Stereochemically Nonrigid Organometallic Molecules. XI. The Molecular Structure of (1,3,5,7-Tetramethylcyclooctatetraene)chromium Tricarbonyl[1,2]

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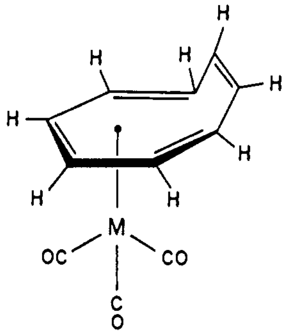
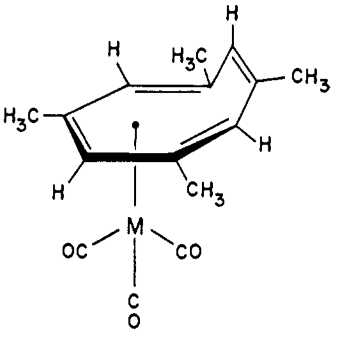
Abstract: The crystal and molecular structures of (1,3,5,7-tetramethylcyclooctatetraene)chromium tricarbonyl have been determined by single-crystal X-ray methods. The crystal data are: space group, $P2_1/c$; $a = 7.512 \pm 0.004$ Å, $b = 18.485 \pm 0.003$ Å, $c = 11.173 \pm 0.006$ Å, $\beta = 114° 5' \pm 3'$; $V = 1416$ Å^3; density measured by flotation, 1.37 ± 0.02 g cm^{-3}. Using a total of 1484 independent, nonzero reflections collected on a manually operated counter-diffractometer with Mo $K\alpha$ radiation, the structure was solved using Patterson and Fourier methods and refined by least squares to final unweighted and weighted residuals of 0.041 and 0.053, respectively. All heavy-atom (Cr, C, O) positions were refined with anisotropic temperature factors, and the positional parameters for the hydrogen atoms were also refined using isotropic temperature factors. The molecule has a structure generally similar to that of (COT)Mo(CO)$_3$, but it is less regular. From the positions of the methyl carbon atoms and ring hydrogen atoms, the type of hybridization at the ring carbon atoms may be inferred.

The fact that many π complexes formed by cyclooctatetraene with metal carbonyl moieties, that is, compounds of the general formula $C_8H_8M_x(CO)_y$, are stereochemically nonrigid, or fluctional, is now well known. Aside from the various molecules in which the metal atom(s) is iron[3-11] or ruthenium,[12] there are the interesting compounds $C_8H_8M(CO)_3$ in which M is Cr[3] or Mo,[3,13] as well as their 1,3,5,7-tetramethylcyclooctatetraene (TMCOT) analogs,[14] (TMCOT)M(CO)$_3$, in which M may be Cr,[15] Mo,[14,15] or W.[15] Both the (COT)M(CO)$_3$ and (TMCOT)M(CO)$_3$ compounds have been shown to exhibit complex, well-defined proton nmr spectra (limiting low-temperature spectra) at temperatures not too far (*ca.* −30°) below room temperature. These limiting low-temperature spectra have been interpreted in terms of the instantaneous structures shown schematically as I and II. In the case of $C_8H_8Mo(CO)_3$, an X-ray crystallographic study[16] has confirmed the essential correctness of I and provided detailed dimensions.



I



II

In view of the very complex behavior of the proton nmr spectra of the (TMCOT)M(CO)$_3$ molecules as a function of temperature,[14,15] it was considered essential to carry out an X-ray structural study of one member of the series in order to see if II is schematically correct and to obtain a more detailed picture of the geometry of the molecule in its instantaneous configuration. Such a study is reported here.

Procedure

The compound was prepared by the method described elsewhere.[15] Deep red single crystals suitable for X-ray work were obtained by slow sublimation at 40° under high vacuum. The compound is air sensitive; hence all subsequent X-ray work was performed on single crystals sealed in thin-walled Lindemann glass capillaries.

Single crystals examined by precession photography were found to be monoclinic. The systematic absences, $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, observed on the precession films of the $h0l$, $h1l$, and $hk0$ levels, uniquely identified the space group as $P2_1/c$ (No. 14). The unit cell dimensions are: $a = 7.512 \pm 0.004$ Å, $b = 18.485 \pm 0.003$ Å, $c = 11.173 \pm 0.006$ Å, and $\beta = 114° 5' \pm 3'$. The angle β was measured from the precession photographs. The quoted values for a, b, and c were derived[17] by plotting

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(2) Preceding paper in this series (part X): M. J. Bennett, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **89**, 6797 (1967).

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the magnitudes obtained for each one at 23° for various 2θ settings on a manually operated General Electric single-crystal orienter against the function $^1/_2[(\cos^2\theta)/(\sin\theta) + (\cos^2\theta)/\theta]$ and linearly extrapolating these plots to $\theta = 90.0°$. Copper radiation (λ Kα_1 1.5405 Å; λ Kα_2 1.5443 Å) was used. The uncertainty intervals quoted for a, b, and c do not represent the precision but rather are the estimated maximum errors judged by the results obtained on the same instrument employing the same procedure for several standard crystals whose unit cell dimensions are accurately known.[18] The main contribution to the uncertainty in a and c comes from the uncertainty in the value of β. This uncertainty represents the estimated precision of the measurements made on the precession films.

The density was measured by flotation in aqueous zinc chloride solution as 1.37 ± 0.02 g cm^{-3}. The density calculated from the formula weight of 296.14, the unit cell volume of 1416 Å^3, and $Z = 4$ is 1.39 g cm^{-3}. With $Z = 4$ in the space group P2$_1$/c, there are no crystallographic symmetry elements imposed on the molecule.

