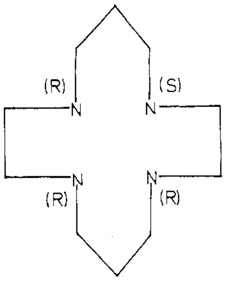
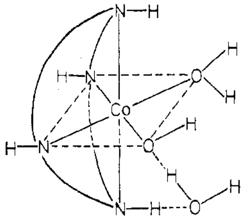


V

change of one axial amine proton, i.e., N(3) or N(4), with concurrent inversion of the nitrogen center giving an unstable cis isomer of structure V. The initially formed trans isomer of structure V is a relatively unstable structure and it may be too labile, with respect to the inversion of a second nitrogen center by means of a second proton exchange to give structure III or IV, to allow detection. The great extent of hydrogen bonding involved in the structure suggests that Poon and Tobe's internal conjugate-base mechanism of isomerization[4] is highly reasonable. It seems, however, that a direct hydrogen bonding between one axial amine proton and the coordinated hydroxide in the isomerizing species[4] *cis*-$[Co(cyclam)OHOH_2]^{2+}$ is rather unlikely in terms of the distance and direction of bonding between the two and that a water molecule, as shown in structure VI, may be needed to transmit this hydrogen-bonding effect.



VI

Acknowledgment. We thank Miss P. K. Chan for preparing a sample of the compound. T.F.L. wishes to thank Dr. R. E. Marsh for valuable discussions and for providing facilities during her visit at California Institute of Technology.

Registry No. *cis*-$[Co(cyclam)en]Cl_3 \cdot 3H_2O$, 59109-91-0; *trans*-$[Co(cyclam)Cl_2]Cl$, 15220-74-3; ethylenediamine, 107-15-3.

Supplementary Material Available: A listing of structure factor amplitudes and a table giving the details of the approximate twofold symmetry of the cyclam group (12 pages). Ordering information is given on any current masthead page.

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Thiocarboxamido and Carbene Complexes Containing Chelating Carbon–Sulfur Linkages. Crystal and Molecular Structures of Dimethylthiocarboxamido(triphenylphosphine)tricarbonylmanganese, $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$, and (Dimethylamino(thiomethoxy)carbene)(triphenylphosphine)tricarbonylmanganese Tetrafluoroborate, $[(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2]BF_4$

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The structures of $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$ (I) and its methylated derivative $[(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2]BF_4$ (II) have been determined by single-crystal x-ray diffraction techniques. The compounds crystallize as follows: I, space group $P\bar{1}$, $a = 9.605$ (11) Å, $b = 11.005$ (12) Å, $c = 11.516$ (12) Å, $\alpha = 77.71$ (6)°, $\beta = 97.83$ (6)°, $\gamma = 97.62$ (7)°; II, space group $P2_1$, $a = 9.581$ (12) Å, $b = 16.559$ (9) Å, $c = 8.727$ (15) Å, $\beta = 101.81$ (6)°. Full-matrix least-squares refinements yielded conventional R factors of 0.089 for I and 0.091 for II. In these complexes the thiocarboxamido and amino(thiomethoxy)carbene ligands are coordinated through both carbon and sulfur atoms. Their structural and bonding features are compared with those of related compounds, and the factors which lead to this unusual mode of bonding are discussed.

Introduction

Recently we have reported a series of thiocarboxamido-manganese and -molybdenum carbonyl complexes in which the dimethylthiocarboxamido group ($C(S)N(CH_3)_2$) acts as a chelating, three-electron donor ligand, coordinated through carbon and sulfur atoms.[1] Although a number of other thiocarboxamido complexes are known, only one other compound, $[MoS(CSN(C_3H_7)_2)(S_2CN(C_3H_7)_2)]_2$, has been reported which shares this unusual structure;[2] in other thiocarboxamido complexes[3-7] the ligand acts as a mono-

Table I. Summary of Crystal Data and Intensity Collection

	$(C_6H_5)_3PMn(CO)_3$-$CSN(CH_3)_2$	$[(C_6H_5)_3PMn(CO)_3$-$C(SCH_3)N$-$(CH_3)_2]BF_4$
Formula (mol wt)	$C_{24}H_{21}O_3NSPMn$ (489.4)	$C_{25}H_{24}O_3NSPMnBF_4$ (591.2)
Space group	$P\bar{1}$	$P2_1$
a, Å	9.605 (11)[a]	9.581 (12)
b, Å	11.005 (12)[a]	16.559 (9)
c, Å	11.516 (12)[a]	8.727 (15)
α, deg	77.71 (6)[a]	
β, deg	97.83 (6)[a]	101.81 (6)
γ, deg	97.62 (7)[a]	
V, Å^3	1172	1355
Z	2	2
d_{exptl} (d_{calcd}), g cm^{-3}	1.388 (1.387)	1.436 (1.449)
F(000), e	504	604
Crystal dimensions, mm (mount axis)	0.50 × 0.36 × 0.14 (*b*)	0.39 × 0.24 × 0.06 (*b*)
	0.30 × 0.25 × 0.12 (*c*)	0.39 × 0.22 × 0.04 (*c*)
μ,[9] cm^{-1}	46.60	59.53
Transmission factors	0.47–0.78	0.54–0.90

[a] These cell dimensions were used throughout the structure solution and refinement because of the near orthogonality of the axes. The dimensions of the corresponding reduced cell[8] are: a = 13.955 Å, b = 14.134 Å, c = 11.005 Å, α = 127.24°, β = 94.84°, γ = 122.02°.

dentate one-electron donor (coordinated through carbon) or as a bridging ligand.

