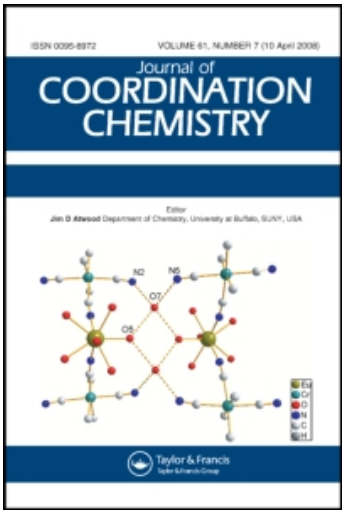

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REACTION AND X-RAY MOLECULAR STRUCTURAL STUDY OF SOME MANGANESE SULFUR CLUSTERS

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REACTION AND X-RAY MOLECULAR STRUCTURAL STUDY OF SOME MANGANESE-SULFUR CLUSTERS

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$[Mn(CO)_3]_2(\mu\text{-}SPh)_2(\mu\text{-dppfe})$ (**1**) has been synthesized by treatment of $Mn_4(SPh)_4(CO)_{12}$ (**2**) with Me_3NO followed by reaction with dppfe (dppfe = 1,1′-bis(diphenylphosphino)ferrocene). **1** is also synthesized from $Mn_2(SPh)_2(CO)_8$ (**3**) by the same procedure as above in an improved yield. The molecular structures of these three manganese-sulfur derivatives have been determined by single crystal X-ray diffraction techniques. The geometry around the manganese atoms in **1** is severely distorted from octahedral, while the distortions from octahedral arrangement are lessened in **2** and **3**. The Mn · · · Mn separation (3.675(5) Å) in **1** is close to those of **2** and **3**.

Keywords: Manganese-sulfur cluster; 1, 1′-bis(diphenylphospino)ferrocene; X-ray structures

INTRODUCTION

In the past two decades, research on the synthesis, structure and properties of iron-sulfur cubane clusters has developed tremendously as synthetic analogues of the active sites of iron-sulfur proteins.[1] In contrast to the plethora of research for iron-sulfur clusters,[2] the chemistry of analogous manganese-sulfur cubane clusters has not to our knowledge been well explored. Recently we have found that higher-nuclearity clusters of the type $[RCCo_3(CO)_8]_2(\mu\text{-diphos})$ are easily synthesized by reaction of $RCCo_3(CO)_9$ with a diphosphine ligand (diphos) after decarbonylation with trimethylamine N-oxide, Me_3NO.[3] As an extension of this finding, we have applied a similar type of reaction to the manganese-sulfur cubane cluster,

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$Mn_4(\mu\text{-}SPh)_4(CO)_{12}$ (**2**). The present paper reports a unique degradation of the tetramer **2** by reaction with dppfe to the dimer, $[Mn(CO)_3]_2(\mu\text{-}SPh)_2(\mu\text{-}dppfe)$, **1**. X-ray structural analyses of **1**, **2** and **3** are also reported.

EXPERIMENTAL

Materials and General Procedures

All manipulations were made under a dry nitrogen and/or argon atmosphere. $Mn_4(SPh)_4(CO)_{12}$ (**2**) and $Mn_2(SPh)2(CO)_8$(**3**) were synthesized by the literature method.[4]

Synthesis of $[Mn(CO)_3]_2(\mu\text{-}SPh)_2(\mu\text{-}dppfe)$ (1)

