

# Synthesis, Structure, and Reactions of Cationic Dimethylmanganese(III) Complexes Containing 1,2-Bis(dimethylphosphino)ethane Ligands

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A stable dimethylmanganese(III) complex,  $[\text{MnMe}_2(\text{dmpe})_2]^+\text{AlMe}_4^-$  (1) has been prepared by the reaction of  $\text{Mn}(\text{acac})_3$  with trimethylaluminum in the presence of 1,2-bis(dimethylphosphino)ethane in ether. An anion-exchange reaction of 1 stabilizes the dimethylmanganese(III) complex to give  $[\text{MnMe}_2(\text{dmpe})_2]^+\text{BPh}_4^-$  (2). X-ray structure analysis reveals that 2 has an octahedral trans configuration: triclinic, space group  $P\bar{1}$ ,  $a = 16.587$  (4) Å,  $b = 17.122$  (8) Å,  $c = 16.539$  (2) Å,  $\alpha = 106.86$  (2)°,  $\beta = 105.76$  (2)°,  $\gamma = 107.64$  (2)°,  $Z = 4$ ,  $R = 0.081$ ,  $R_w = 0.094$ , respectively, with use of 6956 reflections. The average Mn-P bond distance in 2 is longer than that in the isostructural dimethylmanganese(II) complex and shorter than that in octahedral tetramethyl(1,2-bis(dimethylphosphino)ethane)manganese(IV), reflecting the importance of back-bonding in the M-P bond. Reaction of 2 with carbon monoxide in benzonitrile at 90 °C affords  $[\text{Mn}(\text{CO})(\text{PhCN})(\text{dmpe})_2]^+\text{BPh}_4^-$  (3) with liberation of a quantitative yield of acetone. Octahedral trans configuration of 3 is unequivocally determined by X-ray structure analysis: monoclinic, space group  $P2_1/n$ ,  $a = 23.111$  (4) Å,  $b = 14.935$  (3) Å,  $c = 13.602$  (3) Å,  $\beta = 105.14$ °,  $Z = 4$ ,  $R = 0.059$ ,  $R_w = 0.053$ , respectively with use of 3699 reflections. An intermediate unstable purple complex,  $[\text{Mn}(\text{PhCN})(\text{dmpe})_2]^+\text{BPh}_4^-$  (5) has been obtained when the reaction of 2 with carbon monoxide is carried out at 40 °C.

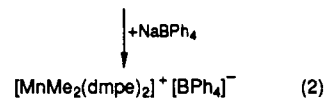
## Introduction

Although a wide variety of valencies of manganese compounds are known, the organometallic complexes of manganese reported to date are limited to the low-valent carbonyl-containing compounds (-1 to +1) as well as to homoleptic dialkyl- and diarylmanganese(II) and their related compounds.<sup>1</sup> Tertiary phosphines, which usually act as effective ligands for late organotransition-metal complexes, are not frequently employed stabilize these manganese-carbon bonds except for those of the  $\text{Mn}^{\text{II}}\text{R}_2\text{L}_n$  type.<sup>2,3</sup> The organometallic chemistry of high-valent manganese complexes is of interest in relation to its role in the oxidation of organic substances<sup>4</sup> as well as in redox reactions of biological systems.<sup>5</sup> However, organomanganese complexes of high oxidation states are scarcely known, except for the recent report of the bis(2,4,6-trimethylphenyl)manganese(III) complex having trimethylphosphine ligands, which was prepared by oxidation of the corresponding Mn(II) diaryl complex,<sup>6</sup> and anionic permethylmanganates(III) and -(IV).<sup>7</sup> Recently, we also reported in a preliminary form trivalent cationic dialkylmanganese(III) complexes  $[\text{MnMe}_2(\text{dmpe})_2]^+\text{X}^-$  ( $\text{X} = \text{AlMe}_4^-$  (1),  $\text{BPh}_4^-$  (2)).<sup>8</sup> This paper discusses details of the

synthesis, structure, and chemical reactivities of these complexes and related compounds.

## Results and Discussion

**Preparation of the Dimethylmanganese(III) Complex.** Treatment of tris(2,4-pentanedionato)manganese(III) with an excess of trimethylaluminum in the presence of 1,2-bis(dimethylphosphino)ethane in diethyl ether gave an air-sensitive, red cationic dimethylmanganese(III) complex having a tetramethylaluminate anion,  $[\text{MnMe}_2(\text{dmpe})_2]^+\text{AlMe}_4^-$  (1), in 45% yield. 1 is thermally very



stable but is decomposed by air and moisture. An ion-exchange reaction of 1 with sodium tetraphenylborate afforded  $[\text{MnMe}_2(\text{dmpe})_2]^+\text{BPh}_4^-$  (2). Surprisingly 2 is stable in water. Large values of the molar electric conductivity of these complex in THF (18 and 45 S cm<sup>2</sup> mol<sup>-1</sup> for 1 and 2, respectively) indicate that these complexes are ionic. Magnetic moments estimated from susceptibility measurements of these complexes give their paramagnetism (3.15 and 3.01  $\mu_B$  for 1 and 2, respectively), the values suggesting a low-spin octahedral d<sup>4</sup> electronic configuration. A similar low-spin electronic structure was previously found in the chromium analogue  $\text{CrMe}_2(\text{dmpe})_2$ .<sup>9</sup> These results may reflect the large ligand field splitting ability of the dmpe ligand.