Intensities were collected using a crystal which was approximately a rectangular parallelepiped with dimensions of $0.30 \times 0.25 \times 0.20$ mm. The crystal was aligned with its a^* axis coincident with the ϕ axis of the goniometer. Mo Kα radiation filtered by zirconium foil was used to measure 2591 independent reflections (index sets hkl and $h\bar{k}\bar{l}$) within the sphere $\theta \leq 25°$. Intensities were measured by a scintillation counter with the pulse-height discriminator set to accept 95% of the Mo Kα peak with the window centered on the Mo Kα peak. The distances from the crystal to the source and from the crystal to the circular screening aperture (2°) were 5.73 and 7.05 in., respectively. A moving-crystal-moving-counter scan technique was employed with a scan range of 2.66° to conform with the mosiac spread of the crystal and take-off angle of 2°. The scan rate was 4°/min.

The integrated intensities (I) were obtained from the total counts (P) of a coupled 2θ-ω scan[19] from $2\theta_{\text{calcd}} - 1.33°$ to $2\theta_{\text{calcd}} + 1.33°$ and stationary background measurements (B_1, B_2) of 20-sec duration at the limits of each scan. Assuming that background varies linearly (or gives an equivalent integrated total) through the scan range, $I = P - B_1 - B_2$. A few strong reflections which exceeded the linear response range of the counter were remeasured using a lower current and were scaled in using four medium intensity reflections measured under both sets of conditions. Three reflections which were checked at frequent intervals exhibited a maximum variation of ±2%, which was random with time. Thus there was no evidence for significant crystal decomposition.

Conversion of experimental data to values of $|F_o|$ and $|F_o|^2$ (on a relative scale) was accomplished with the Fortran II program PMMO written by one of the authors (M. J. B.). As the intensities were calculated, 1103 reflections (as shown in Table I) were rejected using two criteria: (1) $I \leq 0$, (2) $I/(P + B_1 + B_2)^{1/2} < 3$. Only the remaining 1488 reflections were processed further and the corresponding $|F_o|$ and $|F_o|^2$ values used in solving and refining the structure.

Table I. Distribution of Intensities[a] as a Function of Statistical Reliability

Rejected data[b] Range	No.	Accepted data Range	No.
$I < 0$	662	$3 \leq (I/\Delta I) < 4$	129
$0 \leq I/\Delta I < 1$	41	$4 \leq (I/\Delta I) < 6$	204
$1 \leq I/\Delta I < 2$	222	$6 \leq (I/\Delta I) < 10$	208
$2 \leq I/\Delta I < 3$	178	$10 \leq (I/\Delta I) < 20$	371
Total	1103	$20 \leq (I/\Delta I) < 50$	320
		$50 \leq (I/\Delta I) < 100$	117
		$I/\Delta I \geq 100$	39
		Total	1488[c]

[a] Intensity, I, equals $P - B_1 - B_2$; $\Delta I = (P + B_1 + B_2)^{1/2}$. [b] Nearly all rejected reflections were at high angles. [c] Of these 1488 reflections, four were eventually rejected as presumably suffering seriously from extinction.

The linear absorption coefficient, μ, is 8.30 cm^{-1}; for the crystal used, absorption corrections (<4% maximum) are negligible. A check on the variation of several h00 intensities as a function of ϕ showed negligible variation (~3%).

A three-dimensional Patterson map[20] was complicated by the pseudo-special location of the chromium atom ($x \sim 0.0$, $z \sim 0.25$) which caused the Cr–Cr $2x$, $2y$, $2z$ vector to lie on the Harker line 0, v, $^1/_2$. A study of peak heights and shapes led to a tentative assignment of 0.109 for the y coordinate. This choice was substantiated by the successful refinement of the structure. A three-dimensional electron density synthesis,[20] using structure factors with phases calculated from the chromium positions only, gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.498$ (where F_o is the observed and F_c the calculated structure factor) and showed the molecule with its superimposed mirror image. All light atoms, other than hydrogen, were located although several coordinates suffered large errors due to the superposition of images. These large errors were removed by two subsequent difference Fourier maps. A structure factor calculation at this point, with phases based on 1 chromium, 15 carbon, and 3 oxygen atoms, had a discrepancy index $R_1 = 0.411$; the weighted residual, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, using equal (unit) weights for all reflections, was 0.454. The refinement was continued using standard full-matrix, least-squares techniques.[21-23] The course of the refinement is summarized in Table II. It may be noted that a difference Fourier map following the refinements (nine cycles) leading to $R_1 = 0.085$ and $R_2 = 0.109$ revealed all 16 hydrogen atoms.

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(18) "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 122.

(19) D. P. Shoemaker's "MIXG-2, M.I.T. X-ray Goniometer Package," 1962, was used to compute the $2\theta_{\text{calcd}}$ values.

(20) Computed using the program of W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two- and Three-Dimensional Fourier Program for the IBM 709/7090," ERFR-2, 1962.

(21) C. T. Prewitt, "A Full-Matrix Crystallographic Least-Squares Program for the IBM 709/7090, SFLSQ 3," 1962, "A Full-Matrix Crystallographic Least Squares Program for the IBM 360, SFLS5," 1966. In this program the function minimized is $\Sigma w(|F_o| - |F_c|)^2$.

(22) The atomic scattering factors used in the calculation for Cr, C, and O were those listed by J. A. Ibers in ref 18, p 202. The form factors used for hydrogen were those experimentally determined for H atoms in diphenyl by R. Mason and G. B. Robertson. *Cf.* the article by the authors in "Advances in Structure Research by Diffraction Methods," Vol. 2, R. Brill and R. Mason, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1966, p 57.

(23) Anomalous dispersion corrections, real ($\Delta f' = 0.3$ e) and imaginary ($\Delta f'' = 0.8$ e) parts, applied to chromium atomic scattering factors were those listed by C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 468 (1955).

