with the potassium ion, while O(10) forms two pairs of symmetry-related hydrogen bonds, including one with the nitro oxygen atom O(7). This last hydrogen bond stabilizes the nitro group so that the angle between the plane of this group and that of the coordination plane Co, O(3), N(1), N(2), N(3) is 35.9°.

The potassium ions are surrounded by seven oxygen atoms at distances of 2.672 (3)-2.877 (5) Å. One carboxyl oxygen atom in this group makes the shortest contact with one potassium ion and also the longest contact with an adjacent (symmetry-related) potassium. The polyhedra occur in pairs, sharing an edge, as shown in Figure 3.

The configuration of the complex illustrated in Figure 1 can be described using the proposed IUPAC nomenclature[32] as Δ, and the chelate ring conformations as δ-$\lambda\lambda\lambda$. The enantiomer is therefore described as Λ, λ-$\delta\delta\delta$. Ring conformations in complexes of this type have recently been discussed by Lee.[33] The dihedral angle α, defined as the angle between the plane which contains the ring carbon atoms and the cobalt atom and the plane which contains the ligator atoms and the cobalt atom, is listed in Table VI, together with the conventional torsional angle β.

Computer programs used were from the UCLA crystallographic library and included ORXFLS,[34] ORXFFE,[35] and ORTEP.[36]

Registry No. $KCo(C_8N_2O_6H_{11})(NO_2)\cdot 1.5H_2O$, 37448-69-4.

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Crystal and Molecular Structure of an Ortho-Metalated Benzylidineaniline-Manganese Carbonyl Complex, Tetracarbonyl-2-(*N*-phenylformimidoyl)phenylmanganese, $C_6H_5NCHC_6H_4Mn(CO)_4$

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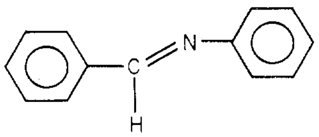
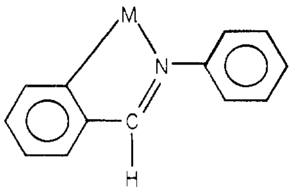
The structure of tetracarbonyl-2-(*N*-phenylformimidoyl)phenylmanganese, a product of the reaction of $CH_3Mn(CO)_5$ with benzylidineaniline, has been determined by a single-crystal X-ray structural analysis. Crystals of $C_6H_5NCHC_6H_4Mn(CO)_4$ are monoclinic, space group $P2_1/c$, with $a = 9.548$ (4), $b = 9.154$ (3), $c = 18.201$ (6) Å, $\beta = 102.07$ (2)°. Observed and calculated ($Z = 4$) densities are 1.48 and 1.47 (1) g/cm^3, respectively. The structure determination was based upon 1530 independent nonzero intensity data with $2\theta \leqslant 50°$ collected by counter methods. Full-matrix anisotropic–isotropic least-squares refinement converged to a final conventional discrepancy factor of 0.071. The crystal structure is composed of monomeric molecular units, in which the manganese atom is coordinated in a distorted octahedral configuration to four carbonyl groups and to the chelating ligand. The ligand is bound *via* a metal–nitrogen bond and a metal–carbon σ bond to the ortho position of the benzylidine phenyl ring, forming a planar five-membered chelate ring. The conformation of the coordinated ligand closely resembles that of free benzylidineaniline; in particular, the aniline phenyl ring is twisted by 57.0° from the CC=NC plane. The Mn–C(phenyl) and Mn–N bond distances are 2.060 (8) and 2.070 (7) Å, respectively. Some apparently significant variation in the Mn–C(carbonyl) distances is observed.

Introduction

The Schiff base benzylidineaniline (bza, I) is isoelectronic



I



II

with azobenzene (azb) and has been shown[1-4] to undergo ortho-metalation reactions similar to those observed for azobenzene.[5,6] In the resulting complexes, the bza has been proposed to be bound to the metal atom in a chelated fashion *via* a nitrogen→metal dative bond and a metal–phenyl carbon σ bond. This mode of coordination was first proposed by Cope and Siekman[7] for a series of palladium(II)-azobenzene derivatives and first demonstrated crystallographically in acetatobis[2-(phenylazo)phenyl]-rhodium.[8] Complexes of bza believed to have structure II

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have been prepared with M = Pd,[1] Rh,[2] Re,[2] Ru,[2] Ni,[3] and Mn.[2,4] Although bza behaves similarly to azb in this respect, it has not to date been shown to display the diversity of modes of metal coordination found for azobenzene.[9-12] The molecular conformations of free azb and bza provide a further comparison of interest. In bza, the two phenyl rings are distinctly noncoplanar (the aniline ring is twisted by 55.2° out of the CN=CC plane),[13] while the isoelectronic molecules stilbene[14] and azobenzene[15] are both nearly coplanar.