A possible route for the formation of 1 is an initial alkylation of tris(2,4-pentanedionato)manganese(III) with trimethylaluminum, giving a trimethylmanganese(III) intermediate, from which one of the methyl groups back-transfers to another trimethylaluminum, giving a cationic dimethylmanganese(III) complex with a tetramethyl-

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Table I. Summary of Crystallographic Data for 2 and 3

	2	3
formula	C <sub>38</sub> H <sub>58</sub> P <sub>4</sub> MnB	C <sub>43</sub> H <sub>67</sub> NOP <sub>4</sub> MnB
fw	704.47	805.53
space group	P $\bar{1}$	P2 <sub>1</sub> /n
cryst syst	triclinic	monoclinic
a, Å	16.587 (4)	23.111 (4)
b, Å	17.122 (8)	14.935 (3)
c, Å	16.539 (3)	13.602 (3)
$\alpha$ , deg	106.86 (2)	
$\beta$ , deg	105.76 (2)	105.14 (1)
$\gamma$ , deg	107.64 (3)	
V, Å <sup>3</sup>	3937 (3)	4532 (2)
Z	4	4
$d_{\text{calc}}$ , g cm <sup>-3</sup>	1.189	1.181
$d_{\text{obsd}}$ , g cm <sup>-3</sup>	1.24	1.18
Mo K $\alpha$ radiation, Å	0.710 68	0.710 68
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	4.73	4.17
temp, °C	room temp	room temp
2 $\theta$ , deg	3 < 2 $\theta$ < 45	3 < 2 $\theta$ < 45
scan type	$\omega/2\theta$	$\omega/2\theta$
no. of data colled	9837	7193
no. of obsd reflns for refinement	6956 ( $F_o > 3\sigma(F_o)$ )	3699 ( $F_o > 3\sigma(F_o)$ )
no. of params	817	460
R	0.081	0.059
R <sub>w</sub>	0.094	0.053
method of phase determination	direct method	heavy-atom method

aluminate anion. A similar alkyl group transfer during alkylation of transition-metal complexes with alkyl-aluminum compounds is known in the formation of [Fe(acac)(dmpe)<sub>2</sub>]<sup>+</sup><sup>10</sup> and [CoMe<sub>2</sub>(bpy)<sub>2</sub>]<sup>+</sup>.<sup>11</sup>

**Molecular Structure of 2.** The structure of 2 has been unequivocally characterized by X-ray structure analysis. Table I summarizes the crystallographic data. Fractional atomic coordinates and selected bond distances and angles are listed in Tables II and III. The triclinic crystal of space group P $\bar{1}$  contains two independent molecules, I and II, in an asymmetric unit of the crystal. These are quite similar to each other, and the ORTEP drawing of molecule I is given in Figure 1. The structure of 2 is that of a typical octahedron in which two methyl groups occupy sites trans to each other. Observed bond distances and angles are normal. It is very interesting to compare the structure of 2 with that of the analogous known *trans*-dimethylbis-(1,2-bis(dimethylphosphino)ethane)manganese(II),<sup>3</sup> since they are isostructural compounds having different metal valencies. The average M–C bond distance (2.11 Å) in 2 is slightly shorter than that in the Mn(II) complex (2.20 Å), while the values are comparable to M–C bond distances (2.12 Å) trans to each other in the analogous Mn(IV) complex, Mn<sup>IV</sup>Me<sub>4</sub>(dmpe).<sup>12</sup> The longer M–C bond length in the low-valent complex may be due to the large ionic radius of Mn(II). A similar trend is also observed in the M–Cl bond in the halomanganese complexes having chelating phosphine ligands.<sup>13</sup> Accidental coincidence of the M–C bond distances in Mn(III) and Mn(IV) complexes in spite of their different metal valencies may arise from the different ligand circumstances in these complexes. On the contrary, M–P bond distances in these complexes show the reverse trend. Namely, the average M–P bond distance (2.32 Å) in 2 is significantly longer than that in the Mn(II) analogue (2.24–2.25 Å)<sup>3</sup> and is shorter than that in the

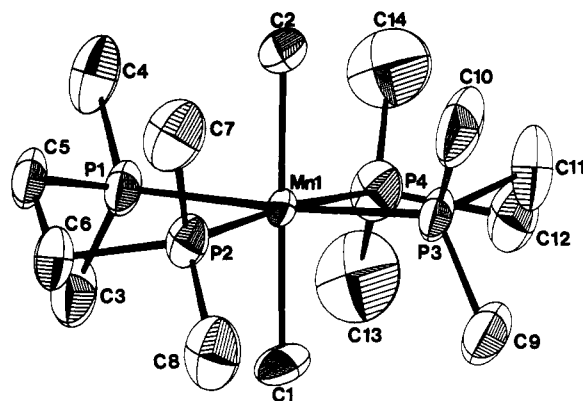


Figure 1. ORTEP drawing of [MnMe<sub>2</sub>(dmpe)<sub>2</sub>]<sup>+</sup>BP<sub>4</sub><sup>-</sup> (2) (Molecule I) showing the atomic numbering scheme used. The counteranion is omitted for clarity. Ellipsoids are drawn at the 30% probability level.

Mn(IV) complex (2.45 Å).<sup>12</sup> The shortening of the M–P bond in the low-valent organomanganese complexes may be interpreted in terms of the increase of the bond strength between Mn and P due to increasingly effective back-bonding. The high-spin electron configuration of Mn<sup>IV</sup>Me<sub>4</sub>(dmpe) also discourages back-bonding. Thus the high electron density in the t<sub>2g</sub> orbital in the octahedral organomanganese compounds having dmpe ligands seems to play an important role in stabilizing the M–P bond.

**Thermolysis of 1 and 2.** Results of the thermolysis of these complexes are summarized in Table IV. Heating the solid sample of 1 and 2 liberated mainly methane accompanied by small amounts of ethylene and ethane. Methane and ethane may be liberated by hydrogen abstraction and coupling of two methyl groups, respectively. Formation of ethylene in these thermolyses is worth noting, since in general ethylene cannot be formed from these complexes. The formation of ethylene is observed more clearly in the thermolysis of 2 in DMSO. Thus a mixture of methane and ethylene was liberated in approximately a 2:1 ratio with a small amount of ethane. The hydrogen source of methane formation is not the solvent, since the methane evolved in the thermolysis in DMSO-d<sub>6</sub> contained only CH<sub>4</sub>. Both 1,2-bis(dimethylphosphino)ethane ligands and the tetramethylaluminate anion are unlikely sources of the ethylene, since [MnBr<sub>2</sub>(dmpe)<sub>2</sub>]<sup>9</sup> liberates no gas when heated at even 195 °C and the thermolysis of [CoMe<sub>2</sub>bpy<sub>2</sub>]<sup>+</sup>AlMe<sub>4</sub><sup>-11</sup> was known to liberate no ethylene at all. Thus the ethylene formed in the thermolysis of 2 is considered to be formed from the Mn–Me group.<sup>14</sup> Although the mechanism is not clear at present, it should include some inter- or intramolecular  $\alpha$ -hydrogen elimination processes from Mn–Me groups. Possible involvement of a simple free carbene species in the mechanism is excluded, since attempted trapping of the carbene intermediate by cyclohexene failed. Although an  $\alpha$ -hydrogen elimination mechanism was proposed previously for the thermolysis of a methyl-iron(II) complex that gave ethylene and methane,<sup>15</sup> the elucidation of the complete mechanism should await further detailed investigation including labeling experiments.

