(26) We note here that binuclear species are known both with symmetrical μ-NO ligands (*e.g.*, ref 27) and with highly unsymmetrical μ-NO ligands (*e.g.*, ref 28).

(27) (π-C_5H_5)(NO)Cr(μ-NO)(μ-NH_2)Cr(NO)(π-C_5H_5): L. Y. Y. Chan and F. W. B. Einstein, *Acta Crystallogr., Sect. B*, **26**, 1899 (1970).

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Crystal and Molecular Structure of Tricarbonyl[(methylsulfidomethyl)phenyl-*2-C,S*]triphenylphosphinemanganese, an Ortho-Metalated Complex of a Sulfur Donor Ligand

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An ortho-metalated structure has been demonstrated for tricarbonyl[(methylsulfidomethyl)phenyl-*2-C,S*]triphenylphosphinemanganese by a crystal structure analysis. This material crystallizes in space group $P\bar{1}$ of the triclinic system with a = 11.022 (7) Å, b = 13.485 (9) Å, c = 9.123 (6) Å, α = 94.52 (1)°, β = 109.90 (1)°, and γ = 98.14 (1)°. Calculated (Z = 2) and observed densities are 1.43 and 1.42 (1) g/cm^3, respectively. The structure analysis was based upon 3385 nonzero intensity data, collected by counter methods and refined by full-matrix least-squares techniques to a final conventional discrepancy factor of 0.057. The complex has a distorted octahedral configuration about Mn, with the organosulfur ligand bound in a chelating fashion *via* Mn–C and Mn–S bonds. The five-membered chelate ring is nonplanar, with the sulfur atom 0.46 Å out of the plane defined by the Mn and three carbon atoms. The triphenylphosphine ligand occupies an axial position and the methyl group lies on the side of the equatorial plane opposite the phosphine ligand. The structural features of this complex are compared with those of closely related compounds derived from nitrogen donor ligands.

Introduction

Intramolecular ortho-metalation reactions continue to be a subject of much interest among organometallic chemists.[1] This type of reaction was first reported in 1965[2] and has subsequently been observed in a large number of systems.[3] By far the majority of these have involved metal complexes of nitrogen or phosphorus donor ligands. However in recent years ortho-metalation reactions have also been reported for systems involving other donor atoms including As,[6-8] Sb,[6] S,[5,8-11] and O.[12] In the case of sulfur donor ligands, ortho-metalated complexes have been obtained from aromatic thioketones,[5,9] benzyl methyl sulfide,[11] and *O*-ethyl thiobenzoate.[10] In certain cases, sulfur donor ligands have failed to yield metalated products when subjected to conditions under which metalation readily occurs with the analogous nitrogen donor.[13,14] The complex $C_6H_4CH_2SCH_3Mn(CO)_3(P(C_6H_5)_3)$ was obtained by triphenylphosphine substitution of $C_6H_4CH_2SCH_3Mn(CO)_4$, the latter compound being a noncrystallizable oil obtained from the reaction of benzyl methyl sulfide with $CH_3Mn(CO)_5$. Our crystal structure analysis of the triphenylphosphine derivative was undertaken to document its proposed metalated structure and to compare its structural details with those of closely related complexes derived from the N donor ligands benzylideneaniline[15] and *N,N*-dimethylbenzylamine.[16] A preliminary report of the synthesis and structure of this complex has appeared.[11]

Experimental Section

Collection and Reduction of Intensity Data. A sample of $C_6H_4CH_2SCH_3Mn(CO)_3P(C_6H_5)_3$ was supplied by Dr. M. I. Bruce of the University of Bristol. Suitable single crystals could be obtained by recrystallization from diethyl ether. Precession photographs showed no evidence of monoclinic or higher symmetry; the assignment of the crystals to the triclinic crystal system was confirmed by a Delaunay reduction. Statistical analysis of normalized structure factors[17] strongly suggested the centrosymmetric space group $P\bar{1}$ and successful solution and refinement of the structure were achieved on the basis of this group. Lattice parameters were determined from least-squares refinement of the setting angles of 16 reflections which had been accurately centered on a Picker four-circle X-ray diffractometer. The three shortest noncoplanar lattice translations define a cell (23°, λ(Mo Kα_1) 0.70930 Å) with a = 11.022 (7) Å, b = 13.485 (9) Å, c = 9.123 (6) Å, α = 94.52 (1)°, β = 109.90 (1)°, and γ = 98.14 (1)°. All results reported are referred to this cell, though a different, arbitrarily chosen, cell was employed during data collection. Calculated (Z = 2) and observed (flotation in aqueous $ZnBr_2$) densities are 1.43 and 1.42 (1) g/cm^3, respectively.