In their reactions with $Fe_2(CO)_9$, benzylidineanilines also undergo ortho-metalation.[16] However a crystal structure analysis of the *p*-toluidine derivative[17] showed that proton transfer to the azomethine carbon atom had occurred and that the resulting chelate was no longer a conjugated system. A similar reductive hydrogen transfer has recently been reported in the reaction of $IrCl(CO)(PPh_3)_2$ with two substituted phenyldiazonium cations.[18]

We now wish to report the results of a crystallographic study of $C_6H_5N{=}CHC_6H_4Mn(CO)_4$, prepared by Bruce, *et al.*, from bza and $CH_3Mn(CO)_5$.[2b] This structural investigation was undertaken in order to document this proposed mode of metal coordination of bza, to compare the structural details of coordinated azb and bza, and to determine whether the nonplanar conformation of bza is maintained in the metal complex. The synthesis and structure of this complex have previously been reported in preliminary form.[4]

Collection and Reduction of the Intensity Data

A sample of $C_{13}N_2H_{10}Mn(CO)_4$ was generously supplied by Dr. M. I. Bruce of the University of Bristol. Precession photographs (*hk*0, *hk*1, *h*0*l*, *h*1*l*) displayed monoclinic symmetry with systematic absences (*h*0*l*, $l \neq 2n$; 0*k*0, $k \neq 2n$) consistent with space group $C_{2h}{}^5$, $P2_1/c$. Lattice parameters were obtained by least-squares refinement of the setting angles of 18 reflections with $2\theta \geqslant 19°$ which had been accurately centered on a Picker four-circle X-ray diffractometer. The unit cell constants (23°, λ(Mo Kα_1) 0.70926 Å) obtained in this manner are a = 9.548 (4), b = 9.154 (3), c = 18.201 (6) Å, β = 102.07 (2)°. The numbers in parentheses are the standard deviations obtained from the least-squares refinement of the setting angles. The density of 1.48 g/cm³ calculated on the basis of 4 formula units per cell agrees well with a density of 1.47 (1) gm/cm³ obtained by flotation in aqueous zinc bromide solution.

Intensity data were collected from a yellow tabular crystal of dimensions 0.33 × 0.23 × 0.20 mm mounted in a thin-walled glass capillary with its longest dimension (the crystallographic [100] direction) parallel to the capillary walls. The 0.23-mm dimension was perpendicular to the well-developed {001} faces; other bounding planes belonged to the {021} and {100} forms. Narrow-source, open-counter ω scans[19] through several reflections displayed an average full width at half-maximum of 0.15°, indicative of satisfactorily low mosaic spread. The data were collected on a Picker automatic diffractometer by use of procedures previously described.[20] A takeoff angle of 1.35° was employed. The diffracted beam was filtered through 3.0-mil Nb foil. The counter aperture was 5 × 5 mm and was positioned 28 cm from the crystal. The pulse-height analyzer was set to admit ~95% of the Mo Kα peak. Data were collected by the θ-2θ scan method. An asymmetric scan range of 0.55° below to 0.70° in 2θ above the calculated scattering angle was employed. For reflections with $2\theta > 45°$ the range was −0.56 to +0.77°. The intensities of all independent reflections with $2\theta \leqslant 50°$ were measured. The $h\bar{k}l$ form was also collected for reflections with $F^2 \geqslant 2.5\sigma(F^2)$, out to 2θ = 38°. The scan rate was 1°/min and stationary background counts of 10 sec were taken at each end of the scan range. Copper foil attenuators were automatically inserted whenever the count rate exceeded ~10,000 counts/sec; only five reflections required attenuation. Four standard reflections, chosen to lie in widely separated regions of reciprocal space, were monitored after every 100 reflections throughout the collection of data. Aside from a small change (*ca.* 1%) which followed repair of an electronic failure, these standards showed no significant variations in intensity during data collection.

Previously described methods were employed in processing the data.[20,21] The *p* factor in the expression for the standard deviation of the observed intensities was assigned a value of 0.05. In averaging the two forms, $\sigma(F^2)$ was estimated both from the average individual σ and from the range of F^2 among equivalent forms. The larger of the two estimates was taken as $\sigma(F^2{}_{\text{av}})$. Of the 2777 independent data collected, 1530 were above background by three or more standard deviations. The observed intensities were scaled to compensate for the change in intensity of the standards. A trial calculation indicated that transmission factors ranged only from 0.83 to 0.86; hence no absorption correction was applied.