We have also found[1] that these chelating thiocarboxamido complexes can be methylated at the sulfur atom of the ligand apparently without altering the mode of attachment of the ligand. The resulting cationic complexes may be regarded as dimethylamino(thiomethoxy)carbene complexes in which the ligand is remarkable in being coordinated through one heteroatom as well as through the carbenoid carbon. It seemed worthwhile to verify this unusual structure by x-ray crystallography and at the same time to investigate the structural and bonding consequences of S-methylation of the chelating thiocarboxamido ligand and (from another point of view) of heteroatom coordination by a carbene ligand.

For these reasons, we have undertaken the x-ray crystal structure determination of $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$ and its methylated derivative $[(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2]BF_4$.

Experimental Section

The compounds $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$ (I) and $[(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2]BF_4$ (II) were synthesized as previously described.[1] Crystals of I were obtained from dichloromethane–heptane; II was recrystallized from acetone–ethyl acetate.

Crystals were mounted on glass fibers using epoxy cement. Lattice dimensions were measured from Weissenberg photographs calibrated with Al powder (axis lengths) and from precession photographs (angles).

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 equal to the total scan time. Cu K$\bar{\alpha}$ radiation (λ 1.541 78 Å) was used throughout. Three reference reflections were measured between levels to monitor electronic and crystal stability; no significant decay was observed for either compound. The data were collected in the usual manner for Lorentz and polarization effects.

Two axes of data were collected for each compound; these were corrected separately for absorption before correlation. A reflection was considered unobserved if the net intensity I was less than $3\sigma(I)$ (where $\sigma(I) = [(0.05I)^2 + N_o + N_b]^{1/2}$; N_o is the total scan count; N_b is the total background count).

Further unit cell, crystal, and intensity collection data for the two compounds are given in Table I.

Table II. Refinement of the Structures

	$(C_6H_5)_3PMn$-$(CO)_3CSN(CH_3)_2$		$[(C_6H_5)_3PMn$-$(CO)_3C(SCH_3)$-$N(CH_3)_2]BF_4$	
Model	*R*	R_w	*R*	R_w
All atoms isotropic	0.112	0.115[a]	0.108	0.116[b]
Phenyl carbon atoms isotropic; idealized phenyl hydrogen positions; all other atoms anisotropic	0.089	0.081	0.091	0.092
Observed data	3884		1813	
No. of variables	154		208	
Final data:parameter ratio	25.2:1		8.7:1	
Max electron density on final diff Fourier map, e Å^{-3}	0.64		0.39	
Error in observn of unit weight, e	5.3		3.1	

[a] Anomalous dispersion corrections for Mn, S, and P atoms.[10]
[b] No anomalous dispersion corrections were made since it was not known whether both crystals contained the same enantiomer.

Determination of the Structures

The structure of compound I was solved by direct methods. Normalized structure factors (*E*'s) were calculated using overall scale and isotropic temperature factors obtained from a Wilson plot. The 499 reflections with $E \geq 1.55$ were used as input to the program MULTAN. Reflections in the starting set were $(47\bar{9})$, $(3\bar{8}6)$, $(1\bar{5}4)$, $(7\bar{4}0)$, $(07\bar{7})$, $(6,\bar{1},\overline{10})$, with the first three used for origin specification. An *E* map computed from one of the sets of phases showing high figures of merit revealed the positions of the manganese, phosphorus, and sulfur atoms. A Fourier synthesis phased on these three positions yielded coordinates for all remaining nonhydrogen atoms.

The structure of compound II was solved by heavy-atom methods. A three-dimensional Patterson map yielded x and z coordinates for the Mn atom; the y coordinate (which is arbitrary for one atom in space group $P2_1$) was set at 0.2500 and maintained at this value throughout the structure solution and refinement. A Fourier synthesis, phased on the manganese atom, yielded an approximate electron density map which possessed false mirror symmetry. This map showed clearly the location of the sulfur atom (very close to the mirror) and two mirror-related images of the phosphorus atom. A second Fourier map phased on the manganese and one image of the phosphorus atom (corresponding to one of two possible enantiomer choices) yielded coordinates for all remaining nonhydrogen atoms.

Details of the least-squares refinement of both structures are given in Table II. The final models included anisotropic thermal parameters for all atoms except those of the phenyl rings; these groups were refined isotropically subject to rigid-body constraints (see Table V, footnote *b*).

All least-squares cycles were based on the minimization of $\sum w||F_o| - |F_c||^2$ where $w = 1/\sigma^2(F_o)$. The atomic scattering factors used for the nonhydrogen atoms were from Hanson et al.[11] while those for hydrogen were from Stewart et al.[12] The values of $|F_o|$ and $|F_c|$ (in electrons × 10) for those reflections used in the refinement are presented in Table III (compound I) and Table IV (compound II) (supplementary material). The positional and thermal parameters for all atoms are given in Table V (I) and Table VI (II). Interatomic distances and angles with estimated standard deviations are presented in Table VII (I) and Table VIII (II).

Computer programs used in this study included locally written programs for data reduction and correlation, Patterson and Fourier maps, and least-squares planes. Also used were modified versions of MULTAN by Main, Woolfson, and Germain; Ibers' NUCLS5 modification of the Busing–Martin–Levy ORFLS for least-squares refinements; the Martin–Busing–Levy ORFFE function and error program; Johnson's ORTEP plotting program; and Stewart's ABSORB from the "X-Ray 72" system for absorption corrections.

