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Transition-Metal Derivatives of Arenediazonium Ions. 9.[1] Isolation and X-ray Crystallographic Characterization of a Bis(arenediazo)molybdenum Complex, (η^5-Methylcyclopentadienyl)bis(p-fluorophenyldiazenido)chloromolybdenum(0)

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The title compound has been isolated as a byproduct of the reaction of (p-FC_6H_4N)(BF_4) with Na(η^5-$CH_3C_5H_4$)Mo(CO)$_3$ and has been characterized crystallographically. Crystals of (η^5-$CH_3C_5H_4$)Mo($N_2C_6H_4$-p-F)$_2$Cl are triclinic, of space group $P\bar{1}$ with two molecules in a unit cell of dimensions a = 7.564 (1) Å, b = 9.814 (1) Å, c = 13.964 (2) Å, α = 114.82 (1)°, β = 78.83 (1)°, and γ = 103.07 (1)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations with anisotropic thermal parameters; R = 0.029 for 2950 reflections (with $I > 3.0\sigma(I)$) measured by diffractometer. The molybdenum coordination is distorted octahedral with three facial sites occupied by the η^5-$CH_3C_5H_4$ ligand (Mo–C = 2.281 -2.412 (6) Å) and the remaining three sites by the chlorine (Mo–Cl = 2.387 (1) Å) and two arenediazo ligands (Mo–N = 1.826 and 1.834 (3) Å). The molybdenum–arenediazo geometry (Mo–N–N = 176.5 and 167.4 (2)° N–N–C = 122.2 and 117.4 (3)°) may be described as "singly bent"; the apparent nonlinearity of one of the Mo–N–N angles is attributed to intermolecular packing effects.

Introduction

In 1964 King and Bisnette[3] reported the synthesis of the (arenediazo)molybdenum complexes (η^5-C_5H_5)Mo(CO)$_2$N$_2$Ar via the reaction of arenediazonium salts with Na[(η^5-C_5H_5)Mo(CO)$_3$]. It was recognized at the time[3-5] that the precise course of the reaction was critically dependent on the conditions employed and that other species of unknown structure accompanied the main product. The present work describes the isolation and complete identification of one of these byproducts, the first crystallographically characterized example of a bis(arenediazo) transition-metal complex.

Results and Discussion

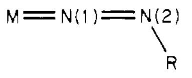
Equimolar quantities of Na[(η^5-MeC_5H_4)Mo(CO)$_3$] and (p-$FC_6H_4N_2$)(BF_4) reacted together in tetrahydrofuran (THF) at −60 °C and worked up by a slightly modified version of King's procedure[4] (omitting the chromatography step) yielded two red neutral complexes I and II. Compound I, the major product, was readily identified as (η-$^5MeC_5H_4$)Mo(CO)$_2$($N_2C_6H_4$-p-F). The IR spectrum of II showed the absence of carbonyl ligands and exhibited four medium-intensity bands in the region 1535–1620 cm^{-1}, suggestive of the presence of at least one coordinated arenediazo ligand. The ^{1}H NMR spectrum indicated the presence of η^5-MeC_5H_4 and $N_2C_6H_4$-p-F ligands in a 1:2 ratio.

Concurrent work in these laboratories[6] had shown that (η^5-C_5H_5)Mo(CO)$_2$N$_2$Ar reacts with arenediazonium salts at −70 °C to yield a highly labile species. On the basis of its reactivity toward nucleophiles and by analogy with the known species[7] [(η^5-C_5H_5)Mo(NO)$_2$CO]$^+$, the reactive arenediazo complex has been assigned the structure [(η^5-C_5H_5)Mo(N_2Ar)$_2$L]$^+$ where L = CO or solvent. It seemed reasonable to assume that the neutral complex II could be accounted for via initial formation of [(η^5-MeC_5H_4)Mo($N_2C_6H_4$-p-F)$_2$L]$^+$, followed by abstraction of halide from CH_2Cl_2 during workup, to yield (η^5-MeC_5H_4)Mo($N_2C_6H_4$-p-F)$_2$Cl. This suggestion was strengthened by the observation that complex II was not formed if CH_2Cl_2 was omitted from the workup, but whereas microanalytical data for C, H, and N were in agreement with the suggested formulaton, the results for halogen (Cl and F) were slightly (but consistently) outside the permitted limits.

