<i>mn</i> 1)-C(<i>mn</i> 6)	119.0 (3)	122.8 (3)	118.6 (3)
C(<i>mn</i> 2)-C(<i>mn</i> 1)-C(<i>mn</i> 6)	119.2 (3)	118.5 (3)	118.4 (4)
C(<i>mn</i> 1)-C(<i>mn</i> 2)-C(<i>mn</i> 3)	120.1 (3)	120.2 (4)	120.7 (4)
C(<i>mn</i> 2)-C(<i>mn</i> 3)-C(<i>mn</i> 4)	120.2 (4)	120.4 (4)	119.8 (4)
C(<i>mn</i> 3)-C(<i>mn</i> 4)-C(<i>mn</i> 5)	120.0 (4)	120.3 (4)	119.5 (5)
C(<i>mn</i> 4)-C(<i>mn</i> 5)-C(<i>mn</i> 6)	121.1 (4)	119.5 (4)	120.7 (5)
C(<i>mn</i> 5)-C(<i>mn</i> 6)-C(<i>mn</i> 1)	119.4 (3)	121.1 (4)	120.8 (5)

**Figure 1.** One molecule of $[(\pi\text{-C}_6\text{H}_5)(\text{C}_6\text{H}_5)\text{AsCH}_2\text{As}(\text{C}_6\text{H}_5)_2]\text{Cr}(\text{CO})_2$ showing the overall stereochemistry and the atom numbering scheme.

of Figure 2. For clarity, the hydrogen atoms and As(2)' have been omitted from both figures, and the thermal ellipsoids have been drawn to include 50% of the probability distribution. Figures 3a and 3b show the principal features of the molecule as viewed perpendicular to the plane of C(211)-C(216). Figure 3b shows the most probable orientation of the disordered π -arene ring C(211)'-C(216)'. Three-dimensional coordinates have not been calculated for the atoms C(211)'-C(216)', and the π -arene ring shown in Figure 3b has been obtained by a rotation of *ca.* 18° about the Cr-CofG axis in the plane of C(211)-C(216).

Discussion

The molecule bis(diphenylarsino)methanechromium dicarbonyl is disordered, and the diffraction data require the free arsenic atom to be distributed between two sites (As(2) and As(2)' in the ratio *ca.* 16:1), giving two distinct conforma-

tional isomers which result from rotation of the ligand about the As(1)-C(12) bond. Atoms of the associated phenyl groups (C(211)-C(216) and C(221)-C(226)) must also be distributed between the two sites. In both isomers, the conformation about the As(1)-C(12) axis is staggered, but the configuration of the π -arene ring with respect to the chromium atom differs. In the major isomer (As(2)), the configuration is partially eclipsed (*i.e.*, midway between configurations I and II), while for the minor isomer, the inferred conformation at the chromium atom is close to being fully staggered. For convenience, the discussion has been largely restricted to the stereochemistry of the major isomer based on As(2).

In the present complex, the geometry at the chromium atom is very similar to those observed for other Cr- π -arene complexes. The bonding is essentially symmetric, and the Cr-C(arene) distances range from 2.165 (4) to 2.195 (4) Å, with the shorter distances being approximately trans to As(1). Similar distances (range 2.152 (2) to 2.224 (2) Å)³⁵ have been observed for the complex $[(\pi\text{-C}_6\text{H}_5)\text{P}(\text{C}_6\text{H}_5)_2]\text{Cr}(\text{CO})_2$,³⁶ where each triphenylphosphine group bridges two inversion symmetry related chromium atoms. In contrast, the Cr-C(arene) distances in $[(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ average some 0.05 Å longer (2.217 (2) to 2.240 (2) Å),¹⁴ while those in $[(\pi\text{-C}_6\text{H}_6)_2\text{Cr}]$ average some 0.04 Å less (2.140 (2) to 2.143 (2) Å),⁸ than the present values.