**Reaction of 2 with Carbon Monoxide.** When carbon monoxide at atmospheric pressure is introduced into a

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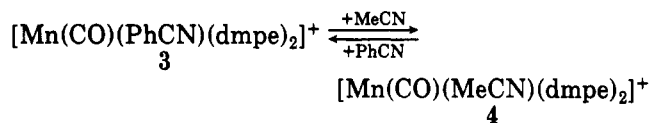
(14) Possible formation of a part of ethylene from the dmpe ligand cannot be completely excluded, since P–C bond cleavage of a coordinated tertiary phosphine ligand, such as 1,2-bis(diphenylphosphino)ethane in (CuR)<sub>2</sub>(dpe)<sub>3</sub> giving alkane and diphenylvinylphosphine, has been reported. Such a P–C bond breakage is known to be accelerated by Lewis acids: Miyashita, A.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1977, 1102.

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benzonitrile solution of **2** at 90 °C, the initially red solution turned purple and finally yellow after 3 h. A quantitative yield of acetone was formed, accompanied by the formation of small amounts of methane, ethylene, and ethane. The resulting yellow complex **3** was characterized as  $[\text{Mn}(\text{CO})(\text{PhCN})(\text{dmpe})_2]^+\text{BPh}_4^-$ . The large value of molar electric conductivity for **3** ( $31 \text{ S cm}^2 \text{ mol}^{-1}$ ) indicates that **3** is also an ionic complex. Photolysis of **3** with a high-pressure mercury UV light in aqueous THF solution liberated carbon monoxide and benzonitrile in 81 and 82% yields/Mn, respectively, supporting its chemical formula. The IR spectrum of **3** shows  $\nu(\text{CN})$  and  $\nu(\text{CO})$  bands at 2217 and  $1818 \text{ cm}^{-1}$ , respectively.

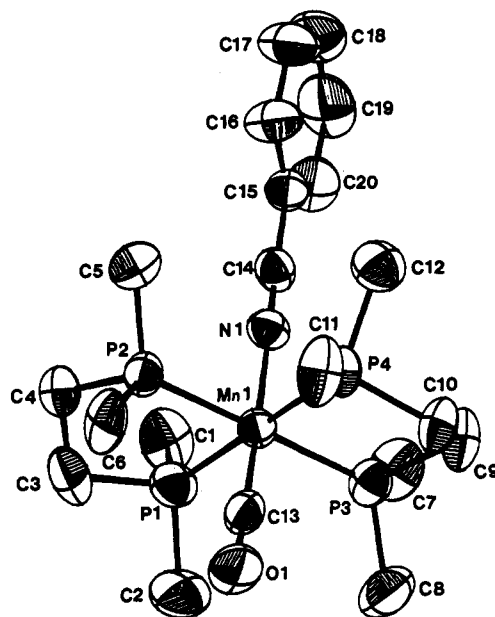
The reaction may be interpreted in terms of the insertion of carbon monoxide into the Mn–C bond followed by reductive elimination of methyl and acetyl groups. The resulting Mn(I) species traps carbon monoxide at atmospheric pressure and benzonitrile to give **3**. Partial dissociation of the dmpe ligand in the initial stages of the reaction, giving a coordinatively unsaturated species, seems to be necessary, since the addition of free dmpe ligand to the reaction mixture considerably retarded the reaction.

Coordinated benzonitrile can be replaced smoothly by acetonitrile, affording  $[\text{Mn}(\text{CO})(\text{MeCN})(\text{dmpe})_2]^+\text{BPh}_4^-$  (**4**), when **3** was heated in acetonitrile to 70 °C for 2 h. An



equimolar amount of benzonitrile was detected in solution. Redissolving the isolated complex **4** in benzonitrile under similar conditions again gave **3** with liberation of acetonitrile, suggesting the reversibility of the reaction.

An intermediate purple complex,  $[\text{Mn}(\text{PhCN})(\text{dmpe})_2]^+\text{BPh}_4^-$  (**5**), can be isolated when the reaction is carried out at 40 °C. Full characterization of **5** was not feasible, since attempted recrystallization of **5** in THF, acetonitrile, DMSO, acetone, and methylene chloride failed. However, the quantitative liberation of benzonitrile on hydrolysis of **5** supports its chemical formula. Complex **5** is considered to be an intermediate in the formation of **3** from **2**, because **5** can be converted to **3** by further reaction with CO in benzonitrile at 90 °C. A noticeable feature in the IR spectrum of **5** is the considerably lower CN stretching band ( $2101 \text{ cm}^{-1}$ ) observed. According to previous studies on the coordination mode of the nitrile ligand, end-on type coordination shows a general increase of the  $\nu(\text{CN})$ , while side-on type coordination decreases  $\nu(\text{CN})$  by 40–540  $\text{cm}^{-1}$ .<sup>16</sup> In the latter case, the value of  $\nu(\text{CN})$  indicates the magnitude of back-bonding in side-on coordination. However, lowering of  $\nu(\text{CN})$  does not necessarily indicate side-on coordination, since the end-on coordination of a nitrile to a ruthenium(II) ammine complex showed considerable lowering of  $\nu(\text{CN})$  ( $43 \text{ cm}^{-1}$ ).<sup>17</sup> Full characterization by X-ray structure analysis is needed in order to confirm the coordination mode in **5**, although the present large shift of  $\nu(\text{CN})$  to lower frequency (127



**Figure 2.** ORTEP drawing of  $[\text{Mn}(\text{CO})(\text{PhCN})(\text{dmpe})_2]^+\text{BPh}_4^-$  (**3**) showing the atomic numbering scheme used. The counteranion is omitted for clarity. Ellipsoids are drawn at the 50% probability level.

$\text{cm}^{-1}$ ) could suggest the a side-on type coordination of benzonitrile.

