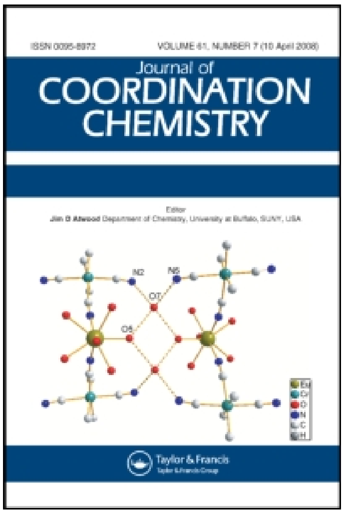

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THE CRYSTAL STRUCTURE OF DIMETHYLDITHIOCARBAMATO(TRIPHENYLPHOSPHINE)-TRICARBONYLMANGANESE(I)

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THE CRYSTAL STRUCTURE OF DIMETHYLDITHIOCARBAMATO(TRIPHENYLPHOSPHINE)-TRICARBONYLMANGANESE(I)

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The structure of $(C_6H_5)_3PMn(CO)_3S_2CN(CH_3)_2$, which is formed as a by-product in the synthesis of $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$, has been determined by single-crystal X-ray diffraction techniques. The compound crystallizes in space group $C2/c$ with 16 molecules in a unit cell of dimensions a = 56.14 Å; b = 8.778 Å; c = 19.75 Å; β = 102.05°. Atomic positions were refined by full-matrix least-squares methods to a final R of 0.083 using 2756 independent reflections. The independent synthesis of this compound is also described.

INTRODUCTION

We have recently described the synthesis[1] and structure[2] of the unusual thiocarboxamido complex $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$ (I), in which the thiocarboxamido ligand is coordinated through both carbon and sulphur atoms. During the course of growing crystals of this compound for X-ray analysis it became apparent that another compound was present as an impurity; however, it was not possible to effect a separation of the two compounds by conventional techniques. Accordingly several crystals of the impurity were selected for X-ray analysis.

Preliminary photographs and a density measurement indicated a formula weight for the compound of approximately 1000 (assuming one molecule per asymmetric unit), suggesting the possibility of a thiocarboxamido-bridged dimer of I, $[(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2]_2$ (F.W. 978). However, solution of the structure revealed that the compound was in fact the dithiocarbamate complex, $(C_6H_5)_3PMn(CO)_3S_2CN(CH_3)_2$, which crystallizes with two independent molecules in the asymmetric unit.

EXPERIMENTAL SECTION

Crystals of $(C_6H_5)_3PMn(CO)_3S_2CN(CH_3)_2$ were separated physically from a mixture of this compound with $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$ which had been recrystallized from dichloromethane-heptane. Crystals were mounted on glass fibers using epoxy cement. Lattice dimensions were measured from Weissenberg and precession photographs, and were corrected for film shrinkage.

Intensity data were collected using a Supper-Pace automated diffractometer having Weissenberg geometry. Variable-length scans in ϕ were used with stationary crystal-stationary counter background counts at the beginning and end of each scan; the total background time was set equal to the total scan time. $CuK_{\bar{\alpha}}$ radiation (λ = 1.54178 Å) was used throughout. Three reference reflections were measured between levels to monitor electronic and crystal stability; approximately 30% decay in intensity was noted, for which a linear correction was

TABLE I
Crystal and intensity collection data

Formula (MW)	$C_{24}H_{21}NO_3PS_2Mn$(521.5)
Space Group	$C2/c$(Z = 16)
a, Å	56.14(11)
b, Å	8.778(9)
c, Å	19.75(3)
β, deg	102.05(6)
V, Å^3	9518.9
d exp(calc), g-cm^{-3}	1.38(1.46)
F(000), electrons	4288
Crystal dimensions	0.45 x 0.15 x 0.10 (b)
(mount axis)	0.50 x 0.10 x 0.10 (c)
μ, cm^{-1}	49.28
Transmission Factors	0.356–0.793