Table II. Summary of the Steps in Least-Squares Refinement[a]

Parameters varied	Equal (unit) weights R_1	Equal (unit) weights R_2	Empirical weighting scheme[b] A R_1	Empirical weighting scheme[b] A R_2	Empirical weighting scheme[b] B R_1	Empirical weighting scheme[b] B R_2	Exptl weighting scheme[c] R_1	Exptl weighting scheme[c] R_2
(1) All atoms, isotropic; H atoms excluded	0.085	0.109						
(2) All atoms, anisotropic;[d] H atoms excluded	0.082	0.091	0.072	0.090				
(3) Cr, C, O anisotropic;[d,e] H's fixed at Fourier coordinates with isotropic *B*'s			0.059	0.075				
(4) Cr, C, O fixed at values obtained from (3); positional coordinates of H atoms[f] varied; isotropic *t* factors fixed			0.055	0.071	0.055	0.066	0.055	0.070
(5) Cr, C, O anisotropic; H atoms, isotropic					0.041	0.050	0.041	0.053

[a] Each set of residuals, R_1 and R_2, listed are those obtained when the indicated type of refinement was cycled to convergence (parameter changes less than esd's). [b] The empirical weighting schemes were chosen according to Cruickshank's criterion (*cf.* D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965, p 113) that $\omega\Delta^2$ should be constant. The details are as follows. Scheme A: for $|F_o| \leq 9.79$, $\omega^{-1} = (5.49 - 0.299|F_o|)$; for $9.79 < |F_o| \geq 18.88$, $\omega^{-1} = 2.53$; for $|F_o| > 18.88$ $\omega^{-1} = (0.184|F_o| - 0.868)$. Scheme B: for $|F_o| \leq 8.60$, $\omega^{-1} = (4.67 - 0.392|F_o|)$; for $8.60 < |F_o| \leq 14.56$, $\omega^{-1} = (1.53 - 0.027|F_o|)$; for $14.56 < |F_o| \leq 25.65$; $\omega^{-1} = (0.008|F_o| + 1.01)$; for $|F_o| > 25.65$, $\omega^{-1} = (0.042|F_o| + 0.259)$. [c] The experimental weighting scheme, according to R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967), was based on the standard deviation of corrected intensities: $\sigma(I) = (\Delta I^2 + pI^2)^{1/2}$ where p, the uncertainty factor, was assigned a value of 0.002. The weighting scheme used was $\sigma = \sigma(F^2)/2F_o$, where $\sigma(F^2)$ is the Lorentz and polarization corrected $\sigma(I)$. [d] A Hamilton *R* factor test (W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965)) showed that the anisotropic model and the one where hydrogen atoms were included could be accepted with a confidence of 99.5%. [e] During the refinement the hydrogen atoms were assigned isotropic temperature factors identical with those of the carbon atoms to which they were attached. [f] A difference Fourier map at this point indicated a rotational disorder of the hydrogen atoms attached to C_{13}. Hence two sets of fractionally occupied positions were assigned to the disordered atoms, as indicated below.

Atoms	*x*	*y*	*z*	Rel wt
H_{131}	0.262	0.034	0.050	0.65
H_{132}	0.128	0.101	−0.011	0.65
H_{133}	0.375	0.087	0.068	0.65
H'_{131}	0.147	0.030	0.037	0.35
H'_{132}	0.267	0.107	0.000	0.35
H'_{133}	0.367	0.033	0.067	0.35

The last cycle of refinement showed no parameter shift greater than $^1/_5$ of one esd except for the disordered hydrogen atoms. The positional and thermal parameters of these atoms were oscillating about a mean value during the last two cycles; hence this mean was assigned to be the true value for these parameters. A final difference Fourier map showed no electron density greater than 0.3 e/Å^3. Calculation of the structure factors for the rejected reflections gave no $|F_c|$ greater than twice the minimum observable. The final standard deviation of an observation of unit weight is 1.24, indicating a slight underestimation in the standard deviation of the intensity data.

Final atomic coordinates with the isotropic temperature factors are shown in Table III. Anisotropic thermal parameters are to be found in Table IV.

Results

The structure is depicted in Figures 1 and 2. These drawings also show the numbering scheme used in the various tables of molecular dimensions. Pertinent intramolecular dimensions are listed in Tables V–VIII. Table IX lists some intermolecular distances which may be of interest. Table X gives the equations for the two major planes into which the eight ring atoms fall and the distances of the atoms from these mean planes. Finally, the vibrational amplitudes, computed from the anisotropic thermal vibration tensors are given in Table XI. It may be seen that the relative magnitudes of these amplitudes are physically reasonable, thus suggesting that the thermal vibration tensors have some physical significance. For example, the oxygen atoms, have, as expected, considerably greater vibration amplitudes in two directions than do the carbon atoms to which they are bound. The methyl carbon atoms also have considerably greater thermal vibration amplitudes than do ring carbon atoms. Finally,

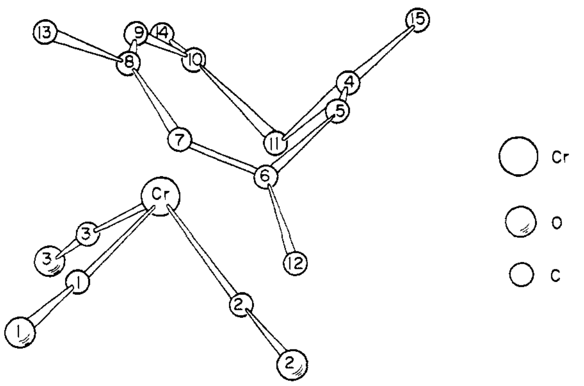

Figure 1. The molecular structure projected on the (011) plane. Hydrogen atoms are omitted for clarity.