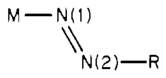
To establish the structure of II unequivocally, we determined its crystal and molecular structure by X-ray methods (details are in the Experimental Section). A view of the molecule, together with our crystallographic numbering scheme, is shown in Figure 1, and a stereoview of the unit-cell contents is in Figure 2. Details of molecular dimensions are in Tables I and II.

The molybdenum atom has distorted octahedral coordination with three facial sites occupied by the η^5-$CH_3C_5H_4$ ligand and the remaining three sites by chlorine and two arenediazo ligands (Figure 1) with N–Mo–N = 93.2 (1)° and Cl–Mo–N = 101.4 and 101.8 (1)°.

The most interesting feature of the structure of II is the geometry of the arenediazo ligands in which recently there has been considerable interest.[8-17] Previous structural studies have shown that these ligands can adopt geometries which have been described as "singly bent" as in III[9-13] or "doubly bent" as in IV[14-16] or as being intermediate between these two forms.[17]



III



IV

One of the arenediazo ligands in II is clearly of the "singly bent" variety with Mo–N(21)–N(22) close to linear (176.5 (2)°) and the N(21)–N(22)–C(21) angle = 122.2 (3)°. The orientation of the ligand with respect to the Mo–Cl bond is

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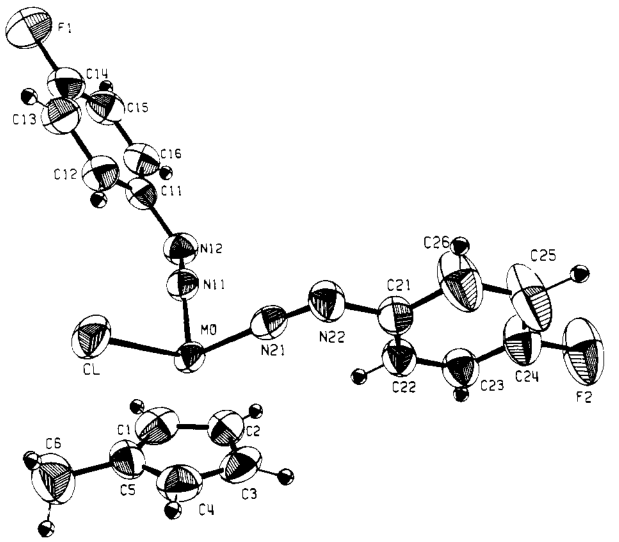

Figure 1. Perspective view of (η^5-$CH_3C_5H_4$)Mo($N_2C_6H_4F$)$_2$Cl showing the molecular geometry and our numbering scheme. The probability ellipsoids are at the 50% level for nonhydrogen atoms; the hydrogen atoms are shown as spheres of arbitrary size.

Table I. Principal Interatomic Distances (Å) and Angles (Deg) for (η^5-$CH_3C_5H_4$)Mo($N_2C_6H_4F$)$_2$Cl with Standard Deviations in Parentheses

(a) Distances from Molybdenum

Mo–Cl	2.387 (1)	Mo–C(4)	2.400 (3)
Mo–C(1)	2.357 (3)	Mo–C(5)	2.446 (3)
Mo–C(2)	2.283 (3)	Mo–N(11)	1.826 (2)
Mo–C(3)	2.354 (3)	Mo–N(21)	1.834 (3)

(b) Distances within the Arenediazo ligands

N(11)–N(12)	1.229 (4)	N(21)–N(22)	1.218 (4)
N(12)–C(11)	1.436 (4)	N(22)–C(21)	1.429 (4)
C(11)–C(12)	1.391 (5)	C(21)–C(22)	1.374 (5)
C(12)–C(13)	1.368 (5)	C(22)–C(23)	1.372 (5)
C(13)–C(14)	1.383 (5)	C(23)–C(24)	1.347 (5)
C(14)–C(15)	1.371 (6)	C(24)–C(25)	1.355 (6)
C(15)–C(16)	1.376 (5)	C(25)–C(26)	1.404 (6)
C(16)–C(11)	1.384 (4)	C(26)–C(21)	1.356 (5)
C(14)–F(1)	1.345 (4)	C(24)–F(2)	1.360 (5)