To a THF solution (15 mL) of **2** (250 mg, 0.25 mmol) was added a methanol solution (~ 1 mL) of Me_3NO (27 mg, 0.36 mmol). The orange color of the THF solution of **2** immediatey faded. After stirring at room temperature for 30 min., an approximately 2/3 volume of the solvent was removed by vacuum. Then, a THF solution (15 mL) of dppfe (140 mg, 0.25 mmol) was added by using a syringe; an orange color was recovered. After the mixture was stirred at ambient temperature for 3 h, the solvent was evaporated under vacuum to leave an orange solid. The solid was dissolved in a minimum of benzene and the solution was subjected to a Yamazen YFLC-600 medium-pressure liquid chromatography (Wako-gel C-200). From a yellow band eluted with benzene, the golden yellow product, [Mn(CO)3]2(μ-SPh)2(μ-dppfe) (**1**) was obtained in 10% yield. The reaction of the dimer, **3** with dppfe at room temperature after decarbonylation with Me_3NO also afforded **1** in improved yield (22%). ^{1}H-NMR (90 MHz, CDC_{13}): δ 3.21 (s, 4H), 4.10 (s, 4H), 7.50 (m, 20H), 8.05, 8.18 (d, 10H). IR (ν(CO) (Nujol)): 2019(m), 2003(*vs*), 1940(s), 1917(m), 1879(s). ^{1}H-NMR spectra were measured with a Hitachi R-90 spectrometer in the Fourier-transform mode. The IR spectra were recorded on a JASCO Valor-III FT-IR spectrometer.

X-Ray Data Collection and Structure Determination

Golden yellow, quartz-like single crystals of **1** were grown from a dichloromethane-hexane (1:1) solution. A crystal with approximate dimensions $0.15 \times 0.15 \times 0.10$ mm^3 was mounted on a MAC MXC^3 diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Diffraction data were collected at 154K by use of an Oxford Cryostream Cooler to improve the intensity. Single crystals of **2** and **3** were grown from chloroform-hexane (1:2). An orange-yellow

crystal of **2** with approximate dimensions of $0.60 \times 0.30 \times 0.25 mm^3$ and a yellow crystal of **3** with approximate dimensions of $0.40 \times 0.30 \times 0.25 mm^3$ were mounted on the same diffractometer. However, data were collected at ambient temperature. The crystal data for **1–3** are collated in Table I. The structures were solved by a direct method (SHELXS-86) based on unique reflections and refined by a full-matrix least-squares method on a Sun SP/Classic work station with a Crystan program package provided by MAC Science. No absorption correction was applied. Refinements on **1** and **2** were made anisotropically for non-hydrogen atoms and refinements on **3** were made anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms. Structural refinements were made on a half molecule of **1** due to the symmetry requirement. The R factors in Table I refer to data with intensities greater than the indicated cutoff in σ. The molecular structures of **1–3** are shown in Figure 1–3. The atomic coordinates are listed in Table II and selected bond lengths angles are given in Table III. The $|F_o|-|F_c|$ tables and anisotropic temperature factor tables are available from the authors.

TABLE I Crystal data

Compound	*$[Mn(CO)_3]_2(\mu\text{-}SPh)_2(\mu\text{-}dppfe)\cdot 2CH_2Cl_2$ (1)*	*$Mn_4(SPh)_4(CO)12$ (2)*	*$Mn_2(SPh)_2(CO)_8$ (3)*
Formula	$C_{52}H_{38}FeMn_2O_6P_2S_2\cdot 2CH_2Cl_2$	$C_{36}H_{20}Mn_4O_{12}S_4$	$C_{20}H_{10}Mn_2O_8S_2$
Formula weight	1216.4	992.52	551.1
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	Pnca	Aa	P^1
a/Å	16.996(5)	16.544(3)	11.158(2)
b/Å	21.245(4)	22.081(3)	12.363(4)
c/Å	14.311(2)	11.529(2)	9.746(2)
α/deg	90	90	104.48(2)
β/deg	90	108.28(2)	113.22(1)
γ/deg	90	90	103.61(2)
V/Å^3	5167(2)	4000(1)	1108.8(5)
Z	4	4	2
d_{calcd}/gcm^{-3}	1.56	1.65	1.65
Crystal dimens/mm^3	0.15×0.15×0.15	0.60×0.30×0.25	0.40×0.30×0.25
μ(Mo kα)/cm^{-1}	7.58	9.44	8.54
Scan type	ω	2θ–ω	ω
Scan range	1.39+0.35tanθ	1.50+0.35tanθ	1.78+0.35tanθ
Scan speed/deg.min^{-1}	4.0	5.0	5.0
2θ max/deg	45	50	50
Temperature (K)	154	298	298
Unique reflections	3378	3529	3910
Reflections with $\|F_o\| \geq n\sigma\|F_o\|$	1658 (n = 5)	2709 (n = 4)	3337(n = 3)
No. of parameters refined	330	509	320
R	0.104	0.040	0.034
Rw	0.128	0.048	0.030

Mo Kα radiation(λ = 0.71073 Å); $R = \||Fo|-|F_c|\|/|F_o|$; $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma(F_o)^2]^{1/2}$ where $w = 1/\sigma^2(F)$.