Intensity data were collected from a yellow tabular crystal of dimensions 0.43 × 0.30 × 0.17 mm mounted in a thin-walled glass capillary. The shortest dimension of the crystal was perpendicular to the well-developed $\{1\bar{1}0\}$ faces; other bonding planes belonged to the $\{010\}$, $\{10\bar{1}\}$, $\{1\bar{3}0\}$, and $\{2\bar{1}\bar{2}\}$ forms. The average full width at half-maximum of peak profiles obtained by narrow-source open-counter ω scans for this crystal was ~0.10°. The general procedures employed in data collection paralleled those previously described.[16] The takeoff angle was 2.1° and the diffracted beam was filtered through 3.0-mil Nb foil. A 4 × 4 mm counter aperture was positioned 28 cm from the crystal. The pulse height analyzer was set to admit ~95% of the Mo Kα peak. A scan range of −0.55° to +0.65° in 2θ from the calculated scattering angle was used for reflections with $2\theta \leq 30°$. This scan range was increased by 0.10° for reflections with $30° < 2\theta < 42.5°$ and by an additional 0.10° for higher angle reflections. A scan rate of 1°/min in 2θ was employed and stationary-background counts of 20 sec were taken at each end of the scan. Four standard reflections were measured at intervals of 100 reflections throughout data collection; the intensities of these reflections showed an average variation of ±1.4%, substantially less than their estimated standard deviations. Owing to instrumental problems, several weeks elapsed between collection of data with 2θ

Table I

Positional and Thermal Parameters for $C_6H_4CH_2SCH_3Mn(CO)_3P(C_6H_5)_3$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	0.36314 (6)[b]	0.20655 (5)	0.33785 (7)	55.8 (9)	41.5 (6)	79.0 (13)	16.7 (4)	25.5 (7)	7.1 (5)
P	0.17018 (11)	0.26931 (8)	0.20077 (13)	57.3 (13)	37.1 (8)	78.5 (17)	12.9 (7)	25.7 (11)	5.4 (8)
S	0.29256 (12)	0.07689 (9)	0.13042 (14)	76.8 (14)	40.5 (8)	122.8 (20)	13.2 (8)	38.4 (13)	−0.7 (9)
C(2)[c]	0.5172 (5)	0.1690 (4)	0.4258 (5)	77 (6)	61 (4)	94 (7)	23 (4)	33 (5)	9 (4)
C(3)	0.4250 (5)	0.3154 (4)	0.4873 (5)	83 (5)	55 (3)	86 (7)	25 (4)	21 (5)	0 (4)
C(4)	0.2982 (5)	0.1360 (4)	0.4623 (6)	80 (5)	58 (3)	123 (8)	26 (4)	48 (5)	17 (4)
C(5)	0.4549 (4)	0.2760 (3)	0.2003 (5)	49 (4)	46 (3)	93 (6)	10 (3)	18 (4)	13 (4)
C(6)	0.5155 (5)	0.3773 (4)	0.2292 (6)	85 (6)	51 (3)	116 (8)	−2 (3)	19 (5)	8 (4)
C(7)	0.5706 (6)	0.4202 (5)	0.1311 (7)	101 (7)	71 (4)	167 (10)	−10 (4)	24 (7)	34 (5)
C(8)	0.5702 (6)	0.3642 (5)	−0.0011 (7)	95 (6)	80 (5)	173 (10)	7 (4)	56 (7)	52 (6)
C(9)	0.5130 (5)	0.2632 (4)	−0.0335 (6)	96 (6)	76 (4)	130 (8)	27 (4)	60 (6)	27 (5)
C(10)	0.4583 (5)	0.2206 (4)	0.0663 (6)	70 (5)	51 (3)	116 (7)	20 (3)	41 (5)	14 (4)
C(11)	0.4033 (7)	0.1119 (4)	0.0293 (7)	194 (9)	52 (4)	206 (11)	4 (5)	145 (9)	−11 (5)
C(12)	0.3412 (7)	−0.0384 (4)	0.1916 (7)	178 (9)	46 (4)	197 (11)	37 (5)	73 (8)	20 (5)
O(2)	0.6170 (4)	0.1474 (4)	0.4852 (5)	87 (4)	122 (4)	179 (7)	60 (3)	41 (5)	52 (4)
O(3)	0.4661 (4)	0.3791 (3)	0.5872 (5)	149 (6)	84 (3)	144 (7)	18 (4)	13 (5)	−40 (4)
O(4)	0.2698 (4)	0.0916 (3)	0.5505 (5)	160 (6)	97 (4)	185 (7)	33 (4)	107 (6)	68 (4)