(c) Distances within the Methylcyclopentadiene Ring

C(1)–C(2)	1.447 (5)	C(2)–C(3)	1.403 (5)
C(3)–C(4)	1.360 (6)	C(4)–C(5)	1.408 (6)
C(1)–C(5)	1.393 (6)	C(5)–C(6)	1.489 (6)

(d) Other Contacts (<3.4 Å) Not Involving H Atoms[a]

Cl···C(5)	3.287	C(14)···F(2)^{III}	3.343
C(13)···F(1)^{I}	3.357	C(15)···F(2)^{III}	3.385
C(21)···F(1)^{II}	3.288	C(1)···C(1)^{IV}	3.213
C(22)···F(1)^{II}	3.352		

(e) Bond Angles

Cl–Mo–N(11)	101.8 (1)	Cl–Mo–N(21)	101.4 (1)
N(11)–Mo–N(21)	93.2 (1)		
Mo–N(11)–N(12)	167.4 (2)	Mo–N(21)–N(22)	176.5 (2)
N(11)–N(12)–C(11)	117.4 (3)	N(21)–N(22)–C(21)	122.2 (3)
N(12)–C(11)–C(12)	123.3 (3)	N(22)–C(21)–C(22)	124.2 (3)
N(12)–C(11)–C(16)	116.6 (3)	N(22)–C(21)–C(26)	115.9 (3)
C(12)–C(11)–C(16)	120.2 (3)	C(22)–C(21)–C(26)	119.9 (3)
C(11)–C(12)–C(13)	120.1 (3)	C(21)–C(22)–C(23)	120.8 (3)
C(12)–C(13)–C(14)	118.7 (3)	C(22)–C(23)–C(24)	118.4 (3)
C(13)–C(14)–C(15)	122.0 (3)	C(23)–C(24)–C(25)	123.0 (4)
C(13)–C(14)–F(1)	118.6 (4)	C(23)–C(24)–F(2)	119.0 (4)
C(15)–C(14)–F(1)	119.4 (3)	C(25)–C(24)–F(2)	118.0 (4)
C(14)–C(15)–C(16)	119.0 (3)	C(24)–C(25)–C(26)	118.2 (4)
C(11)–C(16)–C(15)	119.9 (3)	C(21)–C(26)–C(25)	119.6 (4)
C(2)–C(1)–C(5)	106.7 (3)	C(1)–C(2)–C(3)	107.0 (3)
C(2)–C(3)–C(4)	108.8 (3)	C(3)–C(4)–C(5)	109.3 (3)
C(1)–C(5)–C(4)	108.0 (3)	C(1)–C(5)–C(6)	130.6 (6)
C(4)–C(5)–C(6)	121.2 (4)		

(f) Torsion Angles

N(11)–N(12)–C(11)–C(12)	0.2
N(21)–N(22)–C(21)–C(22)	−7.6

[a] The superscripts refer to the following equivalent positions: I, $2-x$, $1-y$, $1-z$; II, $1-x$, $1-y$, $1-z$; III, $1+x$, $-1+y$, z; IV, $\bar{x}$, $\bar{y}$, $\bar{z}$.

such that the Cl–Mo···N(22)–C(21) system is trans. The remaining arenediazo ligand has an Mo–N(11)–N(12) angle (167.4 (2)°) which is significantly nonlinear and a N(11)–N(12)–C(11) angle of 117.4 (3)°. The Cl–Mo···N(12)–C(11) system is cis. Inspection of the molecular packing diagram (Figure 2) shows, however, that the nonlinearity of the Mo–N(11)–N(12) angle is probably a consequence of crystal packing rather than of electronic effects such as were found[17] in {IrCl($N_2C_6H_5$)[$PCH_3(C_6H_5)_2$]$_3$}$^+$ (where the highly distorted five-coordinate metal coordination could not be adequately described by any idealized geometry and the arenediazo ligand geometry is intermediate between singly and doubly bent with Ir–N–N = 155.2 (7)° and N–N–C = 118.8 (8)°). In the crystal structure of II, the 12.6° bend in the Mo–N(11)–N(12) angle from linearity results in normal intermolecular contacts (Table I); presumably the slight expenditure of energy to produce this results in better crystal packing.