TABLE II Atomic coordinates and isotropic thermal parameters, $B_{eq}(Å)^2$

atom	*x*	*y*	*z*	*B (eq)*
		$[Mn(CO)_3]_2(\mu\text{-}SPh)_2(\mu\text{-}dppfe)\cdot 2CH_2Cl_2$ (*1*)		
Fe	–0.2491800	–0.0000900	0.4510 (2)	1.2 (1)
Mn	–0.1430 (2)	0.0115 (2)	0.1299 (2)	1.5 (1)
S	–0.2616 (3)	0.0685 (3)	0.1594 (4)	1.7 (2)
P	–0.0950 (3)	–0.0037 (3)	0.2856 (3)	1.2 (2)
C 1	–0.085 (1)	0.082 (1)	0.124 (1)	1.9 (6)
C 2	–0.166 (1)	0.024 (1)	0.005 (2)	1.6 (6)
C 3	–0.063 (1)	–0.037 (1)	0.094 (2)	1.9 (7)
O 1	–0.0508 (9)	0.1284 (8)	0.115 (1)	3.0 (5)
O 2	–0.1742 (9)	0.0348 (6)	–0.071 (1)	2.4 (5)
O 3	–0.0086 (9)	–0.0673 (8)	0.070 (1)	2.6 (5)
C 5	–0. 147 (1)	0.025 (1)	0.388 (1)	1.5 (6)
C 6	–0.134 (1)	0.006 (1)	0.486 (1)	1.9 (6)
C 7	–0.220 (1)	0.092 (1)	0.483 (2)	2.1 (7)
C 8	–0.181(1)	0.046 (1)	0.542 (1)	1.3 (6)
C 9	–0.200 (1)	0.0763 (8)	0.386 (1)	0.8 (5)
C 10	–0.268 (1)	0.135 (1)	0.086 (1)	1.9 (6)
C 11	–0.324 (1)	0.190 (1)	–0.051 (2)	2.7 (7)
C 12	–0.289 (1)	0.245 (1)	–0.022 (2)	2.9 (8)
C 13	–0.233 (1)	0.1925 (9)	0.114 (1)	2.3 (7)
C 14	–0.243 (2)	0.246 (1)	0.062 (1)	3.0 (7)
C 15	–0.315 (1)	0.135 (1)	0.002 (2)	2.6 (7)
C 16	–0.003 (1)	0.0420 (9)	0.297 (1)	1.1 (5)
C 17	–0.002 (1)	0.097 (1)	0.350 (2)	1.9 (6)
C 18	0.067 (1)	0.133 (1)	0.353 (1)	1.7 (6)
C 19	0.137 (1)	0.115 (1)	0.305 (1)	1.9 (6)
C 20	0.135 (1)	0.058 (1)	0.256 (2)	2.7 (7)
C 21	0.066 (1)	0.021 (1)	0.250 (1)	1.6 (6)
C 22	–0.062 (1)	–0.083 (1)	0.321 (1)	1.6 (6)
C 23	–0.008 (1)	–0.091 (1)	0.391 (1)	1.8 (6)
C 24	0.018 (1)	–0.152 (1)	0.418 (2)	2.2 (6)
C 25	–0.008 (1)	–0.204 (1)	0.370 (2)	2.6 (7)
C 26	–0.064 (1)	–0.196 (1)	0.293 (2)	2.0 (6)
C 27	–0.088 (1)	–0.135 (1)	0.269 (1)	1.7 (6)
C 11	0.3368 (4)	0.1496 (4)	0.2322 (5)	5.0 (3)
C 12	0.3974 (5)	0.2608 (4)	0.1445 (6)	6.4 (3)
C 30	0.384 (1)	0.179 (1)	0.132 (2)	3.2 (7)
		$Mn_4(SPh)_4(CO)_{12}$(*2*)		
atom	*x*	*y*	*z*	*B (eq)*
Mn 1	–0.1398 (1)	–0.1890 (1)	0.4467 (1)	3.4 (1)
Mn 2	–0.0872 (2)	–0.0689 (2)	0.2702 (4)	3.9 (1)
Mn 3	–0.3007 (2)	–0.0688 (2)	0.2964 (4)	3.7 (1)
Mn 4	–0.24745 (8)	–0.1892 (2)	0.1216 (1)	3.5 (1)
S 1	–0.2807 (3)	–0.1764 (2)	0.3076 (5)	3.2 (1)
S 2	–0.1069 (4)	–0.1763 (2)	0.2636 (6)	3.4 (1)
S 3	–0.1554 (4)	–0.0806 (2)	0.4222 (6)	3.9 (2)
S 4	–0.2317 (4)	–0.0816 (2)	0.1447 (6)	3.5 (2)
C 1	–0.024 (1)	–0.1838 (2)	0.548 (2)	3.7 (2)
C 2	–0.133 (1)	–0.272 (2)	0.453 (2)	6.4 (6)
C 3	–0.177 (1)	–0.193 (1)	0.571 (2)	5.8 (7)
C 4	–0.094 (1)	0.010 (1)	0.271 (2)	5.3 (6)
C 5	0.019 (1)	–0.0690 (9)	0.388 (1)	4.1 (5)