**Structure of 3.** Yellow prisms of **3** suitable for X-ray structure analysis were obtained from THF/ether. Crystallographic data are listed in Table I. Fractional atomic coordinates and selected bond distances and angles are listed in Tables V and VI. An ORTEP drawing of **3** is shown in Figure 2. The structure of **3** is essentially octahedral, in which CO and benzonitrile ligands coordinate trans to each other. Bond distances and angles are quite normal. The average Mn–P bond distance in **3** (2.26 Å) is shorter than those of Mn(III) complex **2** (2.32 Å) and  $\text{Mn}^{\text{IV}}\text{Me}_4(\text{dmpe})$  (2.45 Å). As discussed above, the large degree of back-bonding in the low-valent Mn complex is also considered to be responsible for this trend. However, the observed M–P bond distance in **3** is slightly longer than that in the known Mn(I)–dmpe complex,  $[\text{Mn}^{\text{I}}(\text{AlH}_4)(\text{dmpe})_2]_2$  (2.21 Å),<sup>2d</sup> and is comparable to that in the octahedral dimethylmanganese(II) complex,  $\text{Mn}^{\text{II}}\text{Me}_2(\text{dmpe})_2$  (2.24–2.25 Å).<sup>3</sup> The discrepancy from this trend in spite of the formal oxidation state of Mn(I) may be attributed to the decrease of back-bonding in **3** due to competitive back-bonding between the P nucleus and the electron-accepting carbonyl ligand, which are trans to each other. A considerably lower  $\nu(\text{CO})$  value observed in **3** also supports the strong back-bonding of the CO ligand.

## Experimental Section

**General Considerations.** All manipulations were carried out under nitrogen or argon. Solvents were dried by using the following agents, distilled under nitrogen, and stored under nitrogen before use. Diethyl ether, hexane, and THF were dried over Na/benzophenone ketyl. Acetone was dried over Drierite for 1 week and distilled over fresh Drierite. Dichloromethane and benzonitrile were dried with phosphorus pentoxide. Methanol was dried by refluxing over magnesium methoxide. Acetonitrile, pyridine, and dimethyl sulfoxide were dried over  $\text{CaH}_2$ . Cyclohexene was dried with calcium chloride. 1,2-Bis(dimethylphosphino)ethane (dmpe) was prepared by the literature method.<sup>18</sup> DMSO- $d_6$  was distilled over  $\text{CaH}_2$ . Norcarane was prepared by

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Table II. Fractional Atomic Coordinates ( $\times 10^4$ ) for 2

atom	x	y	z	atom	x	y	z
Molecule I							
Mn(1)	7788 (1)	2576 (1)	5288 (1)	C(17)	9176 (7)	9243 (8)	3679 (8)
P(1)	8186 (2)	3152 (2)	6869 (2)	C(18)	9079 (7)	8516 (9)	2888 (7)
P(2)	9363 (2)	2954 (2)	5708 (2)	C(19)	8431 (7)	7660 (7)	2587 (6)
P(3)	7440 (2)	2124 (2)	3732 (2)	C(20)	7837 (5)	7494 (6)	3074 (5)
P(4)	6216 (2)	2070 (2)	4848 (2)	C(21)	6240 (5)	7925 (5)	3652 (5)
B(1)	7189 (6)	7953 (6)	4337 (6)	C(22)	6218 (7)	8699 (6)	3551 (7)
C(1)	7637 (8)	1292 (6)	5216 (8)	C(23)	5420 (7)	8695 (7)	2944 (8)
C(2)	7937 (7)	3860 (6)	5340 (7)	C(24)	4681 (6)	7929 (7)	2400 (6)
C(3)	7928 (9)	2353 (9)	7416 (8)	C(25)	4705 (6)	7137 (6)	2427 (6)
C(4)	7792 (11)	3988 (11)	7404 (8)	C(26)	5458 (5)	7144 (5)	3049 (6)
C(5)	9428 (8)	3771 (8)	7436 (7)	C(27)	6993 (5)	6996 (5)	4467 (5)
C(6)	9849 (7)	3216 (8)	6959 (8)	C(28)	7577 (6)	6539 (6)	4449 (6)
C(7)	10072 (8)	4018 (10)	5668 (11)	C(29)	7470 (7)	5792 (7)	4669 (7)
C(8)	9763 (7)	2136 (10)	5203 (9)	C(30)	6708 (7)	5482 (7)	4914 (6)
C(9)	7503 (10)	1104 (8)	3076 (8)	C(31)	6110 (7)	5877 (6)	4918 (6)
C(10)	8035 (13)	2942 (10)	3319 (8)	C(32)	6249 (6)	6636 (6)	4711 (6)
C(11)	6268 (9)	1965 (12)	3158 (9)	C(33)	7556 (5)	8713 (5)	5394 (5)
C(12)	5696 (8)	1453 (10)	3534 (10)	C(34)	7034 (7)	9088 (6)	5713 (7)
C(13)	5600 (9)	1244 (13)	5207 (15)	C(35)	7347 (9)	9697 (8)	6659 (8)
C(14)	5727 (11)	2871 (13)	4977 (16)	C(36)	8252 (10)	9908 (7)	7244 (7)
C(15)	7900 (5)	8156 (5)	3853 (5)	C(37)	8804 (8)	9525 (7)	6931 (7)
C(16)	8580 (6)	9035 (6)	4133 (6)	C(38)	8457 (6)	8932 (6)	6023 (6)
Molecule II							
Mn(2)	3391 (1)	2614 (1)	880 (1)	C(55)	7742 (7)	4745 (6)	1851 (7)
P(5)	2334 (2)	1132 (2)	36 (2)	C(56)	7402 (7)	4957 (7)	1116 (9)
P(6)	4075 (2)	2278 (2)	-157 (2)	C(57)	7423 (7)	4530 (7)	289 (8)
P(7)	4411 (2)	4111 (2)	1666 (2)	C(58)	7780 (6)	3889 (6)	181 (7)
P(8)	2708 (2)	2961 (2)	1917 (2)	C(59)	9174 (5)	2975 (5)	140 (5)
B(2)	8488 (6)	2838 (5)	699 (6)	C(60)	9740 (5)	3878 (6)	320 (6)
C(39)	2573 (6)	3016 (6)	15 (6)	C(61)	10413 (6)	4003 (7)	-87 (7)
C(40)	4209 (7)	2206 (7)	1735 (7)	C(62)	10490 (6)	3300 (7)	-665 (6)
C(41)	2256 (9)	354 (7)	619 (8)	C(63)	9932 (6)	2429 (7)	-839 (6)
C(42)	1104 (8)	859 (9)	-568 (10)	C(64)	9301 (5)	2286 (5)	-412 (5)
C(43)	2646 (11)	630 (8)	-907 (9)	C(65)	9124 (5)	2775 (5)	1615 (5)
C(44)	3617 (11)	1041 (9)	-691 (13)	C(66)	9818 (5)	3556 (5)	2369 (5)
C(45)	5320 (8)	2592 (11)	271 (10)	C(67)	10434 (6)	3539 (6)	3131 (6)
C(46)	3920 (10)	2656 (11)	-1079 (9)	C(68)	10372 (6)	2730 (6)	3153 (6)
C(47)	5577 (7)	4400 (8)	2457 (8)	C(69)	9675 (6)	1933 (6)	2420 (6)
C(48)	4640 (9)	4819 (7)	1017 (9)	C(70)	9084 (6)	1991 (50)	1697 (6)
C(49)	3917 (11)	4692 (8)	2366 (11)	C(71)	7525 (5)	1903 (5)	88 (5)
C(50)	3457 (11)	4141 (7)	2765 (10)	C(72)	7147 (5)	1489 (5)	-883 (5)
C(51)	1569 (10)	2964 (15)	1498 (11)	C(73)	6288 (6)	746 (6)	-1384 (6)
C(52)	2591 (9)	2382 (7)	2677 (8)	C(74)	5783 (6)	410 (6)	-913 (7)
C(53)	8138 (5)	3638 (5)	907 (5)	C(75)	6128 (5)	821 (6)	44 (7)
C(54)	8095 (5)	4080 (5)	1732 (6)	C(76)	7004 (5)	1561 (5)	531 (6)