The Mo–N distances (1.826 (2) and 1.834 (3) Å) are in excellent agreement with that reported[9] (1.825 (4) Å) for the corresponding bond in Mo[HB(pz)$_3$](CO)$_2$($N_2C_6H_5$) and are consistent with a significant contribution of the form III to the ground-state structure. The remaining dimensions of the arenediazo groups are in accord with expected values with N–N distances (1.218 and 1.229 (4) Å) and the N–C distances (1.429 and 1.436 (4) Å) being in the range of values previously reported[9-13] (N–N = 1.14–1.23 (1) Å, N–C = 1.40–1.46 (1) Å). In both ligands the N–N bonds are close to being coplanar with the appropriate phenyl rings; the N(11)–N(12)–C-

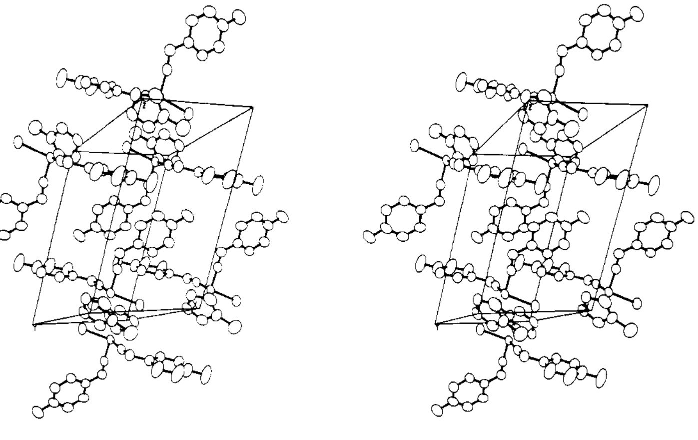

Figure 2. Stereoview of the molecular packing diagram of (η^5-$CH_3C_5H_4$)Mo($N_2C_6H_4F$)$_2$Cl.

Table II. Mean Plane Data for η^5-$(CH_3C_5H_4)Mo(N_2C_6H_4F)_2Cl$[a]

(i) Plane through Cyclopentadiene Ring C(1)–C(5)

Equation: $5.0416x + 2.5102y + 7.3355z = 1.5535$

C(1), 3; C(2), 9; C(3), −19; C(4), 21; C(5), −14; C(6), −139; Mo, 2041; Cl, 3107

rmsd 0.015 Å

(ii) Plane through Aromatic Ring C(11)–C(16)

Equation: $-1.0502x + 8.0255y + 2.4990z = 2.9823$

C(11), 0; C(12), −4; C(13), 3; C(14), 3; C(15), −7; C(16), 6; N(11), 9; N(12), 10; F(1), 8; Mo, −183

rmsd 0.004 Å

(iii) Plane through Aromatic Ring C(21)–C(26)

Equation: $1.1987x - 4.4383y + 13.9426z = 0.5059$

C(21), −10; C(22), −8; C(23), 9; C(24), 7; C(25), −24; C(26), 26; N(21), 31; N(22), −60; F(2), 6; Mo, 61

rmsd 0.016 Å

[a] Equations of mean planes are in the form $ax + by + cz = d$ where x, y, and z are the fractional coordinates given in Table III. Deviations (in Å, $\times 10^3$) of atoms from the planes and root-mean-square deviations (rmsd) of the atoms from the planes are given.

(11)–C(12) and N(21)–N(22)–C(21)–C(22) torsion angles are 0.2 and −7.6°, respectively. The Mo–Cl distance (2.387 (1) Å) is comparable with that found[18] in Mo{HB[Me_2Cl-(pz)]$_3$}(NO)(OC_3H_7)Cl (2.380 (3) Å) and the terminal Mo–Cl bonds in $(Mo_2Cl_9)^{3-}$ (2.384 (6) Å).[19]