TABLE II *(Continued)*

		$Mn_4(SPh)_4(CO)_{12}$ (2)		
atom	*x*	*y*	*z*	*B (eq)*
C 6	–0.052 (1)	–0.068 (1)	0.147 (2)	6.6 (5)
C 7	–0.349 (1)	–0.0707 (8)	0.424 (2)	3.0 (4)
C 8	–0.401 (1)	–0.066 (1)	0.191 (2)	6.5 (8)
C 9	–0.307 (1)	0.0154 (9)	0.282 (2)	4.7 (5)
C 10	–0.210 (1)	–0.194 (1)	–0.012 (2)	4.9 (6)
C 11	–0.257 (1)	–0.2683 (9)	0.138 (2)	3.4 (4)
C 12	–0.354 (1)	–0.190 (1)	0.040 (2)	3.8 (4)
O 1	–0.0430 (7)	–0.1849 (6)	0.592 (1)	6.7 (4)
O 2	–0.120 (1)	–0.3239 (7)	0.439 (2)	7.0 (5)
O 3	–0.206 (1)	–0.194 (1)	0.660 (2)	12.0 (9)
O 4	–0.076 (1)	0.0640 (7)	0.297 (2)	6.8 (4)
O 5	–0.085 (1)	–0.0698 (8)	0.460 (2)	5.9 (4)
O 6	–0.015 (1)	–0.0722 (9)	0.070 (2)	8.3 (7)
O 7	–0.369 (1)	–0.0707 (8)	0.504 (2)	6.7 (6)
O 8	–0.465 (1)	–0.058 (1)	0.114 (2)	7.7 (6)
O 9	–0.294 (1)	0.0635 (8)	0.291 (2)	10.0 (8)
O 10	–0.188 (1)	–0.2046 (9)	–0.085 (2)	8.2 (6)
O 11	–0.261 (1)	–0.3181 (9)	0. 121 (2)	10.6 (7)
O 12	–0.428(1)	–0.1871 (7)	–0.018 (2)	6.1 (5)
C 21	–0.364 (1)	–0.223 (1)	0.328 (2)	3.7 (5)
C 22	–0.350 (1)	–0.277 (1)	0.378 (2)	5.2 (5)
C 23	–0.406 (1)	–0.320 (1)	0.412 (2)	6.1 (8)
C 24	–0.486(2)	–0.296 (1)	0.379 (2)	7.4 (8)
C 25	–0.506 (1)	–0.2420 (9)	0.329 (2)	4.8 (5)
C 26	–0.444 (1)	–0.193 (1)	0.294 (2)	7.7 (7)
C 31	–0.022 (1)	–0.2194 (9)	0.237 (1)	3.8 (5)
C 32	0.061 (1)	–0.2004 (7)	0.264 (2)	3.8 (4)
C 33	0.127 (2)	–0.225 (1)	0.250 (3)	5.8 (7)
C 34	0.1063 (9)	–0.284 (1)	0.194 (2)	5.6 (7)
C 35	0.024 (1)	–0.3080 (9)	0.161 (2)	7.1 (6)
C 36	–0.047 (1)	–0.278 (1)	0.179 (2)	5.7 (6)
C 41	–0.268 (1)	–0.032 (1)	0.020 (2)	5.0 (6)
C 42	–0.299 (2)	–0.0590 (9)	–0.088 (2)	11 (1)
C 43	–0.350 (2)	–0.023 (2)	–0.210 (2)	8.3 (8)
C 44	–0.316 (2)	0.039 (1)	–0.202 (4)	15 (2)
C 45	–0.256 (2)	0.059 (1)	–0.097 (2)	7.7 (8)
C 46	–0.234 (2)	0.020 (1)	0.008 (2)	7.3 (7)
C 51	–0.123 (1)	–0.0388 (9)	0.567 (2)	3.9 (4)
C 52	–0.066 (1)	–0.061 (1)	0.671 (2)	9.8 (8)
C 53	–0.071 (3)	–0.022 (2)	0.765 (2)	13 (2)
C 54	–0.073 (1)	0.027 (1)	0.777 (1)	6.4 (5)
C 55	–0.015 (2)	0.055 (2)	0.670 (5)	17 (2)
C 56	–0.147 (2)	0.027 (1)	0.545 (3)	12 (1)