Results and Discussion

General Description of the Structures. The $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$ molecule (I) and the $(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2^+$ ion (of II) have the structures shown in Figure 1 and 2, respectively. These results clearly

Table V. Parameters for $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$

Final Atomic Parameters

	x	y	z	B, Å^2
Mn	0.2660 (1)	0.3361 (1)	0.8311 (1)	*a*
S	0.1796 (2)	0.1701 (2)	0.9847 (1)	*a*
P	0.1896 (1)	0.2020 (1)	0.6959 (1)	*a*
O(1)	0.5666 (5)	0.3179 (6)	0.8166 (5)	*a*
O(2)	0.3425 (6)	0.5149 (6)	0.9929 (5)	*a*
O(3)	0.2123 (7)	0.5477 (5)	0.6363 (5)	*a*
N	−0.0312 (5)	0.3166 (5)	0.9133 (4)	*a*
C(1)	0.4503 (7)	0.3242 (5)	0.8203 (5)	*a*
C(2)	0.3154 (6)	0.4429 (6)	0.9230 (6)	*a*
C(3)	0.2360 (6)	0.4660 (5)	0.7116 (5)	*a*
C(4)	0.0930 (6)	0.2890 (5)	0.9040 (4)	*a*
C(5)	−0.1251 (9)	0.2361 (9)	0.9972 (7)	*a*
C(6)	−0.0837 (8)	0.4307 (7)	0.8436 (6)	*a*
C(7)	−0.0019 (3)	0.1657 (3)	0.6794 (3)	2.7 (1)
C(8)	−0.0679 (4)	0.0479 (3)	0.7268 (3)	4.0 (1)
C(9)	−0.2153 (4)	0.0276 (3)	0.7204 (4)	4.8 (1)
C(10)	−0.2968 (3)	0.1251 (4)	0.6665 (4)	4.4 (1)
C(11)	−0.2308 (4)	0.2429 (3)	0.6191 (3)	4.3 (1)
C(12)	−0.0834 (4)	0.2631 (3)	0.6256 (3)	3.6 (1)
C(13)	0.2619 (4)	0.0511 (3)	0.7277 (3)	2.7 (1)
C(14)	0.3585 (4)	0.0194 (3)	0.8287 (3)	3.6 (1)
C(15)	0.4175 (4)	−0.0938 (4)	0.8499 (3)	4.2 (1)
C(16)	0.3799 (5)	−0.1754 (3)	0.7701 (4)	5.1 (1)
C(17)	0.2833 (6)	−0.1437 (4)	0.6692 (4)	5.6 (1)
C(18)	0.2243 (4)	−0.0305 (4)	0.6480 (3)	4.6 (1)
C(19)	0.2301 (4)	0.2605 (4)	0.5417 (2)	2.7 (1)
C(20)	0.1337 (7)	0.2416 (14)	0.4430 (3)	4.0 (1)
C(21)	0.1730 (7)	0.2823 (13)	0.3274 (3)	4.8 (1)
C(22)	0.3087 (5)	0.3418 (5)	0.3105 (3)	5.2 (1)
C(23)	0.4051 (7)	0.3606 (15)	0.4091 (4)	5.6 (1)
C(24)	0.3658 (6)	0.3200 (12)	0.5248 (3)	4.3 (1)
H(8)	−0.0126 (5)	−0.0184 (4)	0.7633 (5)	
H(9)	−0.2602 (5)	−0.0524 (3)	0.7526 (5)	
H(10)	−0.3969 (3)	0.1114 (5)	0.6622 (5)	
H(11)	−0.2861 (5)	0.3091 (4)	0.5826 (5)	
H(12)	−0.0385 (5)	0.3432 (3)	0.5933 (5)	
H(14)	0.3841 (7)	0.0748 (5)	0.8829 (4)	
H(15)	0.4832 (6)	−0.1154 (6)	0.9185 (4)	
H(16)	0.4201 (7)	−0.2524 (4)	0.7846 (6)	
H(17)	0.2578 (8)	−0.1991 (5)	0.6150 (5)	
H(18)	0.1586 (6)	−0.0090 (6)	0.5793 (4)	
H(20)	0.0414 (10)	0.2012 (24)	0.4546 (4)	
H(21)	0.1075 (10)	0.2695 (21)	0.2604 (3)	
H(22)	0.3354 (6)	0.3694 (7)	0.2319 (3)	
H(23)	0.4973 (11)	0.4010 (24)	0.3976 (5)	
H(24)	0.4313 (10)	0.3328 (21)	0.5918 (4)	

Anisotropic Temperature Factors[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	562 (10)	717 (9)	533 (7)	20 (6)	73 (6)	−186 (6)
S	1243 (22)	1130 (17)	604 (11)	327 (15)	189 (12)	124 (11)
P	632 (15)	555 (11)	447 (9)	7 (10)	27 (9)	−6 (8)
O(1)	487 (53)	1892 (73)	1476 (52)	46 (46)	139 (40)	−901 (53)
O(2)	1603 (85)	1962 (80)	1556 (59)	−47 (62)	190 (56)	−131 (65)
O(3)	2130 (98)	844 (48)	1199 (48)	168 (52)	307 (53)	69 (43)
N	759 (60)	1006 (51)	643 (36)	51 (43)	305 (36)	−30 (35)
C(1)	946 (82)	705 (52)	737 (46)	−88 (49)	110 (47)	−357 (41)
C(2)	689 (68)	1162 (69)	893 (52)	25 (54)	138 (47)	−530 (54)
C(3)	953 (75)	630 (52)	738 (47)	−143 (47)	240 (46)	−170 (44)
C(4)	647 (63)	799 (52)	515 (38)	−19 (45)	131 (38)	−161 (37)
C(5)	1195 (100)	1664 (100)	1055 (65)	213 (78)	674 (66)	134 (64)
C(6)	1004 (87)	1249 (78)	1037 (59)	474 (65)	193 (57)	−110 (55)