Group Parameters[d]

Group	x_o	y_o	z_o	ϕ	θ	ρ
Ring 1	−0.09247 (19)	0.16285 (15)	0.24652 (22)	−1.1736 (17)	2.6624 (19)	−0.0822 (21)
Ring 2	0.16929 (22)	0.50154 (19)	0.30918 (30)	−3.1273 (25)	2.7857 (19)	1.6683 (25)
Ring 3	0.09153 (20)	0.23904 (15)	−0.17456 (24)	−1.4386 (86)	−1.7970 (16)	−2.0043 (86)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Tabulated β values have been multiplied by 10^4. [b] Numbers in parentheses in all tables and in the text are estimated standard deviations in the least significant figures. [c] The numbering of atoms in the manganese coordination sphere and in the chelate ring corresponds to the system used for the closely related compounds in ref 15 and 16. [d] These parameters are as defined by R. J. Doedens in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, pp 198–200. The origin of each group was taken at its geometric center. Angular coordinates are given in radians.

< 30° and the higher angle data. For this reason, separate scale factors were maintained for the two subsets of data. Copper foil attenuators were automatically inserted in the incident X-ray beam for reflections with counting rates greater than ~10000 counts/sec. The intensities of all independent reflections with $2\theta \leq 50°$ were measured.

Previously described methods[18] were employed in processing the data. The p factor in the expression for the estimated standard deviation of the observed intensities was assigned a value of 0.04. Of the 4372 data collected, 3385 were above background by three or more standard deviations; only these data were employed in subsequent work. A test calculation, based upon a linear absorption coefficient of 8.39 cm^{-1}, showed that neglect of an absorption correction would have a *maximum* effect of <5% on any single intensity. Hence absorption corrections were not applied.

Solution and Refinement of the Structure. The structure was solved by conventional Patterson and Fourier methods. Isotropic least-squares refinement of all nonhydrogen atoms, with phenyl rings of the triphenylphosphine ligand treated as rigid groups, converged to discrepancy factors $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o| = 0.089$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.117$. A single cycle with anisotropic thermal parameters for all nongroup atoms further reduced the residual factors to $R_1 = 0.068$ and $R_2 = 0.093$. A difference Fourier map calculated at this stage showed peaks ranging in height from 0.32 to 0.99 e/Å^3 at reasonable positions for all 24 hydrogen atoms, including those of the methyl group. All positive peaks >0.5 e/Å^3 were within 1.1 Å of a carbon atom. The hydrogen atom positions were idealized (C–H = 0.95 Å, C–C–H = 120° for phenyl rings and 109.5° for methyl and methylene groups) and included at fixed positions in the final refinement. In this refinement phenyl rings were treated as a rigid groups (C–C = 1.392 Å, C–C–C = 120°, individual isotropic temperature factors for group atoms) and all other nonhydrogen atoms were assigned anisotropic temperature factors. Convergence was achieved with $R_1 = 0.057$ and $R_2 = 0.074$; in the final cycle no parameter shifted by more than 0.35σ. The final standard deviation of an observation of unit weight was 2.6. Calculation of structure factors for data with $F_o^2 < 3\sigma(F_o^2)$ showed that for only 6 of the 995 such data did F_c^2 exceed the 3σ cutoff by as much as three standard deviations. Evaluation of mean $w\Delta F^2$ values for subsets of the data as functions of F_o, uncorrected intensity, and $(\sin\theta)/\lambda$ showed no significant trends except for a slight overemphasis of the data with low intensities and high $(\sin\theta)/\lambda$ values. This undoubtedly reflects residual inadequacies in the isotropic–anisotropic thermal model employed.

Throughout the least-squares refinement, the weights of the observed reflections were taken as $w = 4F_o^2/\sigma^2(F_o^2)$ and the function minized was $\sum w(|F_o| - |F_c|)^2$. Scattering factors for Mn, C, S, and O were taken from ref 19 and those of Stewart, *et al.*, were employed for H.[20] Structure factor calculations used the $\Delta f'$ and $\Delta f''$ values of Cromer[21] in correcting for the anomalous scattering by the Mn and S atoms.

Final atomic and group parameters are listed in Table I; parameters of group atoms and hydrogen atoms are tabulated in Table II. Intramolecular distances and angles are given in Tables III and IV, respectively. Principal amplitudes of thermal motion for atoms refined anisotropically are listed in Table V. A table of observed and calculated structure factors is available.[22] See Table VI for molecular planes and dihedral angles.