The η^5-cyclopentadiene ring geometry and bonding to molybdenum (Mo–C = 2.283–2.446 (3) Å, mean C–C = 1.402 (6) Å, mean C–C–C = 108.0 (3)°) are in the same range as reported[20] for η^5-$C_5H_5Mo(CF_3C_2CF_3)(SC_6H_5)L$ (where L = CO or O) with Mo–C values of 2.281–2.412 (6) and 2.349–2.408 (8) Å. In other (η^5-C_5H_5)Mo complexes comparable molybdenum–carbon distances are also found: e.g., 2.303–2.415 (4) Å in η^5-$C_5H_5Mo(CO)_2SC(CH_3)NCH(CH_3)(C_6H_5)$,[21] 2.275–2.410 (15) Å in η^5-$C_5H_5Mo(CO)_2(NC_5H_4CHNCH(CH_3)C_6H_5)$,[22] and 2.270–2.411 (6) Å in η^5-$C_5H_5Mo[C{=}C(CN)_2][P(OCH_3)_3]_2Cl$.[23] Although the atoms of the five-membered ring in II are close to being coplanar (Table II), the methyl carbon C(6) is 0.139 Å out of the ring plane away from the chlorine atom to relieve intramolecular overcrowding between the chlorine atom and the C(5)–C(6) region of the η^5-$C_5H_4CH_3$ ligand (the Cl···C(5) and Cl···C(6) distances are 3.287 and 3.430 Å, respectively). The Mo–C(cyclopentadiene) distances also reflect the effect of the bulky chlorine on the five-membered ring coordination, being longest with C(5) (2.446 (3) Å) and the shortest at C(2) (2.283 (3) Å).

In the crystal structure (Figure 2), the closest contacts between molecules occur between cyclopentadiene rings related through the inversion center at the origin; this results in a C(1)···C(1)^{I} contact of 3.21 Å and the planes of the two (necessarily parallel) cyclopentadienyl rings being separated by 3.1 Å, although the rings themselves only barely overlap in the C(1)···C(1′) region. Other intermolecular contacts correspond to normal van der Waals distances.

Futher byproducts from the reaction of diazonium cations with $[\eta^5$-$C_5H_5Mo(CO)_3]^-$ are currently under investigation.

Experimental Section

Molybdenum hexacarbonyl was purchased from Pressure Chemical Co., Pittsburgh, PA 15201. *p*-Fluorobenzenediazonium tetrafluoroborate was prepared by standard procedures.[24] Infrared spectra were determined on a Perkin-Elmer 257 spectrometer, and NMR spectra were recorded on a Perkin-Elmer/Hitachi R20A instrument, operating at 60 MHz. Microanalyses were carried out by the staff of the microanalytical laboratory of the Chemistry Department of University College, Cork, Republic of Ireland.

Preparation of Complexes I and II. A THF solution of 6.40 g (22.7 mmol) of Na[(η^5-MeC_5H_4)Mo(CO)$_3$] (prepared from MeC_5H_4Na and $Mo(CO)_6$) was cooled to −60 °C (solid CO_2/acetone) under a nitrogen atmosphere, and solid (p-$FC_6H_4N_2$)(BF_4) (4.76 g, 22.7 mmol) was added portionwise with stirring over 30 min. The reaction mixture was allowed to warm spontaneously to room temperature, and the solvent was removed in vacuo on a rotary evaporator without further heating. The red oily residue was dissolved in CH_2Cl_2, and diethyl ether was added to precipitate $NaBF_4$ and other ionic materials. The filtered CH_2Cl_2 solution was concentrated to dryness in vacuo and the residue was extracted with hot pentane, yielding a soluble fraction (I) and sparingly soluble residue (II).

Concentration of the pentane extract and cooling yielded complex I as a bright red solid, 4.83 g (60%). Anal. Calcd for $C_{14}H_{11}FMoN_2O_2$: C, 47.7; H, 3.11; N, 7.91. Found: C, 47.50; H, 3.15; N, 8.00. IR (thin film): 3050 (w), 2925 (m), 2850 (m), 1987 (vs, CO), 1910 (vs, CO), 1615 (s), 1594 (w), 1560 (s), 1490 (s), 1265 (m), 1230 (m), 1162 (m), 1090 (w), 1025 (w), 834 (m), 807 (w), 739 (s) cm^{-1}. The ^1H NMR spectrum (CD_2Cl_2) showed multiplets centered on τ 2.8 and 4.1 and a singlet at τ 7.8 in the ratio 4:4:3, assigned to the C_6H_4, C_5H_4, and CH_3 protons, respectively.