Table III. Final Atomic Coordinates[a] for $(CH_3)_4C_8H_4Cr(CO)_3$

	x	y	z	Isotropic B[b]
Cr	−0.0139 (1)	0.1083 (0)	0.2443 (1)	
C_1	−0.1983 (7)	0.1190 (3)	0.0738 (5)	
C_2	−0.1540 (7)	0.1618 (3)	0.3170 (4)	
C_3	−0.1614 (7)	0.0275 (3)	0.2358 (4)	
C_4	0.3254 (6)	0.1736 (3)	0.4938 (4)	
C_5	0.3022 (7)	0.2239 (3)	0.4068 (5)	
C_6	0.1494 (7)	0.2230 (2)	0.2718 (5)	
C_7	0.1607 (7)	0.1791 (3)	0.1746 (5)	
C_8	0.2343 (6)	0.1069 (3)	0.1810 (4)	
C_9	0.2655 (6)	0.0534 (3)	0.2761 (4)	
C_{10}	0.2301 (6)	0.0487 (2)	0.3914 (4)	
C_{11}	0.2018 (6)	0.1079 (3)	0.4599 (4)	
C_{12}	0.0334 (10)	0.2923 (3)	0.2282 (6)	
C_{13}	0.2539 (13)	0.0821 (4)	0.0567 (7)	
C_{14}	0.2175 (8)	−0.0262 (3)	0.4393 (5)	
C_{15}	0.4779 (9)	0.1755 (4)	0.6332 (6)	
O_1	−0.3162 (6)	0.1220 (2)	−0.0332 (4)	
O_2	−0.2338 (6)	0.1956 (2)	0.3660 (4)	
O_3	−0.2661 (5)	−0.0206 (2)	0.2243 (3)	
H_5	0.372 (6)	0.265 (2)	0.424 (4)	4.1 (9)
H_7	0.090 (6)	0.195 (2)	0.078 (4)	4.2 (9)
H_9	0.294 (5)	0.016 (2)	0.253 (4)	3.0 (8)
H_{11}	0.164 (5)	0.093 (2)	0.523 (4)	3.0 (8)
H_{121}	−0.048 (8)	0.293 (3)	0.146 (6)	6.2 (1.4)
H_{122}	−0.026 (7)	0.303 (3)	0.289 (5)	6.2 (1.2)
H_{123}	0.125 (8)	0.330 (3)	0.236 (5)	7.1 (1.4)
H_{131}	0.272 (15)	0.029 (5)	0.060 (8)	4.5 (1.7)
H_{132}	0.109 (9)	0.094 (3)	−0.018 (6)	3.2 (1.2)
H_{133}	0.362 (12)	0.109 (5)	0.054 (8)	5.8 (1.8)
H'_{131}	0.172 (21)	0.035 (9)	0.025 (14)	4.3 (3.4)
H'_{132}	0.230 (23)	0.127 (8)	−0.005 (14)	7.4 (3.2)
H'_{133}	0.380 (16)	0.053 (7)	0.077 (10)	2.9 (2.0)
H_{141}	0.141 (8)	−0.028 (3)	0.494 (6)	7.6 (1.5)
H_{142}	0.159 (6)	−0.060 (2)	0.370 (4)	3.8 (0.9)
H_{143}	0.333 (7)	−0.041 (2)	0.493 (4)	4.1 (0.9)
H_{151}	0.556 (10)	0.136 (3)	0.643 (6)	8.6 (1.8)
H_{152}	0.554 (8)	0.216 (3)	0.648 (5)	6.3 (1.4)
H_{153}	0.431 (7)	0.184 (3)	0.694 (5)	5.7 (1.3)

[a] The estimated standard deviations, numbers in parentheses, occur in the last significant digit listed in each case. [b] The isotropic thermal parameters for Cr, C, and O can be found in Table IV.

Table IV. Anisotropic Temperature Factors ($\times 10^4$)[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Equivalent isotropic B
Cr	144 (2)	18	54 (1)	2 (1)	30 (1)	1	2.527
C_1	232 (13)	25 (2)	81 (5)	−14 (4)	40 (7)	−1 (3)	3.89
C_2	176 (11)	25 (2)	84 (5)	7 (4)	46 (6)	6 (2)	3.46
C_3	174 (11)	23 (2)	60 (5)	−3 (4)	28 (6)	3 (2)	3.08
C_4	144 (10)	26 (2)	76 (5)	2 (3)	38 (6)	−10 (2)	3.17
C_5	168 (11)	20 (2)	118 (6)	−14 (4)	62 (7)	−12 (3)	3.56
C_6	226 (13)	17 (2)	99 (6)	0 (3)	76 (7)	5 (2)	3.42
C_7	241 (13)	23 (2)	87 (6)	−8 (4)	89 (7)	6 (3)	3.51
C_8	209 (11)	26 (2)	85 (5)	7 (4)	83 (6)	−2 (3)	3.40
C_9	175 (11)	20 (2)	78 (5)	7 (4)	61 (6)	−7 (2)	2.98
C_{10}	123 (9)	18 (1)	66 (4)	5 (3)	23 (5)	2 (2)	2.65
C_{11}	163 (10)	23 (2)	61 (4)	−6 (4)	39 (5)	−1 (2)	2.92
C_{12}	335 (20)	24 (2)	118 (9)	9 (5)	91 (10)	6 (3)	4.74
C_{13}	420 (25)	33 (2)	131 (8)	7 (7)	166 (12)	−4 (4)	5.33
C_{14}	203 (13)	25 (2)	87 (6)	12 (4)	45 (8)	8 (3)	3.69
C_{15}	202 (14)	40 (3)	101 (7)	1 (5)	10 (8)	−26 (3)	4.95
O_1	353 (12)	53 (2)	83 (4)	−1 (4)	−22 (6)	11 (2)	6.64
O_2	345 (12)	45 (2)	132 (5)	56 (4)	128 (7)	9 (2)	5.69
O_3	266 (10)	30 (1)	110 (4)	−31 (3)	55 (5)	−3 (2)	4.70

[a] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Esd's in parentheses occur in the last digit listed in each case.

though this is surely close to the threshold of reliability of the data, the major axis of the elipsoids of (even-numbered) ring carbon atoms bearing methyl groups are consistently smaller than those of the (odd-numbered) ring carbon atoms which do not bear methyl groups. For the minor and medium axes, no consistent distinction is seen.

Discussion

The most significant features of the structure are the following:

(1) The $Cr(CO)_3$ moiety is associated with six of the eight ring carbon atoms (C_6 to C_{11}; Cr–C distances in the range 2.20–2.41 Å) closely enough to indicate Cr–C bonding in this part of the molecule. The long distances from Cr to the other two ring carbon atoms (C_4, C_5; Cr–C distances of 3.155 ± 0.004 Å) indicate that there is no Cr–C bonding.