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TABLE II
Final atomic parameters

Molecule A	x	y	z	β,Å^2	Molecule B	x	y	z	β,Å^2
Mn	0.45320(4)	0.0337(3)	0.3073(1)	a	Mn	0.32623(4)	0.3927(3)	0.4922(1)	a
S(1)	0.41659(7)	0.0355(6)	0.2214(2)	a	S(1)	0.30307(7)	0.3337(6)	0.5764(2)	a
S(2)	0.46111(7)	0.1837(6)	0.2146(2)	a	S(2)	0.34940(6)	0.2137(5)	0.5701(2)	a
P	0.44336(6)	0.2622(4)	0.3568(2)	a	P	0.31224(6)	0.1784(5)	0.4234(2)	a
O(1)	0.5005(2)	0.033(2)	0.4063(7)	5.0(3)	O(1)	0.3621(2)	0.476(2)	0.4130(7)	5.8(3)
O(2)	0.4312(2)	−0.166(2)	0.3964(6)	4.6(3)	O(2)	0.2906(2)	0.590(1)	0.4067(6)	4.2(2)
O(3)	0.4677(2)	−0.236(2)	0.2359(7)	6.0(3)	O(3)	0.3431(3)	0.648(2)	0.5813(8)	6.7(3)
N	0.4211(3)	0.203(2)	0.1125(8)	5.3(4)	N	0.3242(3)	0.114(2)	0.6620(8)	5.0(3)
C(1)	0.4824(3)	0.037(2)	0.3656(9)	3.4(3)	C(1)	0.3473(3)	0.433(2)	0.4419(10)	4.3(4)
C(2)	0.4389(3)	−0.090(2)	0.3623(10)	4.3(4)	C(2)	0.3040(3)	0.508(2)	0.4401(8)	2.9(3)
C(3)	0.4623(3)	−0.130(3)	0.2659(11)	5.0(4)	C(3)	0.3376(3)	0.549(2)	0.5451(10)	4.2(4)
C(4)	0.4320(3)	0.141(2)	0.1765(9)	3.8(4)	C(4)	0.3256(3)	0.208(2)	0.6106(9)	4.0(4)
C(5)	0.3954(4)	0.178(3)	0.0833(13)	7.6(6)	C(5)	0.3020(3)	0.108(3)	0.6900(10)	5.4(4)
C(6)	0.4369(4)	0.294(3)	0.0746(14)	8.0(6)	C(6)	0.3441(4)	−0.001(3)	0.6886(11)	5.6(5)
C(7)	0.4187(1)	0.372(1)	0.3059(5)	1.7(2)	C(7)	0.2929(2)	0.056(1)	0.4631(5)	2.4(3)
C(8)	0.4228(2)	0.510(1)	0.2746(6)	4.4(4)	C(8)	0.2690(2)	0.102(1)	0.4619(5)	2.9(3)
C(9)	0.4033(2)	0.588(1)	0.2335(6)	5.3(5)	C(9)	0.2549(1)	0.022(2)	0.5005(6)	3.9(4)
C(10)	0.3798(2)	0.528(1)	0.2238(6)	5.2(4)	C(10)	0.2647(2)	−0.104(1)	0.5403(5)	4.2(4)
C(11)	0.3757(1)	0.391(1)	0.2551(6)	4.0(4)	C(11)	0.2886(2)	−0.150(1)	0.5415(5)	3.3(3)
C(12)	0.3952(2)	0.313(1)	0.2962(5)	2.2(3)	C(12)	0.3027(1)	−0.070(1)	0.5029(5)	2.3(3)
C(13)	0.4345(2)	0.242(1)	0.4393(4)	2.7(3)	C(13)	0.2953(2)	0.219(1)	0.3361(5)	3.5(3)
C(14)	0.4156(5)	0.327(3)	0.4574(7)	2.9(3)	C(14)	0.2730(3)	0.153(2)	0.3063(6)	4.7(4)