These results suggest, quite unequivocally, that the Cr- π -arene bond strength is inversely related to the π -acid strength of the ligands trans to the π -arene group. Intuitively, there is little reason to expect $d\pi\text{-}p\pi^*$ interactions to provide a major contribution to the Cr- π -arene bond strength. The π acidity of the coordinated π -arene group is certainly low, and in particular, we note the substantial contraction of the Cr-C(arene) distances in $[(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ (average 1.841 Å) compared with those found, for example, in $[(\text{C}_6\text{H}_5\text{O})_3\text{P}]\text{Cr}(\text{CO})_2$ ³⁷ (1.861 Å trans; 1.896 Å cis to phosphorus). The work of Sim, *et al.*,¹⁵⁻¹⁸ however, does suggest that there is some Cr- π -arene bond stabilization resulting from $d\pi\text{-}p\pi^*$ interactions. In particular, with net electron-withdrawing groups (*e.g.*, $-\text{CO}_2\text{CH}_3$),¹⁷ the Cr-C(arene) distances are shorter, and the bonding is stronger than with net electron-releasing groups such as $-\text{OCH}_3$.¹⁵ Although the variation in Cr-C(arene) distances is small (less than 0.03 Å) the concomitant and oppositely directed variation of the Cr-C(carbonyl) distances is more marked (*ca.* 0.07 Å).¹⁵⁻¹⁸ As the Cr-C(carbonyl) distances in the present complex (average 1.827 Å) are similar to those found for $[(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ (average 1.841 (1) Å), it is clear that the Cr-C(arene) bond length differences in $[(\text{DAM})\text{Cr}(\text{CO})_2]$ do not result from any significant variation in the extent of the Cr- π -arene $d\pi\text{-}p\pi^*$ interactions. The similarity of the π -arene carbon-carbon distances in $[(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ ¹⁴ and $[(\pi\text{-C}_6\text{H}_6)_2\text{Cr}]$ ⁸ indicates a similar conclusion. The trans ligand dependence of the Cr- π -arene distances appears, therefore, to be primarily a σ effect associated with global changes in the metal ion valence orbital radius, consequent upon small changes in the effective nuclear charge of the metal ion.

Unlike the situation in $[(\pi\text{-arene})\text{RuX}_2\text{L}]$ (X = Cl and Br; L = tertiary phosphine) where the inequivalence of the trans ligands leads to significant aplanarity of the h^6 -arene ring,³⁸

(35) G. B. Robertson and P. O. Whimp, *J. Organometal. Chem.*, **60**, C11 (1973); G. B. Robertson and P. O. Whimp, unpublished results.

(36) J. A. Bowden and R. Colton, *Aust. J. Chem.*, **26**, 43 (1973).

(37) H. J. Plastas, J. M. Stewart, and S. O. Grim, *J. Amer. Chem. Soc.*, **91**, 4326 (1969).

(38) M. A. Bennett, G. B. Robertson, and A. K. Smith, *J. Organometal. Chem.*, **43**, C41 (1972).

Table IV. Least-Squares Planes

Best Weighted Least-Squares Planes									
Plane		Defined by atoms				Equation ^a			
1		C(111)-C(116)				$-0.6628X - 0.7287Y + 0.1725Z = -1.2457$			
2		C(121)-C(126)				$0.4837X + 0.2367Y + 0.8426Z = 3.7958$			
3		C(211)-C(216)				$-0.3396X - 0.1976Y + 0.9196Z = 5.6850$			
4		C(221)-C(226)				$0.5039X - 0.8637Y + 0.0130Z = -0.1322$			

Deviations of Atoms From the Mean Plane, Å									
Atom	Plane 1	Atom	Plane 2	Atom	Plane 3	Atom	Plane 3	Atom	Plane 4
C(111)	-0.008	C(121)	-0.003	C(211)	-0.010	As(2)'	-0.298	C(221)	0.009
C(112)	0.006	C(122)	0.006	C(212)	0.000	Cr	-1.670	C(222)	-0.006
C(113)	0.001	C(123)	-0.002	C(213)	0.010	C(1)	-2.770	C(223)	0.001
C(114)	-0.007	C(124)	-0.005	C(214)	-0.007	C(2)	-2.751	C(224)	0.002
C(115)	0.002	C(125)	0.005	C(215)	-0.010	O(1)	-3.479	C(225)	0.008
C(116)	0.006	C(126)	-0.001	C(216)	0.018	O(2)	-3.411	C(226)	-0.014
As(1)	0.018	As(1)	0.017	As(2)	-0.233	CofG ^b	0.000	As(2)	0.312
								As(2)'	-1.779