Description and Discussion of the Structure

The crystal structure of tricarbonyl[(methylsulfidomethyl)phenyl-2-*C*,*S*]triphenylphosphinemanganese is made up of discrete molecular units. A distorted octahedral coordination polyhedron is formed by the three carbonyl groups, the triphenylphosphine ligand, and the chelating organosulfur moiety. The latter ligand is bound in an ortho-metalated fashion *via* Mn–C and Mn–S bonds. The overall configuration is thus analogous to those of the previously reported ortho-metalated tetracarbonylmanganese complexes derived from benzylidineaniline[15] and *N*,*N*-dimethylbenzylamine.[16] This crystal structure analysis has thus provided confirmation of the proposed structure of this complex and establishes it as the first structurally documented example of an ortho-metalated complex of a sulfur donor ligand. Two views of the molecular structure are provided in Figures 1 and 2.

As is most clearly evident in Figure 2, the five-membered chelate ring is distinctly nonplanar; the sulfur atom is 0.46 Å out of the plane defined by Mn, C(5), C(10), and C(11). The degree of folding of the ring may be expressed by the parameters α and β,[23] analogous to those which have previously

Table II. Positional and Thermal Parameters of Group Atoms and Hydrogen Atoms

Atom	x	y	z	B, Å^2
	(a) Group Carbon and Hydrogen Atoms			
R1C1[a]	0.0193 (2)[b]	0.2100 (2)	0.2237 (4)	2.56 (8)
R1C2	−0.0780 (3)	0.2646 (2)	0.2271 (4)	3.22 (9)
R1C3	−0.1898 (3)	0.2175 (2)	0.2499 (4)	3.78 (10)
R1C4	−0.2042 (2)	0.1157 (2)	0.2693 (4)	3.89 (10)
R1C5	−0.1069 (3)	0.0611 (2)	0.2660 (4)	3.74 (10)
R1C6	0.0048 (3)	0.1082 (2)	0.2432 (4)	3.05 (9)
R1H2	−0.0682 (5)	0.3341 (2)	0.2138 (6)	. . .[c]
R1H3	−0.2562 (4)	0.2548 (3)	0.2522 (6)	. . .
R1H4	−0.2804 (3)	0.0835 (3)	0.2849 (6)	. . .
R1H5	−0.1167 (5)	−0.0084 (2)	0.2793 (6)	. . .
R1H6	0.0713 (4)	0.0709 (3)	0.2409 (6)	. . .
R2C1	0.1711 (3)	0.4022 (2)	0.2566 (4)	2.85 (8)
R2C2	0.1581 (4)	0.4745 (3)	0.1541 (3)	4.59 (12)
R2C3	0.1563 (5)	0.5738 (2)	0.2067 (4)	6.14 (15)
R2C4	0.1674 (4)	0.6009 (2)	0.3617 (5)	5.96 (15)
R2C5	0.1805 (4)	0.5286 (3)	0.4642 (3)	5.48 (14)
R2C6	0.1823 (4)	0.4293 (2)	0.4117 (3)	4.06 (11)
R2H2	0.1505 (5)	0.4560 (4)	0.0483 (3)	. . .
R2H3	0.1474 (7)	0.6231 (3)	0.1367 (6)	. . .
R2H4	0.1662 (6)	0.6687 (2)	0.3976 (7)	. . .
R2H5	0.1881 (6)	0.5471 (4)	0.5701 (4)	. . .
R2H6	0.1912 (7)	0.3799 (3)	0.4817 (5)	. . .
R3C1	0.1219 (3)	0.2542 (2)	−0.0124 (2)	2.56 (8)
R3C2	0.0096 (8)	0.1870 (8)	−0.1080 (4)	3.21 (9)
R3C3	−0.0207 (8)	0.1718 (9)	−0.2702 (4)	3.78 (10)
R3C4	0.0612 (3)	0.2238 (3)	−0.3367 (2)	4.03 (10)
R3C5	0.1734 (8)	0.2911 (8)	−0.2411 (4)	4.14 (11)
R3C6	0.2038 (8)	0.3063 (9)	−0.0790 (4)	3.20 (9)
R3H2	−0.0463 (13)	0.1515 (13)	−0.0626 (6)	. . .
R3H3	−0.0974 (13)	0.1259 (15)	−0.3354 (6)	. . .
R3H4	0.0404 (4)	0.2134 (4)	−0.4474 (2)	. . .
R3H5	0.2294 (13)	0.3266 (13)	−0.2865 (6)	. . .
R3H6	0.2804 (13)	0.3522 (15)	−0.0137 (6)	. . .
	(b) Nongroup Hydrogen Atoms			
C6H	0.5184	0.4180	0.3207	. . .
C7H	0.6097	0.4899	0.1546	. . .
C8H	0.6088	0.3944	−0.0692	. . .
C9H	0.5116	0.2233	−0.1249	. . .
C11H1	0.4733	0.0749	0.0604	. . .
C11H2	0.3575	0.0957	−0.0809	. . .
C12H1	0.4337	−0.0276	0.2435	. . .
C12H2	−0.2996	−0.0609	0.2618	. . .
C12H3	0.3163	−0.0884	0.1023	. . .