Solution and Refinement of the Structure

The solution of the structure was accomplished by heavy-atom methods. A three-dimensional Patterson function yielded trial coordinates for the Mn atom. Least-squares refinement of positional parameters and an isotropic temperature factor for the metal atom and a scale factor yielded discrepancy factors $R_1 = \Sigma\| F_o| - |F_c\|/\Sigma|F_o| = 0.41$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.49$. Coordinates of the 22 carbon, nitrogen, and oxygen atoms were obtained from difference Fourier maps. Refinement of positional and isotropic thermal parameters for all nonhydrogen atoms, based upon all data with $F_o{}^2 \geqslant 3\sigma(F_o)^2$, converged to R_1 = 0.080 and R_2 = 0.132. Further refinement employed anisotropic thermal parameters for the manganese atom and isotropic *B*'s for all other atoms. The 10 hydrogen atoms were included as fixed contributions to F_c based upon their "ideal" trigonal positions and with temperature factors taken as 1 unit greater than the *B* value for the carbon atom to which they are bound. This final refinement converged to R_1 = 0.071 and R_2 = 0.087, with the largest parameter shift in the last cycle equal to 0.21σ. A difference map at this point showed no residual peaks greater than 0.7 e/Å³.

Throughout the least-squares refinement, the weights of the observed structure amplitudes were taken as $w = 4F_o{}^2/\sigma^2(F_o{}^2)$ and the function minimized was $\Sigma w(F_o - F_c)^2$. The final standard deviation of an observation of unit of weight was 2.2. Calculation of $w(\Delta F)^2$ for subsets of the data as a function of uncorrected intensity, observed *F*, and Bragg angle showed no significant trends; thus confirming that the relative weights were appropriate. Calculation of structure factors for data with $F_o{}^2 \leqslant 3\sigma(F_o{}^2)$ revealed 11 reflections with $|F_o - F_c|/\sigma(F_o) \geqslant 3$; only four of these had $\Delta F/\sigma > 4$. Scattering factors for Mn, C, N, and O were taken from ref 22 and those of Stewart, *et al.*,[23] were employed for H. Structure factor calculations used the $\Delta f'$ and $\Delta f''$ values of Cromer[24] in

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Table I. Atomic Positional and Thermal Parameters for $C_6H_5N{=}CHC_6H_4Mn(CO)_4$[a]

Atom	*x*	*y*	*z*	*B*, Å^2
Mn	0.23423 (13)	0.18922 (14)	0.03026 (6)	*b*
C(1)	0.0530 (9)	0.2118 (10)	0.0460 (5)	3.9 (2)
O(1)	−0.0582 (8)	0.2263 (8)	0.0585 (4)	6.2 (2)
C(2)	0.4211 (11)	0.1744 (12)	0.0279 (5)	4.9 (2)
O(2)	0.5421 (9)	0.1612 (9)	0.0284 (4)	7.5 (2)
C(3)	0.2428 (10)	0.0142 (11)	0.0715 (5)	4.5 (2)
O(3)	0.2486 (8)	−0.0995 (9)	0.1000 (4)	6.3 (2)
C(4)	0.1762 (10)	0.1144 (11)	−0.0623 (5)	4.3 (2)
O(4)	0.1388 (8)	0.0619 (9)	−0.1210 (4)	6.6 (2)
C(5)	0.2985 (8)	0.2928 (9)	0.1322 (4)	3.2 (2)
C(6)	0.3263 (9)	0.2356 (10)	0.2055 (5)	4.0 (2)
C(7)	0.3659 (9)	0.3315 (11)	0.2673 (5)	4.4 (2)
C(8)	0.3755 (10)	0.4805 (11)	0.2583 (5)	4.5 (2)
C(9)	0.3481 (9)	0.5399 (10)	0.1864 (5)	4.3 (2)
C(10)	0.3107 (8)	0.4460 (9)	0.1240 (4)	3.1 (1)
C(11)	0.2769 (8)	0.4993 (9)	0.0478 (4)	3.2 (2)
C(12)	0.2053 (8)	0.4572 (9)	−0.0799 (4)	3.2 (2)
C(13)	0.3095 (9)	0.5336 (10)	−0.1068 (5)	3.9 (2)
C(14)	0.2737 (10)	0.5930 (11)	−0.1796 (5)	4.4 (2)
C(15)	0.1406 (11)	0.5739 (12)	−0.2241 (6)	5.2 (2)
C(16)	0.0368 (11)	0.4931 (12)	−0.1976 (6)	5.3 (2)
C(17)	0.0706 (9)	0.4317 (10)	−0.1248 (5)	4.1 (2)
N	0.2362 (6)	0.4045 (7)	−0.0044 (4)	2.9 (1)
H(6)[c]	0.3182	0.1283	0.2139	
H(7)	0.3877	0.2898	0.3192	
H(8)	0.4021	0.5454	0.3032	
H(9)	0.3548	0.6477	0.1790	
H(11)	0.4079	0.5462	−0.0752	
H(13)	0.3470	0.6505	−0.1993	
H(14)	0.1174	0.6176	−0.2756	
H(15)	−0.0606	0.4790	−0.2300	
H(16)	−0.0013	0.3709	−0.1058	
H(17)	0.2848	0.6053	0.0360	