Group Parameters[b]

	C(7)–C(12)	C(13)–C(18)	C(19)–C(24)
x_c	−0.1493 (3)	0.3209 (3)	0.2694 (3)
y_c	0.1454 (2)	−0.0622 (2)	0.3011 (3)
z_c	0.6729 (2)	0.7489 (2)	0.4261 (2)
δ	−1.534 (2)	0.414 (3)	1.867 (10)
ϵ	3.081 (2)	3.015 (2)	−1.853 (2)
η	0.483 (2)	0.906 (3)	−1.609 (9)

Table V (*Footnotes*)

[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; the resulting thermal coefficients are given with estimated standard deviations. [b] These individual atomic parameters are derived from the refined rigid-body crystallographic coordinates for the phenyl rings which were 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 origin of each ring was chosen at the center of the ring. An isotropic temperature factor was varied for each ring carbon atom, while for the hydrogen atoms the isotropic temperature factor was fixed at 6.0 Å. H(8) is attached to C(8), etc. x_c, y_c, and 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).

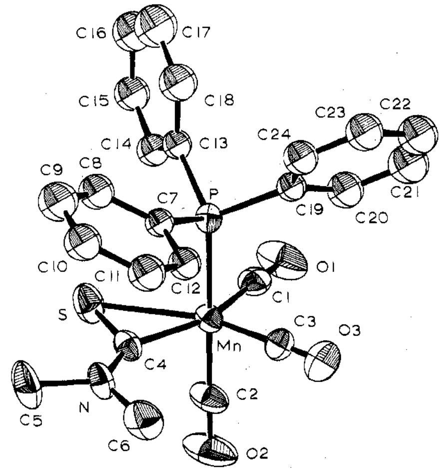


Figure 1. Molecular configuration of $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$.

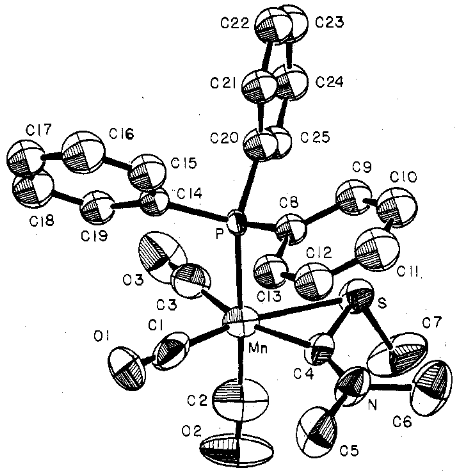


Figure 2. Configuration of the $(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2^+$ ion.

confirm the earlier assignment of the thiocarboxamido ligand as a three-electron donor coordinated through carbon and sulfur atoms and show that this structure is maintained on methylation. The overall coordination geometry about the manganese atom is distorted octahedral in each case, with the thiocarboxamido or carbenoid ligand occupying two coordination positions.

The Mn–P and Mn–CO distances in both complexes are of the expected lengths. The Mn–S distances (2.404 (3) Å in I, 2.363 (6) Å in II) are about the same as the Mn–S distance in $(C_6H_5)_3PMn(CO)_3(o\text{-}C_6H_4CH_2SCH_3)$ (2.382 Å)[13] and comparable to the Cr–S distances in $Cr(S_2CC_6H_5)_3$ (2.37–2.38 Å).[14] They are somewhat longer than the Fe–S distances of 2.19–2.31 Å observed in several iron complexes.[15-18]

The dimethylthiocarboxamido ligand in I is very nearly planar, all of its atoms (S, N, C(4), C(5), C(6), Mn) lying within 0.042 Å of the calculated least-squares plane of best fit. The coplanarity of these atoms is hardly affected when the sulfur is methylated to form the carbenoid ligand in II; all remain coplanar with 0.057 Å. However, the *S*-methyl carbon [C(7)] in II is not in this plane but lies 1.786 Å from it; the C(4)–S–C(7) angle of 103.8 (9)° is somewhat less than the tetrahedral angle.

The C–S bond distance in I (1.682 (6) Å) is virtually identical with that found in the chelating thiocarboxamido ligand in $[MoS(CSNPr_2)(S_2CNPr_2)]_2$ (1.683 Å).[2] This is intermediate between the C—S single-bond distances of 1.79–1.86 Å observed in $Fe_2(CO)_6(SC_2H_5)_2$[15] and $[CH_3SFe_2(CO)_6]_2S$[16] and the C=S double-bond distances of 1.55–1.56 Å observed in CS_2,[19] COS,[20] CSTe,[21] and HCNS.[22] The C–S bond order in this molecule thus appears to be somewhat greater than 1, and the resulting C–S distance compares with similar distances of 1.690 Å in the carbenoid complex $Cr(CO)_5C(CH_3)SC_6H_5$,[23] 1.67–1.71 Å in $Cr(S_2CC_6H_5)_3$,[14] 1.72 Å for the coordinated C–S bond in $[(C_6H_5)_3P]_2Pt(CS_2)$,[24] and 1.72 Å for the bridging C–S group in $[(CH_3O)_3PPd(Cl)CSN(CH_3)_2]_2$.[7]

The distance between these two atoms increases to 1.784 (16) Å on S-methylation; however, this bond remains considerably shorter than the $S\text{–}CH_3$ single bond in II (1.890 (16) Å).