C(15)	0.4103(5)	0.310(4)	0.5231(7)	3.6(3)	C(15)	0.2609(3)	0.197(3)	0.2399(7)	6.6(5)
C(16)	0.4239(2)	0.209(1)	0.5706(4)	4.1(4)	C(16)	0.2712(3)	0.306(1)	0.2033(6)	7.3(6)
C(17)	0.4427(5)	0.124(3)	0.5525(6)	4.1(4)	C(17)	0.2936(4)	0.372(2)	0.2332(6)	7.5(6)
C(18)	0.4480(5)	0.141(4)	0.4869(7)	2.4(3)	C(18)	0.3056(3)	0.329(3)	0.2996(7)	5.6(5)
C(19)	0.4677(2)	0.402(1)	0.3801(5)	2.5(3)	C(19)	0.3344(2)	0.043(1)	0.4027(6)	3.0(3)
C(20)	0.4655(2)	0.522(1)	0.4251(5)	3.6(3)	C(20)	0.3265(1)	−0.094(1)	0.3695(6)	3.8(3)
C(21)	0.4833(2)	0.636(1)	0.4379(5)	3.9(4)	C(21)	0.3434(2)	−0.196(1)	0.3526(6)	4.2(4)
C(22)	0.5033(2)	0.630(1)	0.4086(6)	4.7(4)	C(22)	0.3683(1)	−0.161(1)	0.3689(6)	4.2(4)
C(23)	0.5054(2)	0.511(1)	0.3609(6)	4.3(4)	C(23)	0.3762(1)	−0.024(1)	0.4021(6)	4.2(4)
C(24)	0.4877(2)	0.397(1)	0.3480(5)	3.7(3)	C(24)	0.3592(2)	0.078(1)	0.4190(6)	4.1(4)
H(8)	0.4388(2)	0.550(2)	0.2812(9)		H(8)	0.2623(3)	0.187(1)	0.4349(8)	
H(9)	0.4061(3)	0.682(1)	0.2122(8)		H(9)	0.2386(2)	0.053(2)	0.4997(9)	
H(10)	0.3665(2)	0.581(2)	0.1959(8)		H(10)	0.2550(2)	−0.158(2)	0.5665(8)	
H(11)	0.3597(1)	0.350(2)	0.2485(8)		H(11)	0.2952(3)	−0.235(2)	0.5685(8)	
H(12)	0.3924(3)	0.219(1)	0.3174(7)		H(12)	0.3190(1)	−0.101(2)	0.5037(8)	
H(14)	0.4065(8)	0.396(5)	0.4251(10)		H(14)	0.2660(5)	0.079(3)	0.3311(8)	
H(15)	0.3976(8)	0.368(6)	0.5354(10)		H(15)	0.2457(4)	0.152(4)	0.2196(9)	
H(16)	0.4202(3)	0.198(2)	0.6153(5)		H(16)	0.2630(4)	0.336(2)	0.1582(6)	
H(17)	0.4518(9)	0.055(5)	0.5849(10)		H(17)	0.3006(5)	0.447(3)	0.2084(8)	
H(18)	0.4607(8)	0.083(6)	0.4746(10)		H(18)	0.3209(4)	0.374(4)	0.3199(9)	
H(20)	0.4520(2)	0.526(2)	0.4468(7)		H(20)	0.3096(1)	−0.117(2)	0.3584(9)	
H(21)	0.4818(3)	0.717(1)	0.4685(7)		H(21)	0.3381(3)	−0.289(1)	0.3300(9)	
H(22)	0.5153(2)	0.708(1)	0.4146(9)		H(22)	0.3789(2)	−0.231(2)	0.3574(9)	
H(23)	0.5190(2)	0.507(2)	0.3391(8)		H(23)	0.3931(1)	−0.001(2)	0.4132(9)	
H(24)	0.4892(3)	0.315(1)	0.3175(7)		H(24)	0.3646(3)	0.171(1)	0.4416(9)	