[a] Numbers in parentheses in tables and in the text are estimated standard deviations in the least significant figures. [b] The anisotropic thermal parameters (×10^5) of the manganese atom, referred to an expression of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$, are $\beta_{11} = 1087$ (17), $\beta_{22} = 725$ (14), $\beta_{33} = 256$ (4), $\beta_{12} = -48$ (16), $\beta_{13} = 88$ (6), $\beta_{23} = -14$ (8). [c] Hydrogen atom coordinates are calculated values. The numbering of hydrogen atoms corresponds to that of the carbon atoms to which they are attached. Temperature factors of hydrogen atoms in the metal-bound ring were set at 4.9; for the other hydrogens *B* was assigned a value of 5.5 Å^2.

estimating the real and imaginary parts of anomalous scattering by the manganese atoms.

Final atomic positional and thermal parameters are listed in Table I and intramolecular distances and angles are tabulated in Tables II and III, respectively. Information concerning selected molecular planes and dihedral angles is given in Table IV. A table of observed and calculated structure factors is available.[25]

Description and Discussion of the Structure

Table II. Intramolecular Distances, Å

Mn–C(1)	1.823 (9)	C(5)–C(6)	1.406 (11)
Mn–C(2)	1.799 (10)	C(6)–C(7)	1.414 (12)
Mn–C(3)	1.764 (10)	C(7)–C(8)	1.379 (12)
Mn–C(4)	1.796 (10)	C(8)–C(9)	1.391 (12)
Mn–C(5)	2.060 (8)	C(9)–C(10)	1.409 (12)
Mn–N	2.070 (7)	C(10)–C(5)	1.418 (11)
C(1)–O(1)	1.140 (9)	C(12)–C(13)	1.387 (11)
C(2)–O(2)	1.159 (10)	C(13)–C(14)	1.407 (12)
C(3)–O(3)	1.159 (11)	C(14)–C(15)	1.367 (12)
C(4)–O(4)	1.157 (10)	C(15)–C(16)	1.401 (13)
Mean C–O	1.153 (9)[a]	C(16)–C(17)	1.412 (12)
N–C(11)	1.285 (10)	C(17)–C(12)	1.392 (11)
N–C(12)	1.428 (10)	Mean C–C(phenyl)	1.398 (16)
C(10)–C(11)	1.443 (10)		
C(1)···C(3)	2.534 (13)	C(2)···C(3)	2.500 (14)
C(1)···C(4)	2.652 (13)	C(2)···C(4)	2.619 (14)
C(1)···C(5)	2.640 (12)	C(2)···C(5)	2.662 (12)
C(1)···N	2.771 (11)	C(2)···N	2.733 (12)
C(3)···C(5)	2.786 (12)	C(4)···N	2.870 (11)
C(3)···C(4)	2.555 (13)	C(5)···N	2.639 (10)

[a] The figure in parentheses following mean values of bond distances in this table is the standard deviation of an *individual* distance as estimated by $s = [\{1/(n-1)\} \Sigma_{i=1}{}^{n}(\bar{x} - x_i)^2]^{1/2}$ where x_i is an individual distance and $\bar{x}$ is the mean value of the *n* measurements of presumably equivalent bond distances.