(2) The set of six "bound" carbon atoms is very nearly coplanar, as shown in Table X. Similarly, the two unbound ring carbon atoms together with C_6 and C_{11} define a plane. The dihedral angle between the two "best" planes is 119°.

(3) At each ring carbon atom, the three C–C, or two C–C and one C–H, bonds are virtually coplanar; the only significant exceptions are at C_6 and C_{11}, which define the line of intersection of the two planes. For these, the sums of bond angles are 354 (C_6) and 350° (C_{11}), with the bonds pointing slightly back from the metal side of the ring. Thus, each ring carbon atom uses hybrid orbitals of sp^2 composition (not necessarily trigonal, however) for σ bonding, leaving a $p\pi$ orbital perpendicular to the local plane of the σ bonds. Conjugation is not perfect, in the sense that the sp^2 planes at each ring carbon atom are twisted slightly out of registration with one another, except for the C_8–C_9 pair and the C_4–C_5 pair.

(4) If it is imagined, naïvely, that there are double bonds between the pairs of carbon atoms C_6–C_7, C_8–C_9, C_{10}–C_{11}, then the centers of these bonds together with the CO groups describe a distorted octahedron around the chromium atom. However, the actual pattern of C–C bond lengths in the C_6–C_{11} chain, *viz.*, 1.39, 1.44, 1.40, 1.42, 1.40 Å, each with a

Table V. Intramolecular Distances[a,b]

Atoms	Distance, Å	Atoms	Distance, Å
Cr–C_1	1.852 (5)	C_4–C_5	1.304 (7)
Cr–C_2	1.855 (5)	C_5–C_6	1.477 (7)
Cr–C_3	1.839 (5)	C_6–C_7	1.386 (7)
C_1–O_1	1.163 (6)	C_7–C_8	1.435 (7)
C_2–O_2	1.148 (6)	C_8–C_9	1.400 (7)
C_3–O_3	1.160 (6)	C_9–C_{10}	1.420 (6)
Cr–C_4	3.150 (4)	C_{10}–C_{11}	1.401 (6)
Cr–C_5	3.159 (5)	C_{11}–C_4	1.481 (6)
Cr–C_6	2.406 (5)	C_6–C_{12}	1.513 (8)
Cr–C_7	2.207 (5)	C_8–C_{13}	1.525 (8)
Cr–C_8	2.248 (4)	C_{10}–C_{14}	1.502 (7)
Cr–C_9	2.226 (4)	C_4–C_{15}	1.511 (7)
Cr–C_{10}	2.195 (4)		
Cr–C_{11}	2.289 (4)		
C_5–H_5	0.90 (4)	C_{13}–H'_{131}	1.04 (17)
C_7–H_7	1.04 (4)	C_{13}–H'_{132}	1.05 (14)
C_9–H_9	0.80 (4)	C_{13}–H'_{133}	1.04 (12)
C_{11}–H_{11}	0.90 (4)	C_{14}–H_{141}	0.99 (6)
C_{12}–H_{121}	0.87 (6)	C_{14}–H_{142}	0.95 (4)
C_{12}–H_{122}	0.97 (5)	C_{14}–H_{143}	0.87 (4)
C_{12}–H_{123}	0.96 (6)	C_{15}–H_{151}	0.92 (6)
C_{13}–H_{131}	0.99 (9)	C_{15}–H_{152}	0.91 (6)
C_{13}–H_{132}	1.09 (6)	C_{15}–H_{153}	0.90 (5)
C_{13}–H_{133}	0.96 (9)		

[a] The hydrogen atoms on C_{13} form two sets, H_{13n} and H'_{13n} (n = 1, 2, 3) because of the rotational disorder of the C_{13} methyl group. [b] Numbers in parentheses are estimated standard deviations occurring in the last significant figure listed.

Table VI. Bond Angles[a]

Atoms	Angle, deg	Atoms	Angle, deg
CrC_1O_1	176.6 (4)	C_1CrC_2	94.3 (2)
CrC_2O_2	177.3 (4)	C_2CrC_3	91.0 (2)
CrC_3O_3	175.0 (4)	C_3CrC_1	81.4 (2)
$C_4C_5C_6$	124.5 (4)	$C_5C_6C_{12}$	115.2 (4)
$C_5C_6C_7$	122.4 (4)	$C_7C_6C_{12}$	117.1 (4)
$C_6C_7C_8$	130.7 (4)	$C_7C_8C_{13}$	114.4 (5)
$C_7C_8C_9$	129.5 (4)	$C_9C_8C_{13}$	115.5 (5)
$C_8C_8C_{10}$	134.1 (4)	$C_9C_{10}C_{14}$	116.2 (4)
$C_9C_{10}C_{11}$	125.1 (4)	$C_{11}C_{10}C_{14}$	118.7 (4)
$C_{10}C_{11}C_4$	124.2 (4)	$C_{11}C_4C_{15}$	114.5 (4)
$C_{11}C_4C_5$	121.0 (4)	$C_5C_4C_{15}$	124.5 (4)

[a] See footnote *b* in Table V.

Table VII. Intramolecular H–H Contacts[a]

H_5–H_{121}	3.45	H_5–H_{151}	3.29		
H_5–H_{122}	2.83	H_5–H_{152}	2.48		
H_5–H_{123}	2.48	H_5–H_{153}	3.22		
H_7–H_{121}	2.36	H_7–H_{131}	3.39	H_7–H'_{131}	3.13
H_7–H_{122}	3.46	H_7–H_{132}	2.17	H_7–H'_{132}	2.08
H_7–H_{123}	3.01	H_7–H_{133}	2.68	H_7–H'_{133}	3.42
H_9–H_{131}	2.11	H_9–H'_{131}	2.36	H_9–H_{141}	3.42
H_9–H_{132}	3.13	H_9–H'_{132}	3.42	H_9–H_{142}	2.40
H_9–H_{133}	3.02	H_9–H'_{133}	2.41	H_9–H_{143}	2.78
H_{11}–H_{141}	2.26	H_{11}–H_{151}	2.80		
H_{11}–H_{142}	3.30	H_{11}–H_{152}	3.51		
H_{11}–H_{143}	2.86	H_{11}–H_{153}	2.72		

[a] See footnote *a* to Table V.