By contrast, the (carbenoid) C–N bond length does not change within experimental error on S-methylation; it is indicative of a C=N double bond in both species, as is also the case in $[MoS(SCNPr_2)(S_2CNPr_2)]_2$.[2] The C–N–C bond angles are approximately trigonal (113–126°).

The Mn–C(ligand) distances are both quite short: 1.924 (6) Å in I and 1.843 (17) Å in II. These would appear to be appreciably shorter than the expected length of an Mn–C single bond, for which Churchill[25] has predicted a value of 2.16 Å (based on an estimated manganese covalent radius of 1.39 Å[26]). They are shorter than Mn–C(sp^2) distances of 1.95–2.07 Å found in several other complexes[13,27-31] and may also be compared with Cr–C distances of 2.00–2.16 Å in a number of "carbenoid" complexes.[23,32-37] Weiss and co-workers have previously commented on the resemblance between $[MoS(SCNPr_2)(S_2CNPr_2)]_2$ and "carbenoid" complexes.[2]

The crystal packing in this compound is determined primarily by van der Waals forces, as shown by intermolecular distances, the shortest of which are given in Tables VII and VIII. The packing forces are sufficient to cause significant deviations of the BF_4^- ion from tetrahedral symmetry, as shown by the variations in the B–F distances (1.311–1.369 Å) and F–B–F angles (102.0–112.0°).

Bonding in the Complexes. From the preceding consideration of bond lengths and angles a picture emerges of the bonding in these two complexes. The ligating carbon atom and the nitrogen atom of the thiocarboxamido and carbenoid ligands are trigonally hybridized, and the unhybridized P_z orbital of the carbon atom is in each case in a position to interact with orbitals of appropriate energy and symmetry on the nitrogen, manganese, and sulfur atoms to form delocalized π molecular orbitals potentially involving all four atoms. The observed bond distances clearly indicate that the P_z orbital of the ligand carbon atom in both complexes has sufficient Lewis acidity to interact significantly with all three adjacent atoms. The Mn–C distances are quite short, falling at the low end of the range (1.9–2.1 Å) associated with carbenoid complexes. Considerable π interaction between the carbon and sulfur atoms (bond order ~1.5) and the carbon and

Table VI. Parameters for $[(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2]BF_4$

Final Atomic Parameters

	x	y	z	B, Å^2
Mn	1.3429 (2)	0.2500 (0)	1.0252 (3)	*a*
S	1.3344 (3)	0.2491 (4)	0.7526 (5)	*a*
P	1.1079 (3)	0.1981 (3)	0.9641 (4)	*a*
O(1)	1.2713 (17)	0.3160 (10)	1.3137 (17)	*a*
O(2)	1.6260 (14)	0.3238 (11)	1.1275 (26)	*a*
O(3)	1.4562 (15)	0.0869 (10)	1.1453 (18)	*a*
N	1.2769 (17)	0.4031 (8)	0.8322 (18)	*a*
C(1)	1.2973 (16)	0.2917 (12)	1.2029 (25)	*a*
C(2)	1.5198 (21)	0.2940 (13)	1.0823 (30)	*a*
C(3)	1.4134 (20)	0.1476 (14)	1.1038 (24)	*a*
C(4)	1.3006 (14)	0.3297 (10)	0.8755 (18)	*a*
C(5)	1.2597 (27)	0.4667 (14)	0.9475 (27)	*a*
C(6)	1.2571 (24)	0.4349 (16)	0.6630 (30)	*a*
C(7)	1.5125 (22)	0.2759 (14)	0.7051 (36)	*a*
C(8)	0.9890 (8)	0.2718 (5)	0.8546 (10)	3.0 (3)
C(9)	0.9373 (12)	0.2633 (6)	0.6936 (10)	4.0 (3)
C(10)	0.8532 (12)	0.3241 (7)	0.6098 (9)	5.2 (4)
C(11)	0.8207 (12)	0.3934 (6)	0.6871 (13)	6.3 (5)
C(12)	0.8724 (14)	0.4019 (6)	0.8481 (13)	5.0 (4)
C(13)	0.9565 (10)	0.3411 (6)	0.9139 (9)	3.9 (3)
C(14)	1.0280 (10)	0.1749 (6)	1.1307 (10)	2.9 (2)
C(15)	0.8842 (12)	0.1899 (11)	1.1291 (12)	4.6 (3)
C(16)	0.8246 (9)	0.1652 (13)	1.2549 (14)	5.8 (4)
C(17)	0.9088 (11)	0.1254 (8)	1.3822 (12)	4.7 (3)
C(18)	1.0527 (13)	0.1103 (11)	1.3838 (12)	5.5 (4)
C(19)	1.1123 (9)	0.1350 (13)	1.2581 (13)	3.7 (3)
C(20)	1.0784 (9)	0.1024 (5)	0.8526 (12)	3.8 (3)
C(21)	1.1913 (7)	0.0581 (7)	0.8156 (13)	3.5 (3)
C(22)	1.1652 (8)	−0.0163 (7)	0.7394 (13)	4.4 (3)
C(23)	1.0261 (10)	−0.0464 (6)	0.7001 (14)	4.8 (4)
C(24)	0.9132 (7)	−0.0021 (7)	0.7371 (14)	4.4 (3)
C(25)	0.9394 (7)	0.0723 (7)	0.8134 (13)	3.7 (3)
H(9)	0.9594 (19)	0.2162 (7)	0.6411 (13)	
H(10)	0.8181 (18)	0.3182 (9)	0.5004 (9)	
H(11)	0.7636 (16)	0.4346 (8)	0.6302 (17)	
H(12)	0.8503 (21)	0.4490 (7)	0.9006 (17)	
H(13)	0.9916 (15)	0.3470 (8)	1.0413 (9)	
H(15)	0.8269 (18)	0.2170 (17)	1.0426 (16)	
H(16)	0.7268 (11)	0.1755 (21)	1.2538 (21)	
H(17)	0.8683 (16)	0.1086 (10)	1.4677 (15)	
H(18)	1.1100 (19)	0.0832 (18)	1.4704 (16)	
H(19)	1.2100 (11)	0.1248 (21)	1.2591 (19)	
H(21)	1.2858 (8)	0.0786 (9)	0.8423 (20)	
H(22)	1.2419 (10)	−0.0463 (9)	0.7143 (19)	
H(23)	1.0083 (14)	−0.0969 (7)	0.6483 (19)	
H(24)	0.8187 (8)	−0.0226 (9)	0.7104 (21)	
H(25)	0.8626 (9)	0.1023 (9)	0.8385 (19)	
B	1.5180 (33)	0.0550 (22)	1.5994 (38)	*a*
F(1)	1.5143 (24)	−0.0259 (15)	1.5841 (36)	*a*
F(2)	1.3936 (14)	0.0878 (16)	1.5431 (21)	*a*
F(3)	1.6195 (13)	0.0857 (14)	1.5356 (20)	*a*
F(4)	1.5414 (19)	0.0774 (16)	1.7536 (20)	*a*