the literature method.<sup>19</sup> IR spectra were recorded on JASCO IR A302 and FTIR 5M spectrometers. Molar electric conductivities were measured by using TOA Conduct Meter CM-5B. Magnetic susceptibilities were measured on a Shimadzu Magnetic balance MB-100 by using as a standard compound, and the magnetic moments of the metal were estimated by subtracting the total magnetic susceptibilities of non-metal atoms.<sup>20</sup> Photolyses were performed by using a high-pressure 400-W Hg lamp (RIKO 4000UWL). Elemental analyses were performed by using a Yanagimoto CHN autocorder MT-2. Analyses for Mn were performed by calorimetry.<sup>21</sup> Gases evolved in the reactions were quantitatively analyzed in the gas phase by GC by using an internal standard method. Liquids formed in reactions were also analyzed by GC after the gas analyses.

**Crystal Structure Analysis.** The crystal suitable for X-ray structure analysis was mounted in a capillary tube under nitrogen. Intensity data for 2 and 3 were collected on a Rigaku AFC-5R diffractometer at room temperature. No absorption corrections were applied. Data collections were carried out with the program CRYSTAN (Rigaku) on a FACOM A-70 computer for 2 and 3. Both structures were solved by CRYSTAN and refined by a full-matrix

least-squares method. The final refinement of 2 was performed by a block-diagonal least-squares method using a program, modified Shelx 76, on a HITAC M-680 computer. All the non-hydrogen atoms in 2 and 3 were refined anisotropically. Hydrogen atoms in 2 found in the differential map were refined isotropically. Hydrogen atoms in 3, which were found in the differential map and estimated by calculation, were included in the calculation, but they were not refined.

**trans-Dimethylbis(1,2-bis(dimethylphosphino)ethane)-manganese(III) Tetramethylaluminate (1).** To an ether suspension (50 mL) of the mixture of tris(2,4-pentanedionato)-manganese(III) (3.17 g, 9.00 mmol) and dmpe (3.0 mL, 18 mmol) at -40 °C was added trimethylaluminum (52 mmol). When the solution was allowed to stir at room temperature, its color turned red and a red precipitate was obtained in a few minutes. After stirring the solution for 1 day at room temperature, a red crude material was separated by filtration, washed with ether, and dried in vacuo. Recrystallization from THF/ether at -30 °C gave red crystals. Yield: 1.92 g (45%). Mp: 195 °C dec.  $\mu_B = 3.15$ .  $\Lambda = 18 \text{ S cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for  $C_{18}H_{50}P_4AlMn$ : C, 45.76; H, 10.67; Mn, 11.6. Found: C, 45.41; H, 11.06; Mn, 12.5. IR ( $\text{cm}^{-1}$ ):  $\nu(\text{Mn}-\text{C})$  455;  $\nu(\text{Al}-\text{C})$  693, 542.

**trans-Dimethylbis(1,2-bis(dimethylphosphino)ethane)-manganese(III) Tetraphenylborate (2).** Complex 1 (608.5 mg, 1.288 mmol) was treated with a solution of  $\text{NaBPh}_4$  (440.8 mg, 1.288 mmol) dissolved in a mixture of dichloromethane (30 mL) and acetonitrile (3 mL) at room temperature. The solution was hydrolyzed carefully until the gas evolution was over. Then a

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(20) Morino, Y., Ed. *Kagaku Benran (Chemistry Handbook)*, 2nd ed.; Maruzen: Tokyo, 1975.

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Table III. Selected Bond Lengths and Angles for 2