[a] Group atoms are designated by labels of the form R*n*C(or H)*m*, where *n* denotes the number of the phenyl ring and *m* the number of the atom within the ring. In all rings, C1 is the point of attachment and numbering is sequential around the ring. The number of a H atom corresponds to that of the C atom to which it is bound. [b] Estimated standard deviations of coordinates of group atoms are derived from the esd's of the group parameters by conventional error propagation techniques. They may not meaningfully be used as a basis for estimation of errors in distances or angles within a group. [c] Hydrogen atoms were assigned isotropic thermal parameters 1 unit greater than those of the corresponding carbon atoms. These temperature factors were updated periodically but were not refined.

Table III. Intramolecular Distances (Å)

Mn–C(2)	1.780 (6)	C(2)–O(2)	1.139 (6)
Mn–C(3)	1.802 (6)	C(3)–O(3)	1.121 (6)
Mn–C(4)	1.799 (6)	C(4)–O(4)	1.140 (6)
Mn–C(5)	2.064 (5)	C(5)–C(6)	1.395 (7)
Mn–P	2.382 (4)	C(6)–C(7)	1.363 (8)
Mn–S	2.310 (4)	C(7)–C(8)	1.370 (9)
S–C(11)	1.800 (6)	C(8)–C(9)	1.381 (8)
S–C(12)	1.785 (6)	C(9)–C(10)	1.371 (7)
P–R1C1	1.828 (4)	C(10)–C(5)	1.396 (6)
P–R2C1	1.822 (5)	C(10)–C(11)	1.470 (8)
P–R3C1	1.819 (5)		
P· · ·C(3)	3.061 (7)	C(2)· · ·S	3.000 (7)
P· · ·C(4)	3.165 (7)	C(2)· · ·C(12)	3.294 (9)
P· · ·C(5)	3.130 (8)	C(3)· · ·C(4)	2.569 (9)
P· · ·S	3.207 (5)	C(3)· · ·C(5)	2.769 (8)
C(2)· · ·C(3)	2.456 (8)	C(4)· · ·S	3.047 (8)
C(2)· · ·C(4)	2.532 (8)	C(4)· · ·C(12)	3.471 (9)
C(2)· · ·C(5)	2.565 (8)		

Table IV. Bond Angles (deg)

P–Mn–C(2)	172.6 (2)	R1C1–P–R3C1	101.3 (2)
P–Mn–C(3)	93.0 (2)	R2C1–P–R3C1	104.7 (2)
P–Mn–C(4)	97.4 (2)	Mn–C(2)–O(2)	178.0 (5)
P–Mn–C(5)	89.2 (2)	Mn–C(3)–O(3)	175.6 (5)
P–Mn–S	86.2 (1)	Mn–C(4)–O(4)	173.1 (5)
C(2)–Mn–C(3)	86.6 (2)	Mn–C(5)–C(6)	125.0 (4)
C(2)–Mn–C(4)	90.0 (2)	Mn–C(5)–C(10)	119.7 (4)
C(2)–Mn–C(5)	83.4 (2)	Mn–S–C(11)	101.2 (2)
C(2)–Mn–S	93.5 (2)	Mn–S–C(12)	112.0 (2)
C(3)–Mn–C(4)	91.0 (3)	C(11)–S–C(12)	100.0 (3)
C(3)–Mn–C(5)	91.2 (2)	C(6)–C(5)–C(10)	115.3 (4)
C(3)–Mn–S	174.1 (2)	C(5)–C(6)–C(7)	122.4 (5)
C(4)–Mn–C(5)	172.9 (2)	C(6)–C(7)–C(8)	120.8 (6)
C(4)–Mn–S	94.9 (2)	C(7)–C(8)–C(9)	118.8 (5)
C(5)–Mn–S	82.9 (2)	C(8)–C(9)–C(10)	120.0 (5)
Mn–P–R1C1	116.1 (2)	C(9)–C(10)–C(5)	122.6 (5)
Mn–P–R2C1	116.1 (1)	C(9)–C(10)–C(11)	117.6 (5)
Mn–P–R3C1	116.6 (6)	C(5)–C(10)–C(11)	119.8 (4)
R1C1–P–R2C1	100.9 (2)	C(10)–C(11)–S	111.6 (4)