Table VIII. Angles between Bonds Involving Hydrogen Atoms[a]

$C_4H_5H_5$	123 (2)	$C_8C_9H_9$	111 (3)
$C_6H_5H_5$	112 (3)	$C_{10}C_9H_9$	114 (3)
$C_6C_7H_7$	119 (2)	$C_{10}C_{11}H_{11}$	111 (2)
$C_8C_7H_7$	110 (2)	$C_4C_{11}H_{11}$	114 (3)
$C_6C_{12}H_{121}$	114 (4)	$H_{121}C_{12}H_{122}$	114 (5)
$C_6C_{12}H_{122}$	109 (3)	$H_{122}C_{12}H_{123}$	107 (5)
$C_6C_{12}H_{123}$	107 (3)	$H_{123}C_{12}H_{121}$	105 (4)
$C_8C_{13}H_{131}$	109 (6)	$H_{131}C_{13}H_{132}$	109 (6)
$C_8C_{13}H_{132}$	101 (3)	$H_{132}C_{13}H_{133}$	117 (6)
$C_8C_{13}H_{133}$	105 (5)	$H_{133}C_{13}H_{131}$	115 (7)
$C_8C_{13}H'_{131}$	107 (8)	$H'_{131}C_{13}H'_{132}$	122 (12)
$C_8C_{13}H'_{132}$	108 (8)	$H'_{132}C_{13}H'_{133}$	117 (10)
$C_8C_{13}H'_{133}$	112 (7)	$H'_{133}C_{13}H'_{131}$	90 (10)
$C_{10}C_{14}H_{141}$	113 (3)	$H_{141}C_{14}H_{142}$	107 (4)
$C_{10}C_{14}H_{142}$	113 (2)	$H_{142}C_{14}H_{143}$	112 (4)
$C_{10}C_{14}H_{143}$	110 (3)	$H_{143}C_{14}H_{141}$	103 (4)
$C_4C_{15}H_{151}$	107 (4)	$H_{151}C_{15}H_{152}$	108 (5)
$C_4C_{15}H_{152}$	111 (4)	$H_{152}C_{15}H_{153}$	97 (5)
$C_4C_{15}H_{153}$	115 (3)	$H_{153}C_{15}H_{151}$	118 (5)

[a] See footnotes to Table V.

Table IX. Selected Intermolecular Contacts[a]

Atom P	Atom Q	Vector[b]	Distance, Å
C_3	C_{13}	$(-x, -y, -z)$	3.662
C_{13}	O_3	$(-x, -y, -z)$	3.375
C_{15}	O_2	$(1 + x, {}^1/_2 - y, {}^1/_2 + z)$	3.542
C_{15}	O_1	$(1, 0, 1)$	3.544
C_1	H_{131}	$(-x -y, -z)$	3.06
C_1	H'_{131}	$(-x, -y, -z)$	3.09
C_3	H'_{131}	$(-x, -y, -z)$	3.10
C_3	H_{141}	$(-x, -y, 1 - z)$	2.96
C_5	H'_{132}	$(x, {}^1/_2 - y, z - {}^1/_2)$	3.04
C_9	H_{143}	$(1 - x, -y, 1 - z)$	3.08
C_{10}	H_{143}	$(1 - x, -y, 1 - z)$	3.00
C_{12}	H_{142}	$(-x, y - {}^1/_2, {}^1/_2 - z)$	3.07
C_{14}	H_{151}	$(1 - x, -y, 1 - z)$	3.02
O_1	O_2	$(x, {}^1/_2 - y, z - {}^1/_2)$	3.687
O_1	O_3	$(-1 - x, -y, -z)$	3.528
O_1	H_{153}	$(1, 0, 1)$	3.08
O_1	H_5	$(1 + x, {}^1/_2 - y, {}^1/_2 + z)$	3.03
O_1	H_{131}	$(-x, -y, -z)$	2.85
O_1	H'_{131}	$(-x, -y, -z)$	3.08
O_2	H_{121}	$(x, {}^1/_2 - y, z - {}^1/_2)$	2.87
O_2	H_{152}	$(1 + x, {}^1/_2 - y, {}^1/_2 + z)$	2.82
O_3	H'_{133}	$(1 + x, y, z)$	2.83
O_3	H_{123}	$(-x, {}^1/_2 + y, {}^1/_2 - z)$	2.92
O_3	H_{11}	$(-1 - x, -y, -z)$	2.94
O_3	H_{141}	$(-x, 1 - y, 1 - z)$	3.03
H_{135}	H_5	$(x, {}^1/_2 - y, {}^1/_2 + z)$	2.53
H_{141}	H_{11}	$(-x, -y, 1 - z)$	2.53
H_{141}	H_{141}	$(-x, -y, 1 - z)$	2.41
H_{153}	H_{123}	$(x, {}^1/_2 - y, {}^1/_2 + z)$	2.55

[a] See footnote *a* to Table V. [b] From molecule containing Q to molecule containing P.

Table X. Best Weighted Least-Squares Planes[a]

Atoms	Plane	Equations
$C_6H_7C_8C_9C_{10}C_{11}$	1	$0.8601x + 0.2326y + 0.4540z = 2.0560$
$C_{11}C_4C_5C_6$	2	$-0.8350x + 0.4599y + 0.3022z = 2.8245$

	Distances of Atoms from Planes, Å		
Atoms	Plane 1	Atoms	Plane 2
C_6	0.057	C_{11}	−0.005
C_7	−0.128	C_4	0.012
C_8	0.042	C_5	−0.014
C_9	0.081	C_6	0.007
C_{10}	−0.086		
C_{11}	0.035		
Cr	−1.511		

[a] Direction cosines of the planes refer to the orthogonal axis system *a*, *b*, *c**.