Molecule I			
(a) Bond Lengths (Å)			
Mn(1)-P(1)	2.328 (4)	P(2)-C(6)	1.86 (2)
Mn(1)-P(2)	2.335 (3)	P(2)-C(7)	1.88 (2)
Mn(1)-P(3)	2.307 (4)	P(2)-C(8)	1.81 (2)
Mn(1)-P(4)	2.306 (4)	P(3)-C(9)	1.82 (2)
Mn(1)-C(1)	2.100 (13)	P(3)-C(10)	1.87 (2)
Mn(1)-C(2)	2.109 (12)	P(3)-C(11)	1.81 (2)
P(1)-C(3)	1.86 (2)	C(11)-C(12)	1.48 (3)
P(1)-C(4)	1.85 (2)	P(4)-C(12)	1.92 (2)
P(1)-C(5)	1.82 (1)	P(4)-C(13)	1.83 (3)
C(5)-C(6)	1.51 (2)	P(4)-C(14)	1.78 (3)
(b) Bond Angles (deg)			
C(1)-Mn(1)-C(2)	179.2 (5)	C(2)-Mn(1)-P(2)	92.4 (3)
P(1)-Mn(1)-P(3)	175.4 (1)	C(2)-Mn(1)-P(3)	87.4 (4)
P(2)-Mn(1)-P(4)	174.8 (1)	C(2)-Mn(1)-P(4)	92.5 (3)
P(1)-Mn(1)-P(2)	83.7 (1)	C(3)-P(1)-C(4)	102.2 (8)
P(3)-Mn(1)-P(4)	84.2 (1)	C(7)-P(2)-C(8)	105.2 (8)
P(1)-Mn(1)-P(4)	97.3 (1)	C(9)-P(3)-C(10)	102.2 (9)
P(2)-Mn(1)-P(3)	95.3 (1)	C(13)-P(4)-C(14)	105 (1)
C(1)-Mn(1)-P(1)	92.7 (4)	P(1)-C(5)-C(6)	107.5 (9)
C(1)-Mn(1)-P(2)	87.4 (4)	C(5)-C(6)-P(2)	109 (1)
C(1)-Mn(1)-P(3)	91.8 (4)	P(3)-C(11)-C(12)	107 (1)
C(1)-Mn(1)-P(4)	87.5 (4)	C(11)-C(12)-P(13)	109 (1)
C(2)-Mn(1)-P(1)	88.2 (4)		
Molecule II			
(a) Bond Lengths (Å)			
Mn(2)-P(5)	2.320 (3)	P(6)-C(44)	1.85 (2)
Mn(2)-P(6)	2.332 (3)	P(6)-C(45)	1.84 (2)
Mn(2)-P(7)	2.316 (3)	P(6)-C(46)	1.81 (2)
Mn(2)-P(8)	2.334 (3)	P(7)-C(47)	1.84 (1)
Mn(2)-C(39)	2.108 (11)	P(7)-C(48)	1.86 (2)
Mn(2)-C(40)	2.107 (13)	P(7)-C(49)	1.83 (2)
P(5)-C(41)	1.85 (2)	C(49)-C(50)	1.45 (3)
P(5)-C(42)	1.85 (2)	P(8)-C(50)	1.87 (2)
P(5)-C(43)	1.83 (2)	P(8)-C(51)	1.83 (3)
C(43)-C(44)	1.44 (3)	P(8)-C(52)	1.83 (2)
(b) Bond Angles (deg)			
C(39)-Mn(2)-C(40)	179.5 (5)	C(40)-Mn(2)-P(6)	89.1 (4)
P(5)-Mn(2)-P(7)	177.3 (1)	C(40)-Mn(2)-P(7)	93.2 (4)
P(6)-Mn(2)-P(8)	179.6 (1)	C(40)-Mn(2)-P(8)	91.2 (4)
P(5)-Mn(2)-P(6)	84.2 (1)	C(41)-P(5)-C(4)	102.5 (8)
P(7)-Mn(2)-P(8)	84.5 (1)	C(45)-P(6)-C(8)	100.7 (8)
P(5)-Mn(2)-P(8)	96.2 (1)	C(47)-P(7)-C(48)	100.5 (8)
P(6)-Mn(2)-P(7)	95.2 (1)	C(51)-P(8)-C(52)	101.6 (9)
C(39)-Mn(2)-P(5)	90.2 (3)	P(5)-C(43)-C(44)	113 (1)
C(39)-Mn(2)-P(6)	89.5 (4)	C(43)-C(44)-P(6)	111 (2)
C(39)-Mn(2)-P(7)	87.1 (3)	P(7)-C(49)-C(50)	111 (1)
C(39)-Mn(2)-P(8)	89.2 (3)	C(49)-C(50)-P(8)	113 (1)
C(40)-Mn(2)-P(5)	89.5 (4)		

Table V. Fractional Atomic Coordinates ( $\times 10^4$ ) for 3

atom	x	y	z
Mn(1)	2889.6 (3)	5993.9 (6)	1936.0 (7)
P(1)	2691 (1)	6589 (1)	3340 (2)
P(2)	1960 (1)	6445 (1)	1131 (2)
P(3)	3829 (1)	5544 (1)	2719 (2)
P(4)	3092 (1)	5396 (1)	525 (1)
N(1)	3214 (2)	7168 (4)	1668 (4)
O(1)	2412 (3)	4289 (3)	2425 (4)
C(1)	3194 (3)	7388 (5)	4143 (5)
C(2)	2523 (4)	5803 (5)	4243 (5)
C(3)	1563 (3)	6736 (5)	2083 (6)
C(4)	1994 (3)	7238 (6)	2945 (6)
C(5)	1861 (3)	7453 (5)	348 (6)
C(6)	1437 (3)	5665 (6)	317 (7)
C(7)	4449 (3)	6351 (5)	2895 (6)
C(8)	3997 (4)	4982 (5)	3952 (6)
C(9)	4072 (3)	4717 (5)	1924 (7)
C(10)	3884 (3)	5057 (5)	820 (5)
C(11)	2713 (4)	4345 (5)	40 (6)
C(12)	3007 (4)	6043 (6)	-635 (6)
C(13)	2606 (3)	4976 (5)	2226 (5)
C(14)	3431 (3)	7838 (5)	1582 (5)
C(15)	3760 (3)	8655 (5)	1563 (6)
C(16)	3715 (4)	9085 (5)	635 (6)
C(17)	4061 (5)	9849 (7)	638 (9)
C(18)	4437 (5)	10160 (6)	1520 (11)
C(19)	4438 (4)	9741 (7)	2416 (9)
C(20)	4125 (4)	9000 (6)	2447 (6)
C(21)	4541 (3)	7558 (5)	6689 (5)
C(22)	4426 (3)	8402 (5)	6220 (6)
C(23)	4644 (4)	8649 (5)	5399 (6)
C(24)	4976 (4)	8074 (6)	5000 (6)
C(25)	5100 (3)	7237 (5)	5429 (5)
C(26)	4884 (3)	6994 (5)	6247 (6)
C(27)	4205 (3)	6155 (6)	7634 (6)
C(28)	3891 (4)	5718 (8)	6760 (7)
C(29)	3802 (4)	4785 (8)	6687 (7)
C(30)	4021 (4)	4267 (7)	7527 (8)
C(31)	4345 (4)	4662 (7)	8409 (7)
C(32)	4434 (3)	5586 (7)	8471 (6)
C(33)	4829 (4)	7479 (5)	8745 (6)
C(34)	5435 (4)	7475 (5)	8814 (6)
C(35)	5861 (4)	7611 (5)	9732 (7)
C(36)	5692 (4)	7773 (6)	10612 (6)
C(37)	5099 (4)	7770 (7)	10576 (7)
C(38)	4672 (4)	7634 (7)	9660 (7)
C(39)	3687 (5)	7785 (9)	7667 (8)
C(40)	3705 (5)	8689 (11)	7949 (9)
C(41)	3173 (6)	9241 (10)	7914 (8)
C(42)	2688 (9)	8641 (21)	7684 (15)
C(43)	2540 (9)	7887 (19)	7309 (13)
C(44)	3129 (5)	7392 (9)	7384 (8)
B(1)	4314 (4)	7252 (7)	7688 (7)