		$Mn_2(SPh)_2(CO)_8$ (3)		
atom	*x*	*y*	*z*	*B (eq)*
Mn1	0.13276 (4)	0.83814 (4)	0.20438 (5)	3.42 (2)
Mn2	0.10659 (4)	0.70975 (4)	–0.18826 (5)	3.54 (2)
S 1	0.20149 (7)	0.69498 (6)	0.06953 (8)	3.50 (2)
S 2	0.01387 (7)	0.83689 (7)	–0.06337 (9)	3.71 (2)
C 11	0.2792 (4)	0.9737 (3)	0.2488 (4)	5.4 (1)
C 12	–0.0132 (3)	0.7014 (3)	0.1583 (3)	3.8 (1)

TABLE II *(Continued)*

		$Mn_2(SPh)_2(CO)_8$ (3)		
atom	*x*	*y*	*z*	*B (eq)*
C 13	0.0608 (3)	0.9370 (3)	0.2893 (4)	4.6 (1)
C 14	0.2374 (3)	0.8326 (3)	0.3987 (4)	4.6 (1)
C 21	–0.0494 (3)	0.5732 (3)	–0.2532 (4)	4.2 (1)
C 22	0.2584 (3)	0.8496 (3)	–0.1195 (4)	5.3 (1)
C 23	0.1880 (3)	0.6137 (3)	–0.2567 (4)	4.8 (1)
C 24	0.0302 (3)	0.7236 (3)	–0.3823 (4)	4.5 (1)
O 11	0.3678 (3)	1.0576 (3)	0.2821 (4)	9.8 (2)
O 12	–0.0992 (2)	0.6176 (2)	0.1349 (3)	5.8 (1)
O 13	0.0179 (3)	0.9993 (2)	0.3460 (3)	7.5 (1)
O 14	0.3008 (3)	0.8283 (2)	0.5200 (3)	7.4 (1)
O 21	–0.1421 (2)	0.4887 (3)	–0.2944 (3)	6.5 (1)
O 22	0.3468 (3)	0.9346 (2)	–0.0861 (4)	9.1 (1)
O 23	0.2358 (3)	0.5499 (3)	–0.3025 (3)	8.0 (1)
O 24	–0.0107 (2)	0.7330 (2)	–0.5040 (3)	6.9 (1)
C 31	0.3857 (3)	0.7213 (2)	0.1506 (3)	3.8 (1)
C 32	0.4911 (4)	0.8322 (3)	0.2178 (5)	5.8 (1)
C 33	0.6315 (4)	0.8422 (4)	0.2751 (5)	6.5 (2)
C 34	0.6633 (4)	0.7418 (4)	0.2640 (4)	6.0 (2)
C 35	0.5596 (4)	0.6318 (4)	0.1951 (5)	7.1 (2)
C 36	0.4190 (4)	0.6202 (3)	0.1394 (4)	5.8 (1)
C 41	–0.1741 (3)	0.7688 (3)	–0.1584 (3)	3.9 (1)
C 42	–0.2520 (3)	0.7164 (3)	–0.3245 (4)	4.9 (1)
C 43	–0.3981 (3)	0.6654 (3)	–0.4026 (4)	5.6 (1)
C 44	–0.4671 (3)	0.6675 (3)	–0.3129 (4)	5.8 (1)
C 45	–0.3922 (4)	0.7208 (4)	–0.1493 (5)	6.7 (2)
C 46	–0.2450 (3)	0.7727 (4)	–0.0701 (4)	5.5 (1)
H 32	0.476 (4)	0.904 (4)	0.221 (5)	5.30 (0)
H 33	0.691 (4)	0.924 (4)	0.323 (5)	5.98 (0)
H 34	0.762 (4)	0.756 (3)	0.306 (4)	5.13 (0)