The sparingly soluble residue from the initial separation was extracted with boiling pentane in a Soxhlet apparatus under nitrogen for 24 h. Dark red crystals of complex II (1.5 g (14.5%)) separated from the hot pentane extracts. Anal. Calcd for $C_{18}H_{15}ClF_2MoN_4$: C, 47.4; H, 3.29, Cl, 7.77; F, 8.32; N, 12.27. Found: C, 46.86; H, 3.45; Cl, 8.43; F, 8.92; N, 11.78. IR (thin film): 1620 (m), 1608 (m), 1594 (m), 1570 (w), 1535 (m), 1481 (s), 1290 (w), 1228 (m), 1162 (m), 1140 (w), 1090 (w), 925 (w), 895 (w), 835 (m), 755 (w), 730 (w) cm^{-1}. The ^1H NMR spectrum (CD_2Cl_2) showed multiplets centered on τ 2.8 (C_6H_4) and 4.1 (C_5H_4) and a singlet at τ 7.8 (CH_3) in the ratio 8:4:3.

Collection and Reduction of the X-ray Intensity Data. The dark red crystals of $(CH_3C_5H_4)Mo(N_2C_6H_4F)_2Cl$, $C_{18}H_{15}ClF_2MoN_4$, M_r = 456.7, were examined by Weissenberg and precession photographs which showed that they belonged to the triclinic system; there were no systematic absences. Space group $P\bar{1}$ was assumed and confirmed by this analysis. Unit-cell dimensions a = 7.564 (1) Å, b = 9.814 (1) Å, c = 13.964 (2) Å, α = 114.82 (1)°, β = 78.83 (1)°, and γ = 103.07 (1)° were obtained by a least-squares refinement of the setting angles of 12 general reflections on a Hilger and Watts Y290 four-circle computer-controlled diffractometer (λ(Mo Kα) 0.71069 Å) equipped with a graphite monochromator. The unit-cell volume is 910.8 Å^3, and for Z = 2 the calculated density is 1.67 g cm^{-3}. $F(000)$ = 456. The reduced cell has dimensions a = 7.564 (1) Å, b = 9.814 (1) Å, c = 13.283 (2) Å, α = 107.32 (1)°, β = 92.10 (1)°, and γ = 103.07 (1)°.

Diffraction data were collected from a well-formed red needle with maximum dimensions 0.15 × 0.23 × 0.51 mm and mounted on a eucentric goniometer head with the a axis approximately parallel to the ϕ axis. Its six bounding faces were identified, and their distances from an arbitrary crystal center were measured with a calibrated graticule in a binocular microscope. The θ–2θ scan technique and Mo Kα radiation were used to record the intensities of a unique hemisphere of data within the limits $2 < \theta < 25°$. A symmetric scan range of 0.6° in θ, centered on the calculated peak position (λ(Mo Kα) 0.71069 Å), was composed of 60 steps of 1-s duration. Stationary-crystal, stationary-counter background counts were measured for 15 s at the beginning and end of the scan range. Reflections for which the intensity of the diffracted beam exceeded 10000 counts/s were automatically remeasured with aluminum foil attenuators inserted in order to be within the linear response range of the scintillation counter. The intensities of three standard reflections, monitored at