Table III. Bond Angles, Deg

C(1)–Mn–C(2)	172.2 (4)	Mn–N–C(11)	116.0 (5)
C(1)–Mn–C(3)	89.8 (4)	Mn–N–C(12)	127.0 (5)
C(1)–Mn–C(4)	94.2 (4)	C(11)–N–C(12)	116.9 (7)
C(1)–Mn–C(5)	85.4 (3)	C(5)–C(6)–C(7)	119.3 (8)
C(1)–Mn–N	90.5 (3)	C(6)–C(7)–C(8)	122.2 (9)
C(2)–Mn–C(3)	89.1 (4)	C(7)–C(8)–C(9)	119.6 (9)
C(2)–Mn–C(4)	93.5 (4)	C(8)–C(9)–C(10)	119.0 (8)
C(2)–Mn–C(5)	86.9 (4)	C(5)–C(10)–C(9)	122.1 (7)
C(2)–Mn–N	89.6 (4)	C(5)–C(10)–C(11)	115.4 (7)
C(3)–Mn–C(4)	91.8 (4)	C(9)–C(10)–C(11)	122.4 (8)
C(3)–Mn–C(5)	93.2 (4)	C(10)–C(11)–N	117.0 (7)
C(3)–Mn–N	172.6 (4)	N–C(12)–C(13)	119.4 (7)
C(4)–Mn–C(5)	175.0 (4)	N–C(12)–C(17)	119.2 (7)
C(4)–Mn–N	95.6 (4)	C(13)–C(12)–C(17)	121.4 (8)
C(5)–Mn–N	79.4 (3)	C(12)–C(13)–C(14)	118.4 (8)
Mn–C(1)–O(1)	177.5 (8)	C(13)–C(14)–C(15)	121.4 (8)
Mn–C(2)–O(2)	177.5 (9)	C(14)–C(15)–C(16)	120.1 (9)
Mn–C(3)–O(3)	178.7 (9)	C(15)–C(16)–C(17)	119.5 (9)
Mn–C(4)–O(4)	177.9 (9)	C(16)–C(17)–C(12)	119.1 (8)
Mn–C(5)–C(6)	130.2 (6)		
Mn–C(5)–C(10)	112.1 (6)		
C(6)–C(5)–C(10)	117.7 (7)		

A view of the molecular structure of $C_6H_5N{=}CHC_6H_4Mn(CO)_4$ is shown in Figure 1. The manganese atom is coordinated in a distorted octahedral configuration to the four carbonyl groups and to the chelated ligand. The ligand is bound *via* a metal-nitrogen bond and a metal-carbon σ bond to the ortho position of the benzylidine phenyl ring, as proposed for this complex and for related derivatives of benzylideneaniline.[1-4] This mode of binding is analogous to that found in acetatobis[2-(phenylazophenyl)]rhodium[8] and proposed for numerous other metal complexes derived from azobenzene.[5-7]

On the whole, the conformation of the coordinated bza ligand closely resembles that of free benzylidineaniline.[13] The aniline phenyl ring (C(12)-C(17)) is twisted by 57.0° from the imine (CC=NC) plane in the complex; the corresponding twist in free bza is 55°. The other phenyl ring is nearly coplanar with the imine grouping, forming a dihedral angle of 3.0° with the imine plane, as compared to a value of 10° for the corresponding angle in free bza. The C=N bond is slightly lengthened upon coordination, from 1.237 (3) to 1.285 (10) Å. The N-C(12) and C(11)-C(10) distances of 1.428 (10) and 1.443 (10) Å are both marginally less than the corresponding bond lengths of 1.460 (3) and 1.496 (3) Å in free benzylidineaniline. The chelating coordination of the bza molecule also results in some distortion of the C(5)-C(10)-C(11)-CN grouping, as is most readily evident from the shortening of the C(5)···N distance from 2.92 to 2.639 (10) Å upon coordination.

The marked departure of the coordinated bza from planarity is in contrast to the near-coplanarity of the 2-phenyl-

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(25) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-840.

Table IV. Least-Squares Planes[a]