H 35	0.577 (4)	0.563 (4)	0.198 (5)	5.88 (0)
H 36	0.346 (4)	0.541 (3)	0.095 (4)	4.91 (0)
H 42	–0.211 (4)	0.708 (3)	–0.388 (4)	4.22 (0)
H 43	–0.449 (4)	0.630 (3)	–0.520 (5)	4.99 (0)
H 44	–0.568 (4)	0.626 (3)	–0.372 (4)	4.97 (0)
H 45	–0.435 (4)	0.733 (4)	–0.086 (5)	5.46 (0)
H 46	–0.197 (4)	0.803 (3)	0.041 (4)	4.62 (0)

TABLE III Selected interatomic distances (Å) and angles (deg)

Compound: $[Mn(CO)_3]_2(\mu\text{-}SPh)_2(\mu\text{-}dppfe)\cdot 2CH_2Cl_2$ **(1)**		$Mn_4(SPh)_4(CO)_{12}$ **(2)**		$Mn_2(SPh)_2(CO)_8$ **(3)**	
Distance		*Distance*			
Mn...Mn′	3.675(5)	Mn1...Mn2	3.613(5)	Mn1...Mn2	3.6206(7)
Mn–P	2.390(6)	Mn1...Mn3	3.775(4)	Mn1–S1	2.391(1)
Mn–S	2.394(6)	Mn1...Mn4	3.610(1)	Mn1–S2	2.410(1)
Mn–Cl	1.80(2)	Mn2...Mn3	3.639(6)	Mn2–S1	2.3852(9)
Mn–C2	1.84(2)	Mn2...Mn4	3.767(4)	Mn2–S2	2.413(1)
Mn–C3	1.78(2)	Mn3...Mn4	3.609(5)	Mn1–C11	1.859(4)
Fe–C5	2.02(2)	Mn1–S1	2.395(5)	Mn1–C12	1.859(3)
Fe–C6	2.02(2)	Mn1–S2	2.355(7)	Mn1–C13	1.816(4)
Fe–C7	2.06(2)	Mn1–S3	2.415(6)	Mn1–C14	1.820(4)
Fe–C8	2.00(2)	Mn2–S2	2.394(6)	Mn2–C21	1.869(3)
Fe–C9	2.04(2)	Mn2–S3	2.377(9)	Mn2–C22	1.858(3)
S–C10	1.76(2)	Mn2–S4	2.392(6)	Mn2–C23	1.808(4)
P–C5	1.82(2)	Mn3–S1	2.399(6)	Mn2–C24	1.814(4)
P–C16	1.85(2)	Mn3–S3	2.401(6)	S1–C31	1.798(3)
P–C22	1.85(2)	Mn3–S4	2.386(8)	S2–C41	1.792(3)
C1–O1	1.15(3)	Mn4–S1	2.392(7)	C11–O11	1.120(4)
C2–O2	1.13(3)	Mn4–S2	2.405(5)	C12–O12	1.134(4)
C3–O3	1.18(3)	Mn4–S4	2.396(6)	C13–O13	1.140(5)
		Mn1–C1	1.91(2)	C14–O14	1.136(4)
		Mn1–C2	1.84(2)	C21–O21	1.130(4)
		Mn1–C3	1.73(3)	C22–O22	1.128(5)
		Mn2–C4	1.74(2)	C23–O23	1.146(5)
		Mn2–C5	1.86(2)	C24–O24	1.139(5)
		Mn2–C6	1.70(3)		
		Mn3–C7	1.88(2)		
		Mn3–C8	1.72(2)		
		Mn3–C9	1.86(2)		
		Mn4–C10	1.84(2)		
		Mn4–C11	1.77(2)		
		Mn4–C12	1.72(2)		
		S1–C21	1.80(2)		