standard deviation of about 0.007 Å, suggests that delocalization is fairly extensive. The considerably greater length of the C_7–C_8 bond (1.44 Å) has no obvious physical significance, other than perhaps to suggest that there is somewhat less delocalization over C_6, C_7, C_8 than over C_9, C_{10}, C_{11}. It may also be noted

Table XI. Root-Mean-Square Amplitudes of Vibration (Å) and Their Direction Cosines[a]

Atoms	Minor axis	Medium axis	Major axis
Cr	0.167 (0.155, −0.320, 0.935)	0.177 (−0.071, 0.940, 0.334)	0.191 (0.985, 0.118, −0.123)
C_1	0.195 (0.396, 0.754, 0.524)	0.210 (−0.117, −0.524, 0.843)	0.256 (0.911, −0.395, −0.119)
O_1	0.181 (0.304, −0.140, 0.942)	0.301 (0.262, 0.963, 0.058)	0.359 (0.916, −0.229, −0.330)
C_2	0.191 (−0.456, 0.663, −0.599)	0.212 (0.887, 0.286, −0.362)	0.223 (0.070, 0.692, 0.718)
O_2	0.187 (0.770, −0.575, −0.276)	0.254 (−0.025, −0.461, 0.887)	0.342 (0.637, 0.676, 0.370)
C_3	0.173 (0.121, −0.275, 0.954)	0.196 (0.477, 0.859, 0.188)	0.221 (0.871, −0.432, −0.235)
O_3	0.192 (0.558, 0.800, 0.220)	0.243 (−0.047, −0.235, 0.971)	0.287 (0.829, −0.552, −0.094)
C_4	0.178 (−0.407, 0.665, 0.627)	0.185 (0.852, 0.029, 0.523)	0.233 (0.330, 0.746, −0.578)
C_5	0.166 (0.465, 0.825, 0.321)	0.205 (0.883, −0.459, −0.099)	0.258 (−0.065, −0.329, 0.942)
C_6	0.167 (0.167, 0.955, −0.246)	0.212 (0.799, −0.277, −0.534)	0.239 (0.578, 0.108, 0.809)
C_7	0.160 (0.595, 0.565, −0.572)	0.216 (−0.302, 0.816, 0.492)	0.247 (0.745, −0.120, 0.656)
C_8	0.171 (0.758, −0.155, −0.633)	0.212 (0.165, 0.985, −0.044)	0.234 (0.631, −0.071, 0.773)
C_9	0.156 (−0.591, 0.675, 0.442)	0.209 (0.775, 0.626, 0.080)	0.212 (0.223, −0.390, 0.894)
C_{10}	0.162 (0.634, −0.489, 0.594)	0.183 (0.373, 0.872, 0.327)	0.202 (−0.678, 0.007, 0.735)
C_{11}	0.179 (−0.030, 0.155, 0.987)	0.189 (0.709, 0.700, −0.088)	0.207 (−0.705, −0.697, 0.131)
C_{12}	0.199 (−0.063, 0.974, −0.218)	0.244 (−0.435, 0.170, 0.884)	0.284 (0.898, 0.150, 0.413)
C_{13}	0.191 (−0.638, 0.334, 0.694)	0.244 (0.193, 0.942, −0.276)	0.326 (0.746, 0.042, 0.665)
C_{14}	0.185 (−0.307, 0.744, −0.593)	0.229 (−0.358, 0.487, 0.797)	0.231 (0.882, 0.457, 0.117)
C_{15}	0.177 (0.343, 0.441, 0.829)	0.235 (0.783, −0.622, 0.007)	0.318 (0.519, 0.647, −0.559)

[a] Direction cosines are referred to the orthogonal coordinate system *a*, *b*, *c**.

that the Cr–C_6 distance (2.41 Å) is very significantly longer than the Cr–C_{11} distance (2.29 Å) whereas the other four may be sorted into nearly equal pairs (Cr–C_7 and Cr–C_{10}, 2.20 ± 0.01 Å; Cr–C_8 and Cr–C_9, 2.24 ± 0.01 Å). There is thus an indication that the metal-to-ring bonding favors the C_9, C_{10}, C_{11} half of the group of six "bound" carbon atoms. It is significant that, as shown in a subsequent paper, this is the side toward which the $Cr(CO)_3$ group most easily moves as the molecule manifests its fluxional character.

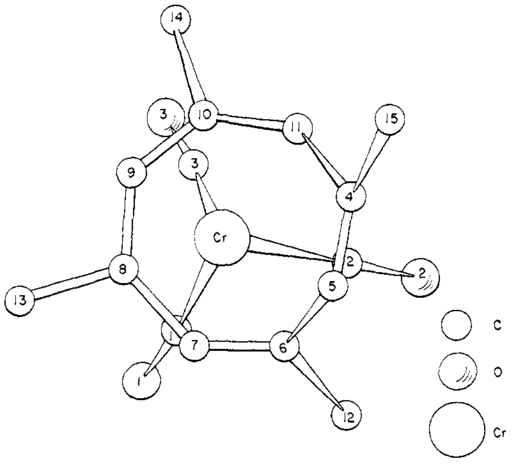

Figure 2. The molecular structure projected on a plane parallel to the mean plane of the atoms C_6, C_7, C_8, C_9, C_{10}, C_{11}. Hydrogen atoms are omitted for clarity.

(5) The set of carbon atoms, C_{11}, C_4, C_5, C_6, and C_{15}, together with the H atom on C_5 form an essentially coplanar group, with a double bond (1.304 ± 0.007 Å) between C_4 and C_5 and single bonds from C_4 and C_5 to the other carbon atoms when the standard length of a single bond between sp^2 hybridized atoms is taken as 1.48 Å (C_{11}–C_4, 1.481 ± 0.006 Å; C_5–C_6, 1.477 ± 0.007 Å) and that between sp^2 and sp^3 hybridized atoms as 1.51 Å (C_4–C_{15}, 1.511 ± 0.007 Å).