Table IV. Thermolysis of Dimethylmanganese(III) Complexes Containing 1,2-Bis(dimethylphosphino)ethane Ligands

complex	solvent	temp, °C	time, h	no. of mol/Mn		
				CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>
1	none	195	8	3.95	0.16	0.05
2	none	195	8	0.57	0.08	0.12
2	DMSO	80	1	1.05	0.45	0.08

large amount of water was added. Extraction of the organic layer with dichloromethane gave a red solution. After removal of all the volatiles in vacuo, the residual red solid was recrystallized from acetone at -30 °C. Yield: 625.1 mg (69%). Mp: 173 °C dec.  $\mu = 3.02 \mu_B$ .  $\Lambda = 45 \text{ S cm}^2 \text{ mol}^{-1}$ . Anal. Calcd for C<sub>38</sub>H<sub>58</sub>BP<sub>4</sub>Mn: C, 64.78; H, 8.30; Mn, 7.8. Found: C, 64.05; H, 8.25; Mn, 8.1. IR (cm<sup>-1</sup>):  $\nu(\text{Mn}-\text{C}) = 455$ .

**Thermolysis of 1 and 2.** Thermolyses of the dimethyl manganese(III) complex were performed by heating the sample in a Schlenk tube with a rubber septum under vacuum. Gases evolved were analyzed quantitatively by GC. Results were summarized in Table IV. Thermolysis of 2 (52.1 mg, 0.074 mmol) in DMSO (1 mL) in the presence of cyclohexene (0.075 mL) 80

°C for 1 h gave gases containing methane (0.055 mmol), ethylene (0.028 mmol), and ethane (0.0045 mmol). No norcarane was detected in solution by GC using a TCP 20% UNIPORT column.

**Carbonyl(benzonitrile)bis(1,2-bis(dimethylphosphino)ethane)manganese(I) Tetrphenylborate (3).** A Schlenk type flask containing a benzonitrile solution (2.0 mL) of complex 2 (213.7 mg, 0.303 mmol) was evacuated. Then carbon monoxide at atmospheric pressure was introduced at room temperature. The solution was heated to 90 °C to give a purple solution immediately. After 3 h, traces of methane, ethylene, and ethane were detected in the gas phase and in solution acetone (0.262 mmol, 73%) was detected by GC. Addition of an excess of ether gave a dark yellow solid, which was recrystallized from THF/ether at -30 °C to give yellow prisms. Yield: 147.4 mg (60%). Mp: 155.5 °C dec.  $\Lambda = 31 \text{ S cm}^2 \text{ mol}^{-1}$ . IR (cm<sup>-1</sup>):  $\nu(\text{CO})$  1830;  $\nu(\text{CN})$  2217. Anal. Calcd for C<sub>44</sub>H<sub>57</sub>NOBP<sub>4</sub>Mn: C, 65.60; H, 7.13; N, 1.74. Found: C, 65.60; H, 7.30; N, 1.69.

Photolysis of 3 (55.9 mg, 0.0694 mmol) in aqueous THF using a high-pressure Hg lamp for 1.5 h at 17 °C liberated carbon monoxide (0.0560 mmol, 81%) and benzonitrile (0.0572 mmol, 82%), which were quantitatively measured by GC.

3 was also obtained by the reaction of 4 (21.1 mg, 0.0284 mmol) with benzonitrile (1.0 mL) at 70 °C for 1.5 h. Acetonitrile (0.0266