^a The equations of the planes $LX + MY + NZ = D$ refer to orthogonal coordinates. The transformation matrix to convert from triclinic to orthogonal coordinates is $X = 7.5282x + 0.0y + 2.1345z$, $Y = 1.1071x + 8.5627y + 2.2244z$, $Z = 0.0x + 0.0y + 18.4209z$. ^b CofG is the center of gravity of the π -arene ring C(211)-C(216).

Table V. Torsion Angles

Axis	Plane 1 ^a	Plane 2 ^a	Torsion angle, deg
As(1)-C(12)	Cr	As(2)	43.7
As(1)-C(12)	Cr	As(2)'	33.5
Cr-CofG ^b	As(1)	C(214)	15.6
Cr-CofG ^b	C(1)	C(212)	14.9
Cr-CofG ^b	C(2)	C(216)	17.2

^a Planes 1 and 2 are three-atom planes defined by the two atoms of the axis together with the appropriate listed atom. ^b CofG is the center of gravity of the π -arene ring C(211)-C(216).

the π -arene carbon atoms of the present derivative (C(211)-C(216)) are planar within experimental error, the maximum deviation from the plane being 0.017 Å (at C(216)). The implied ring tilt is very similar to that found for $[(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ ¹⁴ where there appears to be no possibility of electronically induced asymmetry. The atoms As(2) and As(2)' are 0.233 and 0.298 Å from the π -arene plane, directed toward the chromium atom. In contrast, out-of-plane ring substituents in other Cr- π -arene complexes are directed away from the chromium atom,^{9,15-18} although in $[(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ and $[(\pi\text{-C}_6\text{H}_6)_2\text{Cr}]$ deviations of the hydrogen atoms from the π -arene plane are toward the metal atom.^{14,8} We suggest that the present result is most probably a consequence of steric strain associated with the "bite" size of the DAM ligand. The perpendicular distance from the chromium atom to the π -arene ring is 1.670 Å, *cf.* 1.607 Å for dibenzenechromium,⁴⁻⁸ 1.72 Å for $[(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$,¹³ and 1.73 Å for $[(\pi\text{-}(\text{CH}_3)_6\text{C}_6)\text{Cr}(\text{CO})_3]$.⁹ The perpendicular from the chromium atom and the π -arene ring center of gravity are coincident within experimental error, the difference being 0.012 Å. The perpendicular distance from the π -arene plane to C(1) and C(2) (2.770 and 2.751 Å, respectively) compares favorably with previous observations, *e.g.*, an average value of 2.79 Å for $[(\pi\text{-}(\text{CH}_3)_6\text{C}_6)\text{Cr}(\text{CO})_3]$.⁹

There is no evidence of systematic alternation of the carbon-carbon bond lengths in the π -arene ring. All but two of these distances are in excellent agreement, ranging from 1.394 (7) to 1.413 (6) Å ($\Delta/\sigma \doteq 2.0$). However, the distances C(214)-C(215) (1.357 (8) Å) and C(215)-C(216) (1.433 (6) Å) differ significantly from the mean value of 1.403 Å. For the (π -arene)RuX₂L complexes,³⁸ where the effects of trans ligand asymmetry result in significant ring bending, no C-C bond length variations of this magnitude are observed, and it seems unrealistic to attribute the present deviation ($\Delta =$

0.087 Å, $\Delta/\sigma \doteq 10$) to the inequivalence of the arsenic and carbonyl ligands. The final difference map showed no abnormalities in the vicinity of C(214), C(215), or C(216), and none of these atoms showed any unusual thermal motion. The displacement of C(215) from its expected position may result from the disorder in the structure and may be due to the refinement of a centroid of electron density rather than a discrete atom. The C-C-C angles in the π -arene ring average 120.0° and range from 119.1 (5) to 121.0 (5)°.