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Table III. Positional Parameters for (η^5-$CH_3C_5H_4$)Mo($N_2C_6H_4F$)$_2$Cl with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Mo	0.35538 (3)	0.35678 (2)	0.12364 (2)
Cl	0.6693 (1)	0.3562 (1)	0.0534 (1)
F(1)	0.8945 (4)	0.3256 (3)	0.5271 (2)
F(2)	−0.2944 (4)	0.9425 (3)	0.3622 (3)
N(11)	0.3555 (3)	0.3416 (3)	0.2495 (2)
N(12)	0.3237 (4)	0.3126 (3)	0.3293 (2)
N(21)	0.3471 (3)	0.5614 (3)	0.1874 (2)
N(22)	0.3395 (4)	0.6968 (3)	0.2246 (2)
C(1)	0.1763 (6)	0.1148 (4)	0.0518 (3)
C(2)	0.0663 (4)	0.2338 (4)	0.0875 (3)
C(3)	0.1218 (5)	0.3108 (5)	0.0191 (3)
C(4)	0.2628 (5)	0.2504 (5)	−0.0516 (3)
C(5)	0.2942 (5)	0.1259 (4)	−0.0355 (3)
C(6)	0.4266 (8)	0.0265 (5)	−0.1095 (4)
C(11)	0.4776 (4)	0.3167 (3)	0.3772 (2)
C(12)	0.6578 (5)	0.3520 (4)	0.3379 (2)
C(13)	0.7978 (5)	0.3556 (4)	0.3884 (3)
C(14)	0.7564 (6)	0.3222 (4)	0.4778 (3)
C(15)	0.5797 (6)	0.2856 (4)	0.5172 (3)
C(16)	0.4392 (5)	0.2843 (4)	0.4671 (2)
C(21)	0.1699 (4)	0.7533 (3)	0.2608 (2)
C(22)	0.0015 (5)	0.6629 (3)	0.2466 (3)
C(23)	−0.1554 (5)	0.7258 (4)	0.2814 (3)
C(24)	−0.1401 (6)	0.8785 (5)	0.3285 (4)
C(25)	0.0228 (7)	0.9723 (5)	0.3424 (5)
C(26)	0.1822 (6)	0.9066 (4)	0.3108 (4)
H(11)[a]	0.170	0.043	0.082
H(21)	−0.026	0.256	0.146
H(31)	0.070	0.392	0.022
H(41)	0.330	0.286	−0.104
H(121)	0.684	0.374	0.276
H(131)	0.921	0.380	0.362
H(151)	0.555	0.261	0.578
H(161)	0.316	0.261	0.494
H(221)	−0.007	0.556	0.212
H(231)	−0.272	0.663	0.272
H(251)	0.029	1.080	0.372
H(261)	0.298	0.969	0.325
H(61)	0.546	0.083	−0.111
H(62)	0.390	−0.023	−0.180
H(63)	0.427	−0.051	−0.086

[a] Hydrogen atoms are labeled according to the carbon atoms to which they are bonded; e.g., H(61) is bonded to C(6), H(251) to C(25), etc.

100-reflection intervals, fluctuated by less than 2% during data collection.

Data were corrected for Lorentz and polarization factors as described previously[25] and for absorption[26] (μ(Mo Kα) = 8.0 cm^{-1}). Maximum and minimum values of transmission coefficents are 0.904 and 0.844. Of the 3209 unique reflections measured, 2950 with $I > 3\sigma(I)$ were used in the final refinement of the structure.

Solution and Refinement of the Structure. An estimate of the overall scale and thermal parameters was obtained with use of Wilson's method, and fractional coordinates for the molybdenum and chlorine atoms were derived from a sharpened three-dimensonal Patterson map. A Fourier synthesis based on the molybdenum and chlorine phases revealed all the nonhydrogen atoms. With the anisotropic temperature factors, full-matrix least-squares refinement of this model gave $R = \sum||F_o| - |F_c||/\sum |F_o| = 0.056$. The scattering functions of Cromer and Mann[27] were used for all nonhydrogen atoms, and the curves for the molybdenum and chlorine atoms were corrected for anomalous dispersion.[28]

The top peaks of a difference Fourier map established positions for all the hydrogen atoms; these were then allowed for in chemically expected positions (C–H = 0.95 Å) with isotropic U values and scattering factors from ref 29. In subsequent refinement cycles the hydrogen coordinates were not refined, but separate overall U_{iso} values were refined for the C–H and CH_3 hydrogen atoms. Refinement converged in three more cycles with $R_1 = 0.029$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.036$. The weighting scheme employed was $w^{1/2} = 1/(\sigma^2F + pF^2)^{1/2}$ with $p = 0.0014$. In the final cycle of refinement all shifts were less than 0.3 esd, and a final difference synthesis had no significant features.

Final positional parameters for the atoms, along with their standard deviations as estimated from the inverse matrix, are listed in Table III. Molecular dimensions are in Tables I and II. Listings of observed and calculated structure factors and of thermal parameters are available.

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Supplementary Material Available: Listings of structure factors and of thermal parameters (20 pages). Ordering information is given on any current masthead page.

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