Anisotropic Temperature Factors[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	970 (25)	300 (9)	1422 (41)	−33 (18)	223 (23)	−22 (23)
S	1179 (42)	341 (14)	1551 (62)	−58 (34)	755 (42)	−85 (41)
P	801 (39)	194 (11)	469 (41)	8 (19)	104 (31)	13 (24)
O(1)	3052 (264)	647 (76)	1192 (197)	−257 (122)	705 (193)	−328 (117)
O(2)	993 (158)	706 (82)	5430 (546)	−280 (97)	−259 (216)	−538 (190)
O(3)	2028 (219)	544 (69)	2109 (269)	549 (103)	−216 (181)	4 (122)
N	2305 (234)	2040 (44)	1751 (266)	44 (85)	995 (201)	61 (100)
C(1)	969 (179)	526 (84)	1933 (356)	−237 (102)	121 (202)	421 (167)
C(2)	1261 (246)	440 (81)	3213 (505)	226 (123)	226 (279)	−71 (172)
C(3)	1437 (229)	519 (97)	1689 (322)	−209 (138)	360 (229)	−196 (166)
C(4)	959 (162)	410 (69)	1171 (234)	−213 (90)	878 (160)	−138 (118)
C(5)	3446 (413)	483 (86)	1874 (348)	88 (169)	1699 (323)	−253 (171)
C(6)	2678 (375)	697 (121)	2424 (481)	218 (183)	1552 (342)	207 (215)
C(7)	1710 (260)	721 (134)	4390 (648)	−417 (148)	2041 (348)	−224 (230)
B	2241 (457)	809 (190)	2709 (649)	643 (238)	1417 (443)	175 (290)
F(1)	3999 (388)	954 (128)	8256 (1005)	126 (199)	2430 (541)	−415 (286)
F(2)	1796 (181)	1655 (156)	3906 (391)	613 (144)	699 (205)	133 (209)
F(3)	1845 (179)	1543 (147)	3672 (334)	30 (139)	1313 (206)	−80 (201)
F(4)	3917 (333)	1446 (148)	2391 (289)	500 (189)	1117 (246)	−167 (189)

Table VI (*Continued*)

Group Parameters[b]

	C(8)–C(13)	C(14)–C(19)	C(20)–C(25)
X_c	0.9408 (7)	0.9684 (7)	1.0522 (7)
Y_c	0.3326 (5)	0.1501 (5)	0.0280 (5)
z_c	0.7708 (9)	1.2565 (9)	0.7764 (8)
δ	−2.477 (7)	−0.939 (11)	−0.197 (5)
ϵ	−2.725 (5)	2.089 (6)	−2.687 (7)
η	−1.174 (7)	−2.541 (13)	−0.220 (7)

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

Table VII. Interatomic Distances and Bond Angles in $(C_6H_5)_3PMn(CO)_3CSN(CH_3)_2$

A. Intramolecular Distances, Å

Mn–S	2.404 (3)	P–C(13)	1.831 (4)
Mn–P	2.349 (3)	P–C(19)	1.831 (4)
Mn–C(1)	1.815 (7)	C(1)–O(1)	1.135 (7)
Mn–C(2)	1.800 (6)	C(2)–O(2)	1.149 (7)
Mn–C(3)	1.784 (6)	C(3)–O(3)	1.132 (7)
Mn–C(4)	1.924 (6)	N–C(4)	1.294 (8)
S–C(4)	1.682 (6)	N–C(5)	1.480 (9)
P–C(7)	1.823 (4)	N–C(6)	1.451 (9)