Unlike $[(\pi\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3]$ ¹⁰⁻¹⁴ which adopts configuration I, the major isomer of the present complex adopts a partially eclipsed conformation approaching configuration II. The average torsion angle about the Cr-CofG axis (CofG is the center of gravity of the π -arene ring) is 15.9°, *cf.* 30° for the fully staggered arrangement of configuration I.

The Cr-C(carbonyl) distances (average 1.827 Å) are equal within experimental error (3.0 σ) and are in good agreement with values previously found for (π -arene)Cr(CO)₃ derivatives.^{9,14} As expected, the Cr-C(carbonyl) distances in the present complex are significantly shorter than those found for $[(\text{C}_6\text{H}_5)_3\text{P}]\text{Cr}(\text{CO})_5$ ³⁷ and $[(\text{C}_6\text{H}_5\text{O})_3\text{P}]\text{Cr}(\text{CO})_5$ ³⁷ (*vide supra*). The C-O distances (average 1.156 Å) are equal within experimental error and appear normal. As expected, the Cr-C-O angles show small deviations from linearity; this effect has been attributed to π bonding rather than to crystal packing forces.³⁹

The distance Cr-As(1) (2.406 (1) Å) appears normal but is significantly shorter than the sum of the appropriate σ bond covalent radii ($r_{\text{Cr}} + r_{\text{As}} = 2.69$ Å), reflecting the π -bonding in the Cr-As bond. The As-C distances (average 1.957 Å) vary from 1.941 (3) to 1.978 (4) Å ($\Delta = 0.037$, $\Delta/\sigma \doteq 10$). A similar variation has been found for $[(\text{DAM})_2(\text{Rh}(\text{CO})\text{Cl})_2]$,⁴⁰ where the As-C distances range from 1.925 (8) to 1.981 (8) Å ($\Delta/\sigma \doteq 7$). The geometry of coordinated tertiary arsine ligands has recently been discussed by Pauling, *et al.*⁴¹ The characteristic angular distortions (*i.e.*, M-As-C, *ca.* +10°; C-As-C, *ca.* -10°) from the tetrahedral angle have been attributed to the high s character of the σ -donor orbital. The near equivalence of the distortions at As(1) (coordinated) and As(2) (uncoordinated) further supports this premise. The angles Cr-As(1)-C(12) (109.3 (1)°) and C(12)-As(2)-

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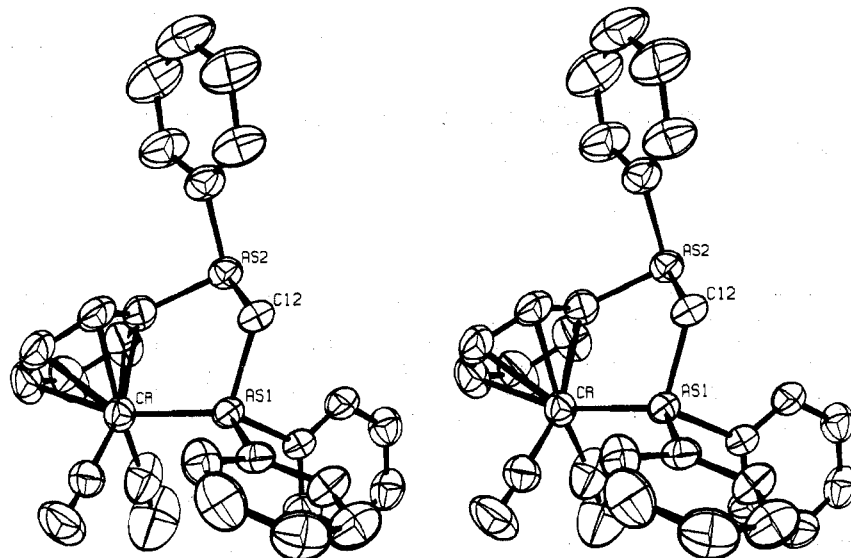


Figure 2. A stereoscopic view of the molecule.