1. Plane Containing C(5), C(6), C(7), C(8), C(9), C(10)

Equation of Plane: $0.9939X - 0.1048Y - 0.0347Z = 1.9722$

Distances to Plane, Å

C(5)	−0.001	C(9)	−0.001
C(6)	−0.004	C(10)	0.003
C(7)	0.006	C(11)	−0.038
C(8)	−0.004	N	−0.098

2. Plane Containing C(3), C(4), C(5), N

Equation of Plane: $0.9927X - 0.0920Y - 0.0780Z = 1.9123$

Distances to Plane, Å

C(3)	0.011	N	0.010
C(4)	−0.011	Mn	−0.008
C(5)	−0.010		

3. Plane Containing C(1), C(2), C(4), C(5)[b]

Equation of Plane: $0.0378X + 0.8978Y - 0.4387Z = 1.4357$

Distances to Plane, Å

C(1)	−0.042	C(5)	0.042
C(2)	−0.042	Mn	−0.035
C(4)	0.043		

4. Plane Containing C(1), C(2), C(3), N

Equation of Plane: $-0.1216X - 0.3447Y - 0.9308Z = -1.4805$

Distances to Plane, Å

C(1)	−0.002	N	0.002
C(2)	−0.002	Mn	0.124
C(3)	0.002		

5. Plane Containing C(12), C(13), C(14), C(15), C(16), C(17)

Equation of Plane: $0.4043X - 0.8367Y - 0.3694Z = -2.0353$

Distances to Plane, Å

C(12)	−0.021	C(16)	0.008
C(13)	0.023	C(17)	0.006
C(14)	−0.009	N	−0.111
C(15)	−0.006		

6. Plane Containing C(10), C(11), C(12), N

Equation of Plane: $0.9881X - 0.1388Y - 0.0670Z = 1.7443$

Distances to Plane, Å

C(10)	0.006	C(12)	0.006
C(11)	−0.006	N	−0.006

7. Plane Containing Mn, C(5), C(10), C(11), N

Equation of Plane: $0.9914X - 0.1084Y - 0.0737Z = 1.8690$

Distances to Plane, Å

Mn	0.006	C(11)	0.010
C(5)	−0.004	N	−0.011
C(10)	−0.001		

Angles between Perpendiculars to These Planes

Planes	Angle, deg	Planes	Angle, deg
1-2	2.6	2-4	90.6
1-4	88.2	2-7	1.0
1-5	59.9	3-4	85.1
1-6	3.0	5-6	57.0
1-7	2.2	5-7	58.7
2-3	90.2		

[a] Unit weights were employed in the calculation of all planes. The equations of the planes are expressed with respect to coordinates (*X, Y, Z*) referred to an orthogonal system (*A, B, C*) oriented with respect to the crystallographic axes such that *A* is parallel to *a*, *B* is parallel to $c^* \times a$, and *C* is parallel to $A \times B$.

[b] These atoms are not strictly coplanar; the plane is included for comparison with results tabulated in the following paper.

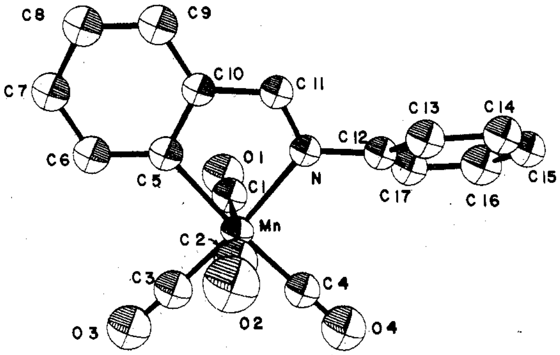

Figure 1. A perspective view of the $C_6H_5NCHC_6H_4Mn(CO)_4$ molecule. Thermal ellipsoids are drawn at the 50% probability level, with the exception that the ellipsoid for C(15) has been reduced in size for clarity.

azophenyl moieties in $(C_6H_4N_2C_6H_5)_2Rh(O_2CCH_3)_2$[8,25a] and $C_6H_4N_2C_6H_5PdCl(PEt_3)_2$.[11] The problem of the conformational variations in the isoelectronic series azobenzene, benzylideneaniline, stilbene has most recently been considered by Burgi and Dunitz.[26] These workers reproduced the experimental structural results by a simple model in which conformations were determined by a delicate balance between π-electron energy and nonbonded repulsions, with the latter factor favoring the nonplanar conformation. Qualitatively similar conclusions had been reached by other workers before detailed structural data became available.[27] The critical nonbonded interactions were taken to be those involving the imine CH group and an ortho CH group of the aniline phenyl ring. It is particularly informative to consider the contact between hydrogen atoms of these two groups in the free ligand and in the complex. This contact is estimated to be 2.63 and 2.68 Å in free bza and in the complexed ligand, respectively. This may be compared with a value of 2.4 Å for twice the van der Waals radius of a hydrogen atom. For a hypothetical planar bza molecule, with the bond lengths and angles of free and complexed bza, the H· · ·H contacts are 2.04 and 1.88 Å, respectively. The corresponding contact in stilbene is estimated to be 2.10 Å, though the structure is not well-refined and this estimate is subject to considerable uncertainty. Reduction of steric interactions appears to be an important factor in accounting for the nonplanarity of both free and coordinated bza. The balance between competing effects believed to be responsible for the conformation of free bza[26] is not sufficiently altered upon metal coordination to cause any major conformational change.[28-32] A recent nmr study of protonated bza suggests that it too has a conformation little different from that of the free molecule.[33]