B. Intermolecular Contacts of Less Than 3.35 Å

O(2)· · ·O(2)	3.066 (12)	O(2)· · ·C(2)	3.280 (9)
O(1)· · ·O(2)	3.119 (7)	O(3)· · ·C(11)	3.338 (7)

C. Bond Angles, Deg

S–Mn–P	87.3 (1)	C(7)–P–C(13)	105.7 (2)
S–Mn–C(1)	109.7 (2)	C(7)–P–C(19)	103.3 (2)
S–Mn–C(2)	93.1 (2)	C(13)–P–C(19)	100.3 (2)
S–Mn–C(3)	150.5 (2)	Mn–C(1)–O(1)	178.0 (5)
S–Mn–C(4)	44.0 (2)	Mn–C(2)–O(2)	176.6 (6)
P–Mn–C(1)	91.8 (2)	Mn–C(3)–O(3)	177.7 (6)
P–Mn–C(2)	176.8 (2)	Mn–C(4)–S	83.3 (3)
P–Mn–C(3)	88.8 (2)	Mn–C(4)–N	147.7 (4)
P–Mn–C(4)	90.7 (2)	S–C(4)–N	128.8 (4)
C(1)–Mn–C(2)	91.1 (3)	C(4)–N–C(5)	122.2 (6)
C(1)–Mn–C(3)	99.6 (3)	C(4)–N–C(6)	121.1 (5)
C(1)–Mn–C(4)	153.5 (3)	C(5)–N–C(6)	116.7 (6)
C(2)–Mn–C(3)	89.3 (3)	C(8)–C(7)–P	122.2 (3)
C(2)–Mn–C(4)	87.3 (3)	C(12)–C(7)–P	117.6 (3)
C(3)–Mn–C(4)	106.8 (3)	C(14)–C(13)–P	120.3 (3)
Mn–S–C(4)	52.6 (2)	C(18)–C(13)–P	119.7 (3)
Mn–P–C(7)	112.2 (2)	C(20)–C(19)–P	122.5 (4)
Mn–P–C(13)	117.2 (1)	C(24)–C(19)–P	117.5 (2)
Mn–P–C(19)	116.5 (2)		

D. Plane Containing Mn, S, C(4), N, C(5), C(6)[a]

Equation of Plane

$$2.0620X + 6.9569Y + 9.0234Z - 10.3971 = 0$$

Distances to Plane, Å

Mn	−0.011	C(4)	−0.038
S	0.042	C(5)	−0.014
N	0.018	C(6)	−0.039

[a] Unit weights assigned to all atoms.

Table VIII. Interatomic Distances and Bond Angles in $[(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2]BF_4$

A. Interatomic Distances, Å

Mn–S	2.363 (6)	C(1)–O(1)	1.122 (23)
Mn–P	2.367 (5)	C(2)–O(2)	1.128 (21)
Mn–C(1)	1.830 (24)	C(3)–O(3)	1.118 (23)
Mn–C(2)	1.818 (22)	N–C(4)	1.279 (20)
Mn–C(3)	1.900 (25)	N–C(5)	1.489 (25)
Mn–C(4)	1.843 (17)	N–C(6)	1.543 (29)
S–C(4)	1.784 (16)	B–F(1)	1.346 (39)
S–C(7)	1.890 (16)	B–F(2)	1.311 (31)
P–C(8)	1.804 (9)	B–F(3)	1.318 (34)
P–C(14)	1.817 (11)	B–F(4)	1.369 (35)
P–C(20)	1.852 (10)		

B. Intermolecular Distances Less than 3.5 Å

O(2)· · ·C(16)	3.299 (25)	F(3)· · ·C(24)	3.332 (18)
O(2)· · ·C(15)	3.319 (22)	F(1)· · ·O(1)	3.334 (28)
F(4)· · ·C(7)	3.319 (36)		

C. Bond Angles, Deg

S–Mn–P	86.3 (1)	C(4)–S–C(7)	103.8 (9)
S–Mn–C(1)	152.9 (6)	Mn–C(1)–O(1)	178.4 (17)
S–Mn–C(2)	96.7 (8)	Mn–C(2)–O(2)	174.6 (21)
S–Mn–C(3)	107.1 (6)	Mn–C(3)–O(3)	177.6 (19)
S–Mn–C(4)	48.3 (5)	Mn–C(4)–S	81.3 (7)
P–Mn–C(1)	86.9 (5)	Mn–C(4)–N	152.9 (13)
P–Mn–C(2)	176.1 (7)	S–C(4)–N	125.2 (12)
P–Mn–C(3)	90.5 (5)	C(4)–N–C(5)	120.7 (16)
P–Mn–C(4)	92.2 (4)	C(4)–N–C(6)	125.9 (15)
C(1)–Mn–C(2)	89.3 (9)	C(5)–N–C(6)	113.4 (16)
C(1)–Mn–C(3)	99.2 (8)	C(9)–C(8)–P	121.3 (7)
C(1)–Mn–C(4)	105.9 (7)	C(13)–C(8)–P	118.6 (6)
C(2)–Mn–C(3)	90.9 (8)	C(15)–C(14)–P	122.0 (7)
C(2)–Mn–C(4)	88.0 (8)	C(19)–C(14)–P	117.8 (8)
C(3)–Mn–C(4)	154.9 (8)	C(21)–C(20)–P	121.9 (7)
Mn–P–C(8)	110.0 (3)	C(25)–C(20)–P	118.0 (7)
Mn–P–C(14)	115.7 (3)	F(1)–B–F(2)	111.8 (32)
Mn–P–C(20)	117.7 (3)	F(1)–B–F(3)	110.4 (23)
C(8)–P–C(14)	104.1 (5)	F(1)–B–F(4)	111.3 (30)
C(8)–P–C(20)	106.8 (9)	F(2)–B–F(3)	112.0 (26)
C(14)–P–C(20)	101.2 (5)	F(2)–B–F(4)	102.0 (20)
Mn–S–C(4)	50.4 (5)	F(3)–B–F(4)	108.9 (30)
Mn–S–C(7)	111.9 (10)		