TABLE III (*Continued*)

Compound: $[Mn(CO)_3]_2(\mu\text{-}SPh)_2(\mu\text{-}dppfe)\cdot 2CH_2Cl_2$ (*1*)		$Mn_4(SPh)_4(CO)_{12}$ (*2*)		$Mn_2(SPh)_2(CO)_8$ (*3*)	
Distance		*Distance*			
		S2–C31	1.81(2)		
		S3–C41	1.76(2)		
		S4–C51	1.84(2)		
Angle					
Mn–S–Mn′	100.4(2)	S1–Mn1–S2	80.6(2)	S1–Mn1–S2	81.71(3)
S–Mn–S′	75.8(2)	S1–Mn1–S3	76.2(2)	S1–Mn2–S2	81.77(3)
P–Mn–S	101.0(2)	S2–Mnl–S3	79.8(2)	Mnl–S1–Mn	98.59(3)
S–Mn–Cl	92.5(7)	S2–Mn2–S3	79.8(2)	Mn1–S2–Mn	97.29(4)
S–Mn–C2	97.8(6)	S2–Mn2–S4	76.3(2)	S1–Mn1–C11	95.7(1)
S–Mn–C3	170.9(7)	S3–Mn2–S4	79.5(2)	S1–Mn1–C12	83.6(1)
P–Mn–Cl	88.3(7)	S1–Mn3–S3	76.4(2)	S1–Mn1–C13	173.70(8)
P–Mn–C2	172.1(7)	S1–Mn3–S4	80.3(2)	S1–Mn1–C14	91.6(1)
P–Mn–C3	86.2(7)	S3–Mn3–S4	79.1(2)	S2–Mn1–C11	87.3(1)
C1–Mn–C2	87.0(9)	S1–Mn4–S2	79.6(2)	S2–Mn1–C12	92.4(1)
C1–Mn–C3	93 (1)	S1–Mn4–S4	80.3(2)	S2–Mn1–C13	94.3(1)
C2–Mn–C3	88 (1)	S2–Mn4–S4	76.0(2)	S2–Mn1–C14	172.8(1)
Mn–C1–O1	176 (2)	Mn1–S1–Mn3	103.9(2)	S1–Mn2–C2	86.9(1)
Mn–C2–O2	174 (2)	Mn1–S1–Mn4	97.9(2)	S1–Mn2–C22	92.7(1)
Mn–C3–O3	177 (2)	Mn1–S2–Mn2	99.1(3)	S1–Mn2–C23	90.9(1)
Mn–P–C16	107.6(6)	Mn1–S2–Mn4	98.6(2)	S1–Mn2–C24	177.8(1)
Mn–P–C22	118.7(7)	Mn1–S3–Mn2	97.8(2)	S2–Mn2–C21	90.6(1)
Mn–P–C5	122.8(7)	Mn1–S3–Mn3	103.2(2)	S2–Mn2–C22	86.9(1)
Mn–S–C10		Mn2–S2–Mn4	103.4(2)	S2–Mn2–C23	172.6(1)
		Mn2–S3–Mn3	99.2(3)	S2–Mn2–C24	96.1(1)
		Mn2–S4–Mn3	99.2(3)	C11–Mn1–C12	179.3(2)
		Mn2–S4–Mn4	103.8(2)	C11–Mn1–C13	88.9(2)
		Mn3–S1–Mn4	97.8(2)	C11–Mn1–C14	90.5(2)
		Mn3–S4–Mn4	98.0(2)	C12–Mn1–C13	91.8(2)
		S1–Mn1–C1	169.1(6)	C12–Mn1–C14	89.7(1)
		S1–Mn1–C2	100.2(7)	C13–Mn1–C14	92.6(2)
		S1–Mn1–C3	92.3(7)	C21–Mn2–C22	177.5(2)