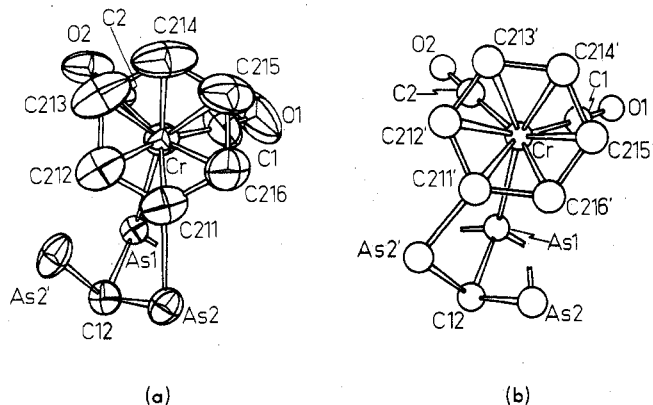


Figure 3. The principal features of the molecule as viewed perpendicular to the plane of the π -arene ring; view b shows the inferred location of the disordered π -arene ring.

C(211) ($94.0(1)^\circ$) are significantly less than their expected values (*ca.* 120 and 100° , respectively), indicating some steric strain in the chelated DAM ligand. The angle As(1)-C(12)-As(2) ($106.6(2)^\circ$) may be strain affected to a similar (energetic) degree, although previous observations have shown that this angle in the DAM ligand varies from 92^{42} to 114° ⁴⁰ in differing chelate situations. In $[\text{W}(\text{CO})_3(\text{DAM})_2\text{Br}_2]$,⁴² where the DAM ligand is monodentate, the As-C-As angle is 116.5° .

Within the three "free" phenyl rings, the C-C distances average 1.380 \AA , while the C-C-C angles average 120.0° . Bond length variation is characteristic of libration shortening, while the angular deviations at C(*mn*2)-C(*mn*1)-C(*mn*6) are indicative of joint libration effects and electronegativity differences between As- and H-bonded carbon atoms.⁴³

(42) M. G. B. Drew, A. W. Johans, A. P. Wolters, and I. B. Tomkins, *Chem. Commun.*, 819 (1971).

The minor isomer (*ca.* 5% of the sample) results from rotation about the As(1)-C(12) bond. Both isomers are staggered forms relative to the As(1)-C(12) axis, although the torsion angles about this axis (Table V) are less than the 60° normally expected for a fully staggered conformation. It was not possible to locate either the disordered π -arene ring or the "free" phenyl ring bonded to As(2)'. The distance C(12)-As(2)' ($1.998(8) \text{ \AA}$) is longer than C(12)-As(2) ($1.960(3) \text{ \AA}$), but the lack of a complete geometry for the minor isomer precludes us from commenting on this apparent anomaly. The angle As(1)-C(12)-As(2)' ($104.8(3)^\circ$) is only slightly smaller than As(1)-C(12)-As(2). The proposed π -arene ring (C(211)'-C(216)') adopts an almost fully staggered configuration relative to the chromium atom. As there are no unusual short inter- and intramolecular contacts, it appears that the fully staggered conformation is less energetically favorable than the partially eclipsed configuration adopted by the major isomer.

Acknowledgments. We thank Drs. R. Colton and C. J. Rix, University of Melbourne, for the sample of $[(\text{DAM})\text{Cr}(\text{CO})_2]$. We are grateful for generous allocations of time on the IBM 360/50 and Univac-1108 computers of The Australian National University Computer Centre.

Registry No. $\{[(\pi\text{-C}_6\text{H}_5)(\text{C}_6\text{H}_5)\text{AsCH}_2\text{As}(\text{C}_6\text{H}_5)_2]\text{Cr}(\text{CO})_2\}$, 50803-56-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche ($105 \times 148 \text{ mm}$, $24\times$ reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1047.

(43) J. M. Guss and R. Mason, *J. Chem. Soc., Dalton Trans.*, 2193 (1972).