Anisotropic temperature factors[a]

Molecule A	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Mn	21(1)	782(34)	212(8)	13(5)	17(2)	−59(16)
S(1)	32(2)	1297(68)	275(15)	−11(9)	22(4)	−145(30)
S(2)	31(1)	1457(75)	242(14)	−18(9)	28(4)	−23(30)
P	16(1)	632(53)	139(11)	−7(7)	9(3)	−10(22)

TABLE II (continued)

Molecule B						
Mn	20(1)	760(36)	246(9)	19(5)	14(2)	2(16)
S(1)	27(1)	1521(74)	209(13)	16(9)	11(3)	−67(29)
S(2)	25(1)	1060(67)	268(14)	3(8)	6(3)	1(26)
P	22(1)	578(54)	198(13)	13(7)	13(3)	−1(25)

Group parameters[b]

Molecule A	C(7)–C(12)	C(13)–C(18)	C(19)–C(24)	Molecule B	C(7)–C(12)	C(13)–C(18)	C(19)–C(24)
x_c	0.3992(1)	0.4291(1)	0.4855(1)	x_c	0.2788(1)	0.2833(2)	0.3513(1)
y_c	0.4502(9)	0.2256(8)	0.5162(8)	y_c	−0.0241(8)	0.2625(11)	−0.0589(9)
z_c	0.2648(4)	0.5050(4)	0.3930(4)	z_c	0.5017(4)	0.2697(5)	0.3858(4)
δ	−2.140(6)	−1.103(23)	2.370(6)	δ	−0.836(7)	−2.093(13)	0.803(6)
ϵ	−2.712(7)	1.806(6)	3.108(6)	ϵ	2.416(6)	−2.150(8)	−2.751(7)
η	−2.794(7)	−2.774(23)	0.827(7)	η	−2.911(8)	0.399(14)	0.269(7)

[a] Anisotropic temperature factors of the form

$$\exp -[\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$$

were used for these atoms.

[b] The individual atomic parameters for the phenyl carbon and hydrogen atoms are derived from refined rigid-body crystallographic coordinates based on the following model: Each ring was presumed to be a regular hexagon with C–C bond lengths of 1.398 Å and C–H bond lengths of 0.950 Å. The centroid of each ring was chosen as the origin. An isotropic temperature factor was varied for each carbon atom, while the isotropic temperature factor for the hydrogen atoms were fixed at 6.0 Å². H(8) is attached to C(8), etc. x_c, y_c, z_c are the fractional coordinates of the group centroid; δ, ϵ, and η (in radians) are defined conventionally (S. J. La Placa and J. A. Ibers, *Acta. Crystallogr.*, 18, 511 (1965)).

made. The data were also corrected in the usual manner for Lorenz and polarization effects.

Two axes of data (*b, c*) were collected; these were corrected separately for absorption before correlation. A total of 8277 independent reflections were obtained, of which 2756 were considered observed; a reflection was considered observed if the net intensity I was greater than $4\sigma(I)$ (where $\sigma(I) = [(0.051)^2 + No + Nb]^{1/2}$; No = total scan count; N_b = total background count).

Further unit cell, crystal, and intensity collection data are given in Table I.

Structure Determination and Refinement

The structure of the compound was solved by heavy-atom methods. The observed systematic absences (*h* 0 *l*, *l* odd; *h k l*, *h* + *k* odd) indicated that the space group was C_c or $C_{2/c}$. The results of a Wilson plot suggested a centric space group, so that $C_{2/c}$ was chosen; this choice was confirmed by the successful solution and refinement of the structure. A three-dimensional Patterson map yielded coordinates for the two manganese atoms. A Fourier map phased on these atoms clearly showed the locations of the two phosphorous and four sulfur atoms. After least-squares refinement of these eight positions, a second Fourier map yielded coordinates for all remaining nonhydrogen atoms.