Table VI. Selected Bond Lengths and Angles for 3

(a) Bond Lengths (Å)			
Mn(1)–P(1)	2.259 (2)	P(3)–C(7)	1.839 (8)
Mn(1)–P(2)	2.246 (2)	P(3)–C(8)	1.824 (8)
Mn(1)–P(3)	2.257 (2)	P(3)–C(9)	1.825 (8)
Mn(1)–P(4)	2.273 (2)	C(9)–C(10)	1.538 (10)
Mn(1)–C(13)	1.741 (8)	P(4)–C(10)	1.825 (8)
Mn(1)–N(1)	1.978 (6)	P(4)–C(11)	1.840 (8)
C(13)–O(1)	1.138 (10)	P(4)–C(12)	1.833 (8)
P(1)–C(1)	1.817 (7)	C(14)–C(15)	1.441 (11)
P(1)–C(2)	1.814 (8)	C(15)–C(16)	1.396 (12)
P(1)–C(3)	1.837 (8)	C(16)–C(17)	1.393 (13)
C(3)–C(4)	1.527 (10)	C(17)–C(18)	1.37 (2)
P(2)–C(4)	1.824 (9)	C(18)–C(19)	1.34 (2)
P(2)–C(5)	1.823 (8)	C(19)–C(20)	1.368 (14)
P(2)–C(6)	1.829 (8)	C(20)–C(15)	1.377 (10)
(b) Bond Angles (deg)			
C(130)–Mn(1)–N(1)	177.5 (3)	C(4)–P(2)–C(5)	102.1 (4)
C(13)–Mn(1)–P(1)	88.9 (3)	C(4)–P(2)–C(6)	101.9 (4)
C(13)–Mn(1)–P(2)	90.3 (2)	C(5)–P(2)–C(6)	102.0 (3)
C(13)–Mn(1)–P(3)	90.3 (2)	P(2)–C(4)–C(3)	108.5 (6)
C(13)–Mn(1)–P(4)	91.2 (3)	Mn(1)–P(3)–C(7)	119.1 (3)
N(1)–Mn(1)–P(1)	88.7 (2)	Mn(1)–P(3)–C(8)	121.3 (3)
N(1)–Mn(1)–P(2)	90.2 (2)	Mn(1)–P(3)–C(9)	109.3 (2)
N(1)–Mn(1)–P(3)	89.3 (2)	C(7)–P(3)–C(8)	102.2 (4)
N(1)–Mn(1)–P(4)	91.2 (2)	C(7)–P(3)–C(9)	99.8 (4)
P(1)–Mn(1)–P(2)	85.1 (1)	C(8)–P(3)–C(9)	102.0 (4)
P(2)–Mn(1)–P(4)	95.0 (1)	P(3)–C(9)–C(10)	107.6 (5)
P(3)–Mn(1)–P(4)	84.1 (1)	Mn(1)–P(4)–C(10)	109.7 (3)
P(1)–Mn(1)–P(3)	95.8 (1)	Mn(1)–P(4)–C(11)	117.2 (3)
P(1)–Mn(1)–P(4)	179.9 (1)	Mn(1)–P(4)–C(12)	121.7 (3)
P(2)–Mn(1)–P(3)	179.0 (1)	C(10)–P(4)–C(11)	101.4 (4)
O(1)–C(13)–Mn(1)	179.6 (10)	C(10)–P(4)–C(12)	102.2 (4)
C(14)–N(1)–Mn(1)	175.0 (5)	C(11)–P(4)–C(12)	102.6 (4)
Mn(1)–P(1)–C(1)	121.8 (3)	P(4)–C(10)–C(9)	108.4 (6)
Mn(1)–P(1)–C(2)	116.4 (3)	N(1)–C(14)–C(15)	173.7 (7)
Mn(1)–P(1)–C(3)	108.6 (3)	C(14)–C(15)–C(16)	119.4 (6)
C(1)–P(1)–C(2)	103.6 (3)	C(15)–C(16)–C(17)	117.9 (7)
C(1)–P(1)–C(3)	101.7 (3)	C(16)–C(17)–C(18)	121.0 (10)
C(2)–P(1)–C(3)	102.1 (4)	C(17)–C(18)–C(19)	120.3 (10)
P(1)–C(3)–C(4)	108.1 (5)	C(18)–C(19)–C(20)	120.5 (9)
Mn(1)–P(2)–C(4)	108.7 (2)	C(19)–C(20)–C(15)	120.2 (9)
Mn(1)–P(2)–C(5)	119.4 (3)	C(20)–C(15)–C(16)	120.2 (7)
Mn(1)–P(2)–C(6)	120.0 (3)	C(20)–C(15)–C(14)	120.5 (7)

mmol, 94%) was detected in solution. Addition of an excess of ether led to the precipitation of 4 (18.2 mg).

**Reaction of 2 with Carbon Monoxide in Benzonitrile in the Presence of dmpe.** Carbon monoxide (1 atm) was introduced into a benzonitrile solution (1.0 mL) of 2 (0.0795 mmol) at 60 °C. After stirring for 5 min, acetone was detected in 49% yield. A

similar experiment of 2 (0.0812 mmol) in the presence of dmpe (0.0839 mmol) under the same reaction conditions afforded acetone in 23% yield.

**Carbonyl(acetonitrile)bis(1,2-bis(dimethylphosphino)ethane)manganese(I) Tetrphenylborate (4).** Complex 3 (99.4 mg, 0.123 mmol) was dissolved in acetonitrile (2 mL) and stirred for 2 h at 70 °C. The yellow solution became light yellow. Benzonitrile (0.103 mmol) was detected in solution by GC. Addition of an excess of ether caused precipitation of a colorless powder, which was recrystallized from THF/ether at –30 °C as colorless needles. Yield: 87.4 mg (75%). Mp: 169–170 °C dec.  $\Lambda = 34 \text{ S cm}^2 \text{ mol}^{-1}$ . IR (cm<sup>-1</sup>):  $\nu(\text{CO})$  1850;  $\nu(\text{CN})$  2217. Anal. Calcd for C<sub>39</sub>H<sub>55</sub>NOBP<sub>4</sub>Mn: C, 63.00; H, 7.46; N, 1.88. Found: C, 62.97; H, 7.43; N, 1.74.

**(Benzonitrile)bis(1,2-bis(dimethylphosphino)ethane)manganese(I) Tetrphenylborate (5).** Complex 2 (149.3 mg, 0.202 mmol) was dissolved in benzonitrile (2.0 mL) and degassed. An excess of carbon monoxide at atmospheric pressure was brought in contact with the solution at room temperature. The solution was heated at 40 °C for 35 h to give a deep purple solution. Small amounts of methane (0.024 mmol), ethylene (0.003 mmol), and ethane (0.002 mmol) were also detected. Addition of a large excess of hexane gave a deep purple solid, which was repeatedly washed with hexane and dried in vacuo. Yield: 147.9 mg (94%). IR (cm<sup>-1</sup>):  $\nu(\text{CN})$  2101. No bands due to free benzonitrile were observed. One water molecule seems to be included in the solid sample of 5, since  $\nu(\text{OH})$  due to included water was observed at 3500 cm<sup>-1</sup> in spite of prolonged vacuum drying (10<sup>-3</sup> mmHg). Anal. Calcd for C<sub>43</sub>H<sub>59</sub>NOBP<sub>4</sub>Mn: C, 64.92; H, 7.48; N, 1.76. Found: C, 64.35; H, 7.43; N, 1.35.

Further reaction of 5 with CO in benzonitrile at 90 °C for 2 h led to the formation of 3.

Hydrolysis of 5 (26.1 mg, 0.0336 mmol) in THF (1.0 mL) led to a color change from purple to red. GC analysis of the solution revealed the liberation of benzonitrile (0.0227 mmol, 68%).

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**Supplementary Material Available:** Tables of crystal data, fractional atomic coordinates, anisotropic thermal parameters, and bond distances and bond angles (16 pages); listings of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.