Table V. Principal Root-Mean Square Amplitudes (Å) of Thermal Motion

Atom	Max	Intermed	Min
Mn	0.198 (1)	0.170 (1)	0.156 (2)
P	0.187 (2)	0.172 (2)	0.160 (2)
S	0.221 (2)	0.202 (2)	0.175 (2)
C(2)	0.239 (7)	0.191 (8)	0.180 (7)
C(3)	0.246 (7)	0.188 (7)	0.174 (7)
C(4)	0.236 (7)	0.207 (7)	0.177 (7)
C(5)	0.203 (6)	0.189 (7)	0.158 (7)
C(6)	0.247 (7)	0.213 (7)	0.188 (7)
C(7)	0.308 (8)	0.228 (8)	0.204 (8)
C(8)	0.300 (8)	0.234 (8)	0.187 (8)
C(9)	0.265 (7)	0.221 (7)	0.188 (7)
C(10)	0.220 (7)	0.202 (7)	0.173 (7)
C(11)	0.351 (8)	0.223 (8)	0.177 (8)
C(12)	0.309 (8)	0.265 (8)	0.187 (8)
O(2)	0.340 (5)	0.256 (5)	0.170 (6)
O(3)	0.336 (6)	0.280 (6)	0.185 (6)
O(4)	0.325 (5)	0.277 (5)	0.180 (6)

been used for metal-coordinated ethylenediamine rings and for the chelate ring in the metalated dimethylbenzylamine complex (henceforth designated Mn(dmb)). In the present case, the values of these parameters are α = 12.5° and β = 19.1°. This indicates a more nearly planar ring than is observed in Mn(dmb) (for which α = 19.2° and β = 32.0°) or in ethylenediamine chelate rings. Comparison of bond angles indicates that the organosulfur chelate ring as a whole is less strained than the analogous organonitrogen ring in Mn(dmb). This is particulary evident in the angles at C(5) and C(10), which approach closely to their ideal trigonal values in the present complex. This is made possible mainly by the acceptance by the S atom of a smaller bond angle [Mn–S–C(11) = 101.2 (2)°] than that at the N atom in Mn(dmb) [106.4 (2)°]. In accord with the general picture of a less strained chelate ring in the organosulfur complex, the S–Mn–C(5) angle of 82.9° is closer to the ideal octahedral value than the corresponding angle of 80.2° in Mn(dmb).[16]

The configuration adopted by the $C_6H_4CH_2SCH_3Mn(CO)_3P(C_6H_5)_3$ molecule is one of several potential isomeric forms. As anticipated, the triphenylphosphine ligand is found in an axial coordination site, trans to a CO group. This position is less hindered sterically than the equatorial coordination sites; it also corresponds to the location of one of the longer Mn–CO bonds in three closely related tetracarbonylmanganese complexes derived from organonitrogen ligands.[15,16,24] Other possibilities for isomerism involve the relationship of the S–CH_3

Table VI. Molecular Planes and Dihedral Angles[a]

1. $-0.7871X + 0.3150Y - 0.5303Z = -2.8686$			
C(5)	0.011	C(8)	0.004
C(6)	−0.006	C(9)	0.002
C(7)	−0.001	C(10)	−0.009
2. $-0.8072X + 0.4242Y - 0.4105Z = -2.2955$			
S	0.054[b]	C(5)	−0.059
C(3)	0.066	Mn	0.053
C(4)	−0.061		
3. $0.0351X - 0.7324Y - 0.6800Z = -3.5744$			
P	−0.021[b]	C(5)	0.026
C(2)	−0.031	Mn*	−0.018
C(4)	0.026		
4. $0.5975X + 0.6020Y - 0.5297Z = 1.5479$			
P	0.012	C(3)	−0.016
S	−0.012	Mn*	−0.118
C(2)	0.016		
5. $-0.7705X + 0.3002Y - 0.5623Z = -2.8833$			
Mn	0.006	C(11)	−0.009
C(5)	−0.016	S*	0.463
C(10)	0.018		
Angles (deg) between Perpendiculars to these Planes			
1–2	9.4	2–4	90.4
1–5	2.2	3–4	93.4
2–3	93.4		

[a] In the calculation of all planes, unit weights were given to all atoms listed except those marked with an asterisk, which were given zero weight. Equations of planes are expressed with respect to coordinates (X, Y, Z) referred to an orthogonal system (A, B, C) oriented such that A is parallel to a, B is parallel to $c^* \times a$, and C is parallel to $A \times B$. [b] The groupings of atoms 2 and 3 are not strictly coplanar but are included to permit comparison with corresponding planes in closedly related molecules.