At this point rigid-body parameters were calculated for the phenyl group carbon atoms, constraining these atoms to an idealized geometry which was maintained throughout the least-squares refinement.

Isotropic refinement of all atoms yielded $R = \Sigma \| F_c | - | F_o \| / \Sigma | F_o | = 0.110$; $R_w = [\Sigma(w \| F_o | - | F_c \|)^2 / \Sigma(w | F_o |)^2]^{1/2} = 0.147$. Anisotropic temperature factors were then introduced for the manganese, sulfur, and phosphorus atoms, and the form factors of these atoms were corrected for anomalous dispersion.[3] The final refinement yielded R = 0.083, R_w = 0.089; the error in an observation of unit weight was 4.33. No parameter shifted by more than 0.1σ during the last refinement cycle. A Fourier difference map showed no peaks higher than 0.63e–Å^{-3}; however, the methyl group hydrogen atoms were not located. The final data-to-parameter ratio was 12.2:1.

All least-squares cycles were based on the minimization of $\Sigma(w \| F_o | - | F_c \|)^2$ where $w = \sigma(F_o)^{-2}$. The atomic scattering factors for non-hydrogen atoms

TABLE III
Interatomic distances and bond angles

A. Intramolecular distances (Å)

	Molecule A	Molecule B		Molecule A	Molecule B
Mn–P	2.347(5)	2.357(5)			
Mn–S(1)	2.377(6)	2.373(6)	S(1)–C(4)	1.646(18)	1.706(18)
Mn–S(2)	2.373(6)	2.385(5)	S(2)–C(4)	1.694(17)	1.698(17)
Mn–C(1)	1.795(16)	1.734(19)	N–C(4)	1.396(22)	1.324(21)
Mn–C(2)	1.831(20)	1.762(16)	N–C(5)	1.455(27)	1.465(23)
Mn–C(3)	1.783(23)	1.760(21)	N–C(6)	1.501(29)	1.515(25)
P–C(7)	1.810(11)	1.819(11)	C(1)–O(1)	1.155(17)	1.165(19)
P–C(13)	1.810(10)	1.821(11)	C(2)–O(2)	1.100(19)	1.145(16)
P–C(19)	1.824(10)	1.825(11)	C(3)–O(3)	1.172(22)	1.129(21)

B. Intermolecular distances less than 3.4 Å

O(1B)–C(23B)	3.208(18)	O(2A)–C(20A)	3.330(17)
C(10B)–C(10B)	3.275(20)	O(1B)–C(22B)	3.339(18)
C(5A)–O(3B)	3.299(30)	O(2A)–C(21A)	3.353(16)