D. Plane Containing Mn, S, C(4), N, C(5), C(6)[a]

Equation of Plane

$$9.2442X + 3.4833Y - 0.3776Z - 12.8903 = 0$$

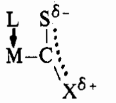
Distances to Plane, Å

Mn	0.007	C(5)	0.023
S	0.029	C(6)	−0.004
N	0.004	C(7)	1.786
C(4)	−0.057		

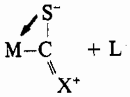
[a] Unit weights assigned to all atoms.

nitrogen atoms (bond order ~2) is also evident. Again this is similar to the π interaction between the carbenoid carbon and adjacent heteroatoms in carbenoid complexes.

This picture provides some insight into the reasons for the occasionally observed behavior of $C(S)NR_2$ groups as three-electron donors, while in all reported instances the similar groups C(S)OR and C(S)SR behave as one-electron donors coordinating only through carbon.[38–40] In a nonchelating, "one-electron" thiocarboxamido complex (**1a**, X = NR_2), some



1a



1b

π-electron delocalization would be expected to occur as in the case, for example, of organic amides. The result is a net transfer of electron density from the nitrogen toward the sulfur atom, increasing the Lewis basicity of the latter. In addition, the C–S bond is lengthened, increasing the potential chelating "bite" of the group. Both of these influences favor the coordination of the sulfur atom (**1b**). If, on the other hand, X = OR or SR, π-electron delocalization is not expected to be significant since these groups cannot accept the resulting positive charge as readily as an NR_2 group, and thus sulfur coordination is less likely to occur. The possibility is not precluded, however, especially for X = SR, and efforts directed at synthesizing such complexes are in progress.

The shortening of the C—S bond in going from I to II indicates that π bonding between the carbon and sulfur atoms decreases on S-methylation. At the same time there is no discernible effect on the C═N bond. In this situation, one would predict a corresponding increase in metal–carbon π bonding in the S-methylated species. This expection is borne out, and the change is manifested in two ways. First, the (carbenoid)C–Mn bond distance decreases dramatically from 1.924 to 1.843 Å. The Mn–C distance in the latter species is well within the range expected for Mn–CO distances; indeed it appears to be the shortest Mn–C bond yet reported except for carbonyl distances. Second, the Mn–CO distance trans to the carbenoid carbon *increases* markedly on S-methylation from 1.815 to 1.900 Å, extraordinarily long for an Mn–CO bond. This reflects the enhanced degree of π donation from the metal to the carbenoid carbon atom; as this carbon competes more effectively as a π acceptor, π donation to the trans carbonyl is decreased, resulting in a longer Mn–CO bond. A smaller increase can be seen for the Mn–CO distance cis to the carbenoid carbon (1.784 to 1.830 Å). By contrast, the Mn–CO distance trans to phosphorus (which is perpendicular to the plane of the carbenoid ligand and thus is effectively isolated from changes in its π-acceptor strength) remains unchanged within experimental error.

Except for the attachment of the sulfur to the metal atom, the carbenoid ligand in this complex resembles those in other carbenoid complexes in its general features, i.e., in the shortness of the carbon–metal and carbon–heteroatom bonds. In this connection it is interesting to compare the details of the structure of the $(C_6H_5)_3PMn(CO)_3C(SCH_3)N(CH_3)_2^+$ ion with those of the $(CH_3NC)_2Pt[C(SC_2H_5)NHCH_3]_2^{2+}$ ion, previously reported by Butler and Enemark,[41] which also contains amino(thioalkoxy)carbene ligands but whose sulfur atoms are not coordinated to the metal. In the latter complex, the (carbenoid)C–S bond distance is only 1.681 Å, 0.1 Å shorter than in the S-coordinated manganese complex, while the Pt–C distance of 2.058 Å appears to be about the expected value for a platinum–carbene bond (cf. 1.98 Å in $(C_2H_5)_3PPtCl_2C(OC_2H_5)NHC_6H_5$[42] and 2.00 Å in $(C_2H_5)_3PPtCl_2C[N(C_6H_5)CH_2]_2$[43]). Thus it seems that in the S-coordinated carbenoid complex there is less C–S π bonding and more metal–carbon π bonding than in the "normal" carbenoid complex. The causes of this difference cannot be identified with certainty but it may be a response to the strains resulting from S-coordination. In this situation a decrease in (carbenoid)C–S π bonding is favored since ring strain is relieved and since the concomitant lengthening of the C–S bond allows these atoms more effectively to occupy two coordination sites. As C–S π bonding decreases, Mn–C π bonding increases as noted above.

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Registry No. I, 58894-31-8; II, 58894-38-5.

Supplementary Material Available: Tables III and IV, listing structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

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