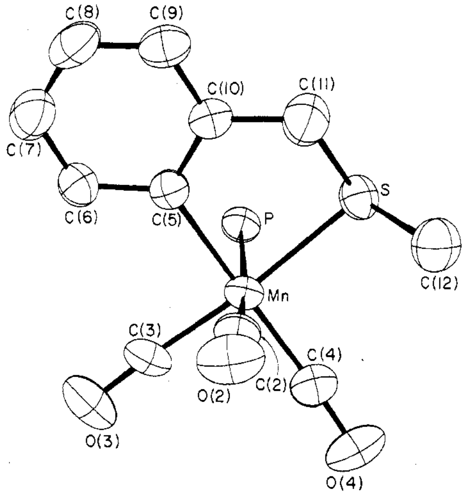

Figure 1. The molecular structure of $C_6H_4CH_2SMeMn(CO)_3PPh_3$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the phenyl rings of the PPh_3 ligand have been omitted for clarity. The atomic numbering scheme corresponds to that used in ref 15, with C(1) and O(1) replaced by the PPh_3 group.

group to the plane defined by Mn, C(5), C(10), and C(11). In the configuration observed, the sulfur atom and the methyl group lie on opposite sides of this plane with the methyl group directed away from the triphenylphosphine ligand. At first sight, the shape and orientation of the thermal ellipsoid for C(11) is suggestive of inversion about S; however none of the other expected effects of such motion are observed. Finally it may be noted that the molecule is asymmetric and that the sample studied was hence a racemate.

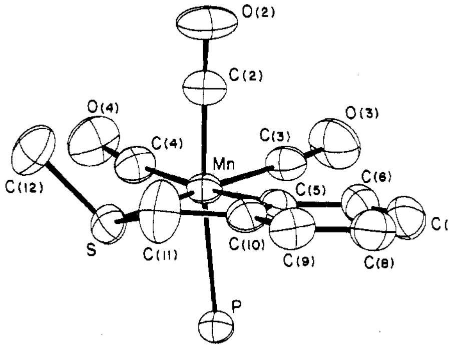

Figure 2. An alternative view of the molecular structure, chosen to illustrate the conformation of the chelate ring.

The major distortions from regular octahedral coordination about the manganese atom are related to the angle of 82.9 (2)° subtended by the chelating C and S atoms, to a nonlinearity of the P–Mn–C(2) angle, and to deformation of the equatorial coordination plane (defined by C(3), C(4), C(5), and S) related to the nonplanarity of the chelate ring. This last mentioned effect is substantially greater in the present case than for Mn(dmb), for which the four equatorial atoms are planar within ~0.025 Å. In the organosulfur complex, deviations from the "best" equatorial plane are of the order of 0.06 Å. As is evident by comparing Figure 2 with the analogous figure of ref 16, the phenyl ring in the present complex lies much more nearly in the equatorial plane than the corresponding ring in Mn(dmb). These observations are consistent with the presence of less steric strain in the sulfur donor complex, owing primarily to the greater capacity of the sulfur atom to accept distortions from a regular tetrahedral geometry.

Bond distances within the metal coordination sphere fall, for the most part, within their expected ranges. The three Mn–C(carbonyl) distances are equal within experimental error, indicating no major differences in structural trans effect among the three other ligands. The Mn–C(5) distance of 2.064 (5) Å agrees well with other Mn–C(phenyl) distances, which have been observed in the range 2.03–2.07 Å.[15,16,24,25] The Mn–P distance of 2.382 (4) Å is near the long end of the range of 2.247 (7)–2.398 (4) Å previously observed for Mn–PR_3 distances.[26-29] It may be noted that, in analogous tetracarbonylmanganese complexes,[15,16,24] one of the apical Mn–C bonds tends to be elongated; also the P···S contact is a relatively short 3.207 (5) Å. The Mn–S distance of 2.310 (4) Å is shorter than would have been estimated by simple covalent radius considerations (using values of ~1.39 Å for Mn[30] and 1.04 Å for S[31]) but well within the range observed for Fe–S distances in various organosulfur–iron complexes.[32] Other distances and angles within the molecule are normal and require no further comment.