C. Bond angles (degrees)

	Molecule A	Molecule B		Molecule A	Molecule B
P–Mn–S(1)	92.8(2)	93.7(2)	C(7)–P–C(13)	103.2(5)	106.5(5)
P–Mn–S(2)	86.9(2)	85.3(2)	C(7)–P–C(19)	103.1(5)	102.0(5)
P–Mn–C(1)	89.1(6)	91.0(6)	C(13)–P–C(19)	99.9(5)	99.2(6)
P–Mn–C(2)	95.0(6)	90.6(5)	Mn–S(1)–C(4)	85.2(6)	87.1(6)
P–Mn–C(3)	175.1(7)	178.0(6)	Mn–S(2)–C(4)	84.3(6)	86.9(6)
S(1)–Mn–S(2)	73.6(2)	73.1(2)	S(1)–C(4)–S(2)	116.9(10)	112.7(10)
S(1)–Mn–C(1)	174.4(5)	170.4(6)	S(1)–C(4)–N	121.9(12)	123.5(13)
S(1)–Mn–C(2)	90.4(6)	96.3(5)	S(2)–C(4)–N	121.0(13)	123.8(13)
S(1)–Mn–C(3)	88.0(6)	86.4(6)	C(4)–N–C(5)	120.7(17)	120.0(16)
S(2)–Mn–C(1)	101.2(6)	99.1(6)	C(4)–N–C(6)	117.8(15)	121.7(15)
S(2)–Mn–C(2)	164.0(6)	168.3(5)	C(5)–N–C(6)	121.5(18)	118.0(16)
S(2)–Mn–C(3)	88.7(7)	92.9(6)	Mn–C(1)–O(1)	175.5(15)	171.6(17)
C(1)–Mn–C(2)	94.6(8)	92.0(8)	Mn–C(2)–O(2)	177.3(16)	175.7(14)
C(1)–Mn–C(3)	89.7(8)	88.6(9)	Mn–C(3)–O(3)	177.0(18)	174.1(17)
C(2)–Mn–C(3)	89.8(9)	91.4(8)	P–C(7)–C(8)	122.1(8)	118.7(7)
Mn–P–C(7)	116.3(4)	112.3(4)	P–C(7)–C(12)	117.9(7)	120.6(7)
Mn–P–C(13)	115.2(4)	115.8(6)	P–C(13)–C(14)	123.0(9)	124.3(10)
Mn–P–C(19)	116.8(4)	119.1(3)	P–C(13)–C(18)	116.9(11)	115.7(9)
			P–C(19)–C(20)	120.4(7)	120.0(7)
			P–C(19)–C(24)	119.4(7)	120.0(8)

D. Planes containing S(1), S(2), N, C(4), C(5), C(6)

Molecule A: Unit vector: $20.454x - 7.216y - 9.954z - 6.027 = 0$

Molecule B: Unit vector: $16.568x + 5.973y + 11.739z - 13.783 = 0$

	Distance from plane, Å	
Atom	Molecule A	Molecule B
Mn[a]	0.059	−0.254
S(1)	−0.034	−0.001
S(2)	0.057	−0.025
N	0.001	0.040
C(4)	−0.032	0.023
C(5)	0.054	−0.032
C(6)	0.047	−0.006

[a] This atom was not included in the calculation of the least-squares plane. Unit weights were used for all other atoms.

were from Hanson *et al.*[4] while those for hydrogen were from Stewart *et al.*[5] The positional and thermal parameters for all atoms are given in Table II. Interatomic distances and angles with estimated standard deviations are given in Table III.

Computer programs used in this study included locally-written programs for data reduction and correlation and least-squares planes. Also used were modified versions of Zalkin's FORDAP for Patterson and Fourier maps; Ibers' NUCLS5 for least-squares refinements; the Martin–Busing–Levy ORFFE function and error program; Johnson's ORTEP plotting program; and Stewart's ABSORB for absorption corrections.

Synthesis of $(C_6H_5)_3PMn(CO)_3S_2CN(CH_3)_2$

Once the identity of $(C_6H_5)_3PMn(CO)_3S_2CN(CH_3)_2$ had been established, its independent synthesis was carried out as follows: 0.500 g of $(C_6H_5)_3PMn(CO)_4Br$ (1.04 mmol) and 0.180 of $N(CH_3)_2H_2[S_2CN(CH_3)_2]$ (1.05 mmol) were stirred in 50 ml of acetone. After 4 hr the reaction was complete. The solvent was removed and chromatography of the residue over alumina gave the product as a yellow band eluting with 2:1 hexane:chloroform. The compound was recrystallized from dichloromethane-heptane. Yield, 0.291 g (0.559 mmol, 54%). Yellow crystals, decompose without melting at 125°C. Analysis: Calcd. for $C_{24}H_{21}NO_3PS_2Mn$: C, 55.2; H, 4.03; N, 2.69; S, 12.28. Found: C, 54.8; H, 3.83; N, 2.77; S, 12.53. NMR spectrum: C_6H_5, 2.64τ(15); CH_3, 7.32τ(6). Infrared spectrum: ν_{CO} (heptane): 1978(s), 1904(s), 1873(s) cm^{-1}. Other peaks (KBr disc): 3000(w), 2875(w), 1480(s), 1450(s), 1405(s), 1364(s), 1290(w), 1235(m), 1166(w), 1134(m), 1078(m), 1072(m), 1015(w), 983(m), 752(m), 742(m), 738(m), 690(s), 660(s), 624(s), 610(s), 598(s), 638(m), 510(s), 483(m), 435(m), 415(w), 408(w) cm^{-1}.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structures of the two crystallographically independent molecules of $(C_6H_5)_3PMn(CO)_3S_2CN(CH_3)_2$ are shown in Figure 1. The two molecules differ only slightly, the main difference being in the orientations of the phenyl rings with respect to the rest of the molecule. For the most part the bond distances in the two molecules agree within experimental error; there is more variation among the bond angles.