(6) The three Cr–CO distances are nearly identical, with a mean value of 1.848 ± 0.007 Å. This may be compared with the mean values for structually similar $Cr(CO)_3$ groups in $C_6H_6Cr(CO)_3$ (1.842 ± 0.007 Å),[24] $(CH_3)_6C_6Cr(CO)_3$ (1.814 ± 0.007 Å),[25] and (diethylenetriamine)$Cr(CO)_3$ (1.816 ± 0.005 Å).[26] It has been argued in the dien$Cr(CO)_3$ case that there can be no significant amount of metal-to-ligand back bonding and that Cr–CO bond lengths around 1.82 Å can be taken as indicative of this in other molecules as well. Thus, in the present instance, as in the $C_6H_6Cr(CO)_3$ and $(CH_3)_6C_6Cr(CO)_3$ cases, the metal-olefin bonding would be interpreted, on this criterion, as consisting

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(24) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1314 (1965).
(25) M. F. Bailey and L. F. Dahl, *ibid.*, **4**, 1298 (1965).
(26) F. A. Cotton and D. C. Richardson, *ibid.*, **5**, 1851 (1966).

essentially of olefin-to-metal donation. Whether this be valid or not, it is interesting that the $C_6H_6Cr(CO)_3$, $(CH_3)_6C_6Cr(CO)_3$, dien$Cr(CO)_3$, and (TMCOT)$Cr(CO)_3$ molecules are so similar in respect to the Cr–CO bond lengths.

(7) Finally, it is appropriate to compare the (TMCOT)$Cr(CO)_3$ structure with the structures of the two closely related compounds (COT)$Mo(CO)_3$[16] and (cycloocta-1,3,5-triene)$Cr(CO)_3$.[27] The (COT)$Mo(CO)_3$ molecule is more symmetrical than (TMCOT)$Cr(CO)_3$, possessing rigorous, crystallographic mirror symmetry. Aside from this, it is structually very similar. The dihedral angle between the two planes formed by the ring is 130°, compared to 119° in (TMCOT)$Cr(CO)_3$. This and some other differences may be a consequence of changing Cr for Mo, but a detailed analysis is elusive. It is interesting that, in all three compounds, the pattern of OC–metal–CO bond angles is the same, one angle being about 80° while the other two are 91–94°.

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[27] V. S. Armstrong and C. K. Prout, *J. Chem. Soc.*, 3770 (1962).

Electrophilic Aromatic Substitution Reactions by Platinum(II) and Palladium(II) Chlorides on N,N-Dimethylbenzylamines

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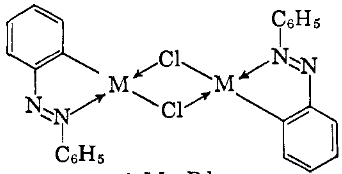
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received May 26, 1967

Abstract: Potassium tetrachloroplatinate(II) and lithium tetrachloropalladate(II) react readily with N,N-dimethylbenzylamine to give di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)diplatinum(II) and -dipalladium(II), respectively. These stable crystalline complexes possess both *ortho*-attached covalent metal–carbon bonding and coordinate metal–nitrogen bonding to the benzylamine. Similar bond formation by palladium(II) is observed in its complexes with the *p*-methoxy and 3,5-dimethoxy derivatives of N,N-dimethylbenzylamine. However, no palladium–carbon bonds are present in the palladium(II) chloride complexes obtained from *p*-nitro-N,N-dimethylbenzylamine and the N,N-dimethyl-2-phenyl-1-ethyl- and 3-phenyl-1-propylamines or from benzylamine and various secondary benzylamines.

The observation by Cope and Siekman[2] that azobenzene reacts with platinum(II) chlorides and palladium(II) chlorides to give complexes **1** and **2** having carbon-to-metal σ bonds has led us to search for similar reactions with other aromatic systems. This work was carried out in an attempt to obtain information concerning the structural requirements for aromatic substitution by platinum and palladium and whether the substitution reaction is confined to azobenzene and its derivatives. The systems investigated were limited to benzylamines and other classes of aromatic compounds containing groups which could coordinate to the metal and form structures similar to **1** and **2** if *ortho* substitution into the ring takes place.



1, M = Pd
2, M = Pt

Results and Discussion

The reactions of both the simple unsubstituted benzylamine and the secondary benzylamine, N-methylbenzylamine, with potassium tetrachloroplatinate(II) in aqueous methanol solvent did not meet with any success. Only intractable black products were obtained. Reaction of these amines with lithium tetrachloropalladate(II) in methanol did give good yields of crystalline complexes. Analyses, however, showed that these (**3** and **4**) were of the usual dichlorobis(amine)palladium(II) type[3] in which the two amines are coordinated through nitrogen to the metal, and no metal–carbon σ bonding is involved. Attempts to facilitate the aromatic substitution by palladium with the secondary benzylamines by changing the substituent on nitrogen from methyl to benzyl or phenyl, or by reaction with the highly activated N-phenyl-3,5-dimethoxybenzylamine, were unsuccessful. Again only the usual dichlorobis(amine)palladium(II) type complexes **5**, **6**, and **7** were obtained.

In contrast to the results obtained with the primary and secondary benzylamines, N,N-dimethylbenzylamine was found to react smoothly with the platinum(II) and palladium(II) chlorides to give crystalline products whose elemental analyses suggested that the desired di-μ-chloro-bis(N,N-dimethylbenzylamine-2-C,N)diplatinum(II) and -dipalladium(II) complexes had been formed. These materials have structures **8** and **9** similar to the type found by Cope and Siekman[2] with azobenzene. Thus, when a solution of N,N-dimethylbenzylamine and a half-molar quantity of potassium tetrachloroplatinate(II) in aqueous methanol was allowed to stand at room temperature for 45 hr, a dark brown pre-

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[1] (a) Deceased; (b) Department of Chemistry, University of California, Davis, Calif. 95616.

[2] A. C. Cope and R. W. Siekman, *J. Am. Chem. Soc.*, 87, 3272 (1965).

[3] E. Pietsch, Ed., "Gmelins Handbuch der Anorganischen Chemie–Palladium," Vol. 65, 8th ed, Verlag Chemie, GMBH, Weinheim/Bergstrasse, 1942, p 391.