In summary, this crystal structure analysis has provided the first documented instance of an ortho-metalated structure involving a sulfur donor ligand. The structure found in the solid state is one of several possible isomeric configurations for this molecule. It has been shown that the MnC_3S chelate ring in the organosulfur complex exists in a less strained configuration than does the MnC_3N ring in the analogous complex derived from dimethylbenzylamine. It would be of interest to determine whether these conformational variations could be related to any trends in chemical behavior of these metalated complexes, *e.g.*, tendencies to undergo insertion[33] or displacement reactions.

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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, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals

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Crystal and Molecular Structure of Dibenzotellurophene Diiodide, $C_{12}H_8TeI_2$[1]

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The structure of dibenzotellurophene diiodide, $C_{12}H_8TeI_2$, has been determined by the use of three-dimensional X-ray data collected on an automated diffractometer with monochromatized Mo Kα radiation. The compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 8.807$ (3) Å, $b = 8.182$ (2) Å, $c = 12.001$ (6) Å, $\alpha = 121.16$ (3)°, $\beta = 101.63$ (3)°, $\gamma = 103.05$ (3)°, and $V = 666.2$ (4) Å^3. The density of 2.660 (2) g cm^{-3} calculated on the basis of two molecules per unit cell agrees with the measured density of 2.66 (2) g cm^{-3}. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to a conventional R index of 2.6% based on 2376 observed reflections. The dibenzotellurophene moiety is nearly planar but shows a twist of 3.3° between the two six-membered rings. Tellurium forms bonds with two carbon atoms at 2.111 (4) and 2.113 (4) Å with a C–Te–C bond angle of 81.8 (2)°. Approximately normal to the C–Te–C plane, tellurium forms axial bonds with iodine atoms at 2.944 (1) and 2.928 (1) Å. The I–Te–I bond angle is 178.47 (1)°. Tellurium also forms weak bonds with iodine atoms in each of two neighboring molecules with Te···I distances of 3.717 (1) and 3.696 (1) Å. The C–Te···I bond angles are 175.1 (1) and 171.1 (1)° so that the configuration about tellurium is octahedral. The intermolecular Te···I bonds link the molecules into infinite chains along the b axis. The observed C–C bond distances in the six-membered rings range from 1.362 (7) to 1.409 (6) Å (average 1.387 Å) and the C–C bond distance between the rings is 1.469 (6) Å.

Introduction

Crystals of organotellurium diiodides display a range of colors from red-orange through dark violet. Structural studies of five of these compounds have disclosed a variety of intermolecular bonding arrangements and suggest a possible relationship between the types of secondary bonds and the colors of the crystals.[2] Investigations to date indicate that the red crystals involve only Te···I intermolecular bonds and that the dark violet color results when I···I intermolecular bonds are present. Dibenzotellurophene diiodide, $C_{12}H_8TeI_2$, which forms brilliant red crystals, provided another interesting case for structural study. Not only did this present an additional opportunity to observe intermolecular bonding in these compounds, but also of even greater interest was the determination of the structural details of the dibenzotellurophene moiety.

Experimental Section

Dibenzotellurophene diiodide was prepared by grinding the dichloride[3] with a twofold excess of potassium iodide under methyl ethyl ketone. After filtration, the solution deposited deep red prismatic crystals suitable for the X-ray study.

A preliminary investigation of several crystals by means of precession photographs showed them to be triclinic and tentative assignments of the cell dimensions, space group, and number of molecules per unit cell were made. The specimen used for the intensity measurements was 0.13 mm × 0.20 mm × 0.36 mm in directions normal to the $\{10\bar{1}\}$, $\{01\bar{2}\}$, and $\{010\}$ faces, respectively. It was mounted with b^* approximately along the ϕ axis of a four-circle computer-controlled diffractometer (Syntex $P\bar{1}$ autodiffractometer) equipped with a scintillation counter and a graphite monochromator. The automatic centering, indexing, and least-squares routines of the instrument were applied to 15 selected reflections, ten of which were in the 2θ range from 15 to 28°. The lattice parameters at 23° based on Mo Kα = 0.71069 Å are $a = 8.807$ (3) Å, $b = 8.182$ (2) Å, $c = 12.001$ (6) Å, $\alpha = 121.16$ (3)°, $\beta = 101.63$ (3)°, $\gamma = 103.05$ (3)°, and $V = 666.2$ (4) Å^3. The measured density of 2.66 (2) g cm^{-3} compares favorably with the calculated value of 2.660 (2) g cm^{-3} for $Z = 2$. The space group was therefore taken as $P\bar{1}$.

The intensity data were collected with Mo Kα radiation, a scan rate of 2° min^{-1}, and a scan range from 1.00° below the Kα_1 peak to 1.00° above the Kα_2 peak. Background counts were taken for half