The coordination about the manganese atoms is distorted octahedral, with the major distortion resulting from the small angle (73.6° and 73.1° in molecules A and B, respectively) subtended by the two sulfur atoms of the dimethyldithiocarbamate ligand. The angle between the two carbonyl groups (C(1)–Mn–C(2)) opens only slightly to compensate (94.6°, 92.0°). In molecule A, the dimethyldithiocarbamate ligand is skewed toward C(2); the angles S(1)–Mn–C(2) and S(2)–Mn–C(1) are 90.4° and 101.2°, respectively. In molecule B this distortion is less, the corresponding angles being 96.3° and 99.1°. These distortions presumably arise from intramolecular interactions between these atoms and those of the triphenylphosphine ligand. A similar situation has been observed in $[(C_6H_5)_3P]_2Mn(CO)_2O_2CCH_3$, where the corresponding angles are 106.7° and 102.5°.[6]

The Mn–P distances are of the expected length. The Mn–S distances (2.373–2.385 Å) compare with those found in $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$ (2.404 Å)[2], $[(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2]BF_4$ (2.363 Å)[2], and $(C_6H_5)_3PMn(CO)_3(o\text{-}C_6H_4CH_2SCH_3)$ (2.382 Å).[7]

The Mn–CO distances are typical of those found in many manganese carbonyl complexes. Within a given molecule, the Mn–C distances *trans* to the sulfurs and *trans* to phosphorus are equal within experimental error. This suggests that the sulfur atoms of the dithiocarbamate ligand are not behaving extensively either as π-acceptors (in which case they would compete in π-bonding with the *trans* carbonyl groups, resulting in long Mn–CO distances) or as π-donors (resulting in short Mn–CO distances).

The distances within the dimethyldithiocarbamate ligand are typical of those found in dithiocarbamate complexes. The C–S distances in the ligand (1.646–1.706 Å) are also comparable to that in $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$ (1.682 Å)[2]. The ligands in both molecules are fairly planar, with all of the atoms (S(1), S(2), N, C(4), C(5), C(6)) lying within 0.06 Å of the calculated least-squares plane of best fit.

The crystal packing is determined primarily by van der Waals forces, as shown by the intermolecular distances, the shortest of which are given in Table III.

The question of the origin of this compound during the synthesis of $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$ from $(C_6H_5)_3PMn(CO)_4^-$ and $ClCSN(CH_3)_2$ is an intriguing one. The starting materials were carefully freed of dithiocarbamate impurities, and it seems