The coordination about the manganese atom is distorted octahedral; the principal distortions are related to the angle of 79.4 (3)° subtended by the chelating atoms and to a non-

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[25a] Note Added in Proof. A complete report of the structural analysis of this compound has very recently become available [R. J. Hoare and O. S. Mills, *J. Chem. Soc., Dalton Trans.*, 2138 (1972)]. The torsion angles about the C-N bonds to the two free phenyl rings are 14 and 22°, respectively. In the closely related complex $(C_6H_4N_2C_6H_5RhClCO)_2$, the free phenyl rings are twisted by angles of 53.6 and 45.1° from the plane of the chelate ring to which they are bound [R. J. Hoare and O. S. Mills, *ibid.*, 2141 (1972)]. Clearly, the degree of twisting of the free phenyl ring in azobenzene derivatives of this type depends sensitively upon the details of its environment.

(26) H. B. Burgi and J. D. Dunitz, *Helv. Chim. Acta*, **54**, 1255 (1971).

(27) This earlier work is cited in ref 26.

(28) Recently reported work[29] indicates that *p*-chlorobenzylidine-*p*-chloroaniline is planar in the solid state. Apparently crystal packing forces and/or electronic effects of the halogen substituent are sufficient to overcome the energy barrier between the twisted and planar forms. In solution, the nonplanar form appears to predominate.

(29) C. J. Eckhardt and J. Bernstein, *J. Amer. Chem. Soc.*, **94**, 3247 (1972).

(30) In the structurally related iron carbonyl complex $(C_6H_4CHCC_6H_5)Fe_2(CO)_6$, on the other hand, the organic ligand adopts a twisted conformation (dihedral angle 57°)[31] in preference to the planar conformation of the parent molecule, stilbene.[32]

(31) Y. Degreve, J. Meunier-Piret, M. van Meersche, and P. Piret, *Acta Crystallogr.*, **23**, 119 (1967).

(32) J. M. Robertson and I. Woodward, *Proc. Roy. Soc., Ser. A*, **162**, 568 (1937).

(33) A. van Putten and J. W. Pavlik, *Tetrahedron*, **27**, 3007 (1971).

linearity of the C(1)-Mn-C(2) vector. This latter distortion involves an angular displacement of C(1) and C(2) away from C(4) and toward C(5), with a resulting C(1)-Mn-C(2) angle of 172.2 (4)°. The Mn-C(5) distance of 2.060 (8) Å is identical within experimental error to the Mn-C(sp^2) distance of 2.072 Å found in *cis*-($CH_3NHCO)Mn(NH_2CH_3)(CO)_4$[34] and is shorter by about 0.06 Å than the value predicted by Churchill[35] (on the basis of a Mn single-bond covalent radius of 1.39 Å[36]) for the length of a single Mn-C(sp^2) bond. The Mn-N distance of 2.070 (7) Å agrees well with that estimated from a manganese covalent radius of 1.39 Å and an N(sp^2) radius of *ca.* 0.68 Å.

The C-C distances within the phenyl rings average to 1.398 (16) Å and no individual distance deviates significantly from this value. The standard deviation of an individual C-C(phenyl) distance, as estimated from the variation in observed distances on the assumption of equivalent distances, is greater than their mean least-squares esd by a factor of about 1.3. The variations in C-C distances are comparable for the two rings. The mean Mn-carbonyl C and C-O bond distances of 1.795 and 1.153 (9) Å are of normal magnitudes; there appears to be some variation in the individual Mn-C-(carbonyl) distances. None of the Mn-C-O angles deviate from linearity by more than 2.5°.

A comparison of this structure with that of the closely related *N*,*N*-dimethylbenzylamine complex $(CH_3)_2NCHC_6H_4Mn(CO)_4$ may be found in the following paper.[37]

Registry No. $C_6H_5NCHC_6H_4Mn(CO)_4$, 36594-09-9.

Acknowledgment. Support of this work by the National Science Foundation (Grant GP-20603) is gratefully acknowledged.

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[34] D. M. Chipman and R. A. Jacobson, *Inorg. Chim. Acta*, 1, 393 (1967).

[35] M. R. Churchill, *Perspect. Struct. Chem.*, 3, 91 (1970).

[36] F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, 5, 1851 (1966).