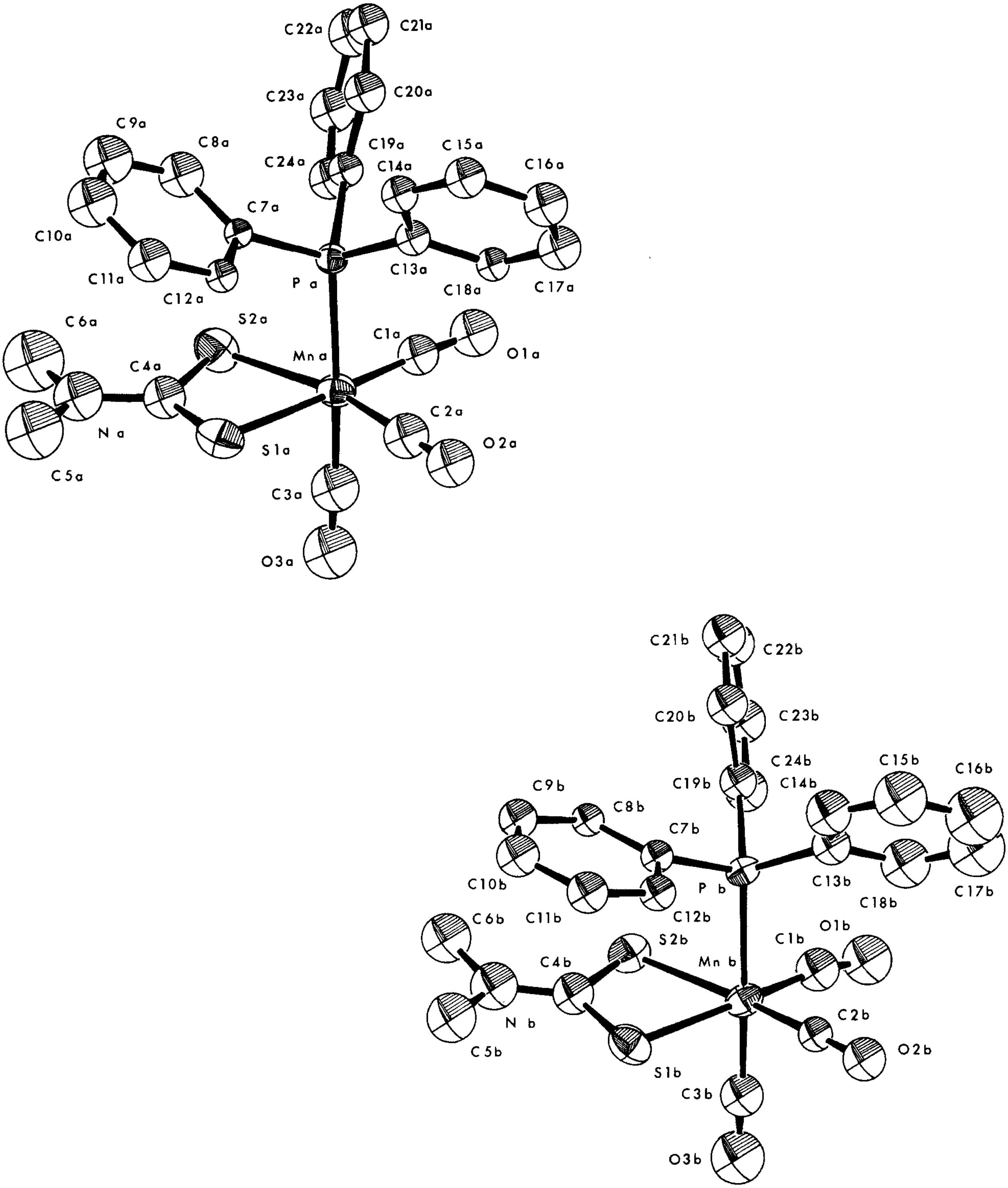
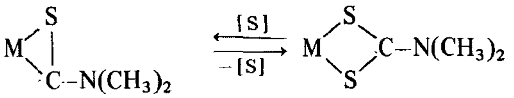


FIGURE 1 Configurations of the two crystallographically independent $(C_6H_5)_3PMn(CO)_3S_2CN(CH_3)_2$ molecules.

possible that the dithiocarbamate complex arises from the abstraction by thiocarboxamido complex of a sulfur atom with insertion into the metal–carbon bond:



The feasibility of this reaction and its reverse, and the identity of the sulfur-supplying substrate, are now under investigation.

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