[37] R. G. Little and R. J. Doedens, *Inorg. Chem.*, 12, 844 (1973).

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Crystal and Molecular Structure of an Ortho-Metalated *N*,*N*-Dimethylbenzylamine-Manganese Carbonyl Complex, Tetracarbonyl-2-(dimethylaminomethyl)phenylmanganese, $C_6H_4CH_2N(CH_3)_2Mn(CO)_4$

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A single-crystal X-ray structural investigation has established the crystal and molecular structure of the ortho-metalated manganese carbonyl complex derived from *N*,*N*-dimethylbenzylamine. Crystals of tetracarbonyl-2-(dimethylaminomethyl)phenylmanganese are monoclinic, with eight molecules in a unit cell of dimensions $a = 27.36$ (1), $b = 6.805$ (4), $c = 15.12$ (1) Å, $\beta = 93.30$ (3)°. The space group is $C2/c$. Observed and calculated densities are 1.43 and 1.35 (5) g/cm^3, respectively. Full-matrix anisotropic least-squares refinement, based upon 1989 independent nonzero diffractometer data, converged to a conventional discrepancy factor of 0.047. The discrete monomeric $C_6H_4CH_2N(CH_3)_2Mn(CO)_4$ molecules contain a manganese atom bound in a distorted octahedral configuration to four carbonyl groups and to the chelating ligand. The ligand is bound *via* a metal-nitrogen bond and a metal-carbon σ bond to the ortho position of the phenyl ring. The five-membered chelate ring is distinctly puckered. The Mn-C and Mn-N distances are 2.139 (3) and 2.070 (7) Å, respectively. Comparison of the details of the structures with those for two closely related tetracarbonylmanganese complexes leads to a number of generalizations concerning this structure type.

Introduction

In the preceding paper, we reported the results of a crystal structure analysis of the ortho-metalated product obtained from the reaction of benzylidineaniline with $CH_3Mn(CO)_5$.[1] Ortho-metalation reactions[2] are also known for benzyldialkylamines, $C_6H_5CH_2NR_2$.[3] In this paper, the results of a crystal structure analysis of a product of such a reaction, $[C_6H_4CH_2N(CH_3)_2]Mn(CO)_4$, are reported. This investigation was undertaken in order to compare the details of the structure of this compound with those for the benzylidineaniline complex and thereby to help establish the structural systematics of this important structure type.

Experimental Section

Collection and Reduction of Intensity Data. A sample of $C_6H_4CH_2N(CH_3)_2Mn(CO)_4$ was generously supplied by Dr. M. I. Bruce of the University of Bristol. Suitable single crystals were prepared by recrystallization from light petroleum ether. Precession photographs (*h*0*l*, *h*1*l*, 0*kl*, 1*kl*) displayed monoclinic symmetry with systematic absences ($h0l$, $l \neq 2n$; hkl, $h + k \neq 2n$) consistent with the space groups Cc and $C2/c$. Successful solution of the structure was achieved in the latter centrosymmetric space group. Lattice parameters were obtained by least-squares refinement[4] of the setting angles of 14 reflections with $2\theta \geq 40°$ which had been accurately centered on a Picker four-circle X-ray diffractometer. The unit cell constants (23°, λ(Mo Kα_1) 0.70926 Å) obtained in this manner are $a = 27.36$ (1), $b = 6.805$ (4), $c = 15.12$ (1) Å, and $\beta = 93.30$ (3)°. The numbers in parentheses are the standard deviations obtained from the least-squares refinement of the setting angles. Calculated ($Z = 8$)

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[1] R. G. Little and R. J. Doedens, *Inorg. Chem.*, 12, 840 (1973).

[2] G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).

[3] A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, 90, 909 (1968).

[4] Programs employed in this structural analysis included local versions of PICK (J. A. Ibers) for cell refinement and generation of diffractometer settings; PICKOUT (R. J. Doedens, J. A. Ibers) for data processing; GONO (W. C. Hamilton) for absorption correction; FORDAP (A. Zalkin) for Fourier summation; UCIGLS (derived from Busing, Martin, and Levy's ORFLS) for structure factor calculations and least-squares refinement; ORFFE (Busing, Martin, and Levy) for function and error calculations; PLANET (D. L. Smith) for least-squares plane calculations; DANFIG (R. J. Dellaca, W. T. Robinson) and ORTEP (C. K. Johnson) for preparation of figures; and RSCAN (R. J. Doedens) for evaluation of the weighting scheme. All computations were carried out on the local PDP-10 computer.