TABLE III (*Continued*)

Compound: $[Mn(CO)_3]_2(\mu\text{-}SPh)_2(\mu\text{-}dppfe)\cdot 2CH_2Cl_2$ (*1*)		$Mn_4(SPh)_4(CO)_{12}$ (*2*)		$Mn_2(SPh)_2(CO)_8$ (*3*)	
Distance		*Distance*			
		S2–Mn1–C1	94.1(8)	C21–Mn2–C23	89.7(2)
		S2–Mn1–C2	97 (1)	C21–Mn2–C24	92.7(1)
		S2–Mn1–C3	172.3(8)	C22–Mn2–C23	92.8(2)
		S3–Mn1–C1	93.6(6)	C22–Mn2–C24	87.6(2)
		S3–Mn1–C2	175.7(7)	C23–Mn2–C24	91.2(2)
		S3–Mn1–C3	95.8(9)	Mn1–S1–C31	118.4(1)
		S2–Mn2–C4	168.6(8)	Mn1–S1–C41	113.9(1)
		S2–Mn2–C5	96.3(6)	Mn2–S1–C31	11.6(1)
		S2–Mn2–C6	93.3(8)	Mn2–S2–C41	110.8(1)
		S3–Mn2–C4	93 (1)		
		S3–Mn2–C5	91.09(7)		
		S3–Mn2–C6	170.1(7)		
		S4–Mn2–C4	93.7(7)		
		S4–Mn2–C5	168.7(7)		
		S4–Mn2–C6	92.1(7)		
		S1–Mn3–C7	91.2(6)		
		S1–Mn3–C8	98.8(8)		
		S1–Mn3–C9	174.(4)		
		S3–Mn3–C7	96.6(5)		
		S3–Mn3–C8	171.9(9)		
		S3–Mn3–C9	100.4(6)		
		S1–Mn4–C10	173.0(7)		
		S1–Mn4–C11	88.2(7)		
		S1–Mn4–C12	90.2(8)		
		S2–Mn4–C10	94.0(6)		
		S2–Mn4–C11	98.1(5)		
		S2–Mn4–C12	168.5(8)		
		S4–Mn4–C10	95.4(8)		
		S4–Mn4–C11	167.8(7)		
		S4–Mn4–C12	97.2(8)		

RESULTS AND DISCUSSION

Our first objective for reaction of **2** with dppfe after treatment with Me_3NO was to synthesize a dppfe-briged dimer such as $[Mn_4(SPh)_4(CO)_{11}]_2(\mu$-dppfe). However, the product obtained is $[Mn(CO)_3]_2(\mu$-$SPh)_2(\mu$-dppe)(**1**) as described in the Experimental section. This suggested that the tetramer **2** was degraded to dimer, $Mn_2(SPh)_2(CO)_6$ by treatment with Me_3NO and this dimer was reacted with dppfe to yield **1**. Therefore, we have attempted reaction of **3** with dppfe after treatment with Me_3NO, which is an excellent decarbonylating reagent. The same product **1** is obtained in improved yield. Next, we attempted thermal reaction of **2** with dppfe; equimolar amounts of **2** and dppfe were heated at 80°C in toluene for 3 h. However, no reaction took place except decomposition. These findings suggest that degradation of the tetramer **2** by treatment with an oxidizing reagent Me_3NO is a key step for the formation of **1**. Fading of orange-color of **2** by treatment with Me_3NO also supports degradation of the tetramer. We do not have further evidence at present on whether the degraded fragment is dimer, $Mn_2(SPh)_2(CO)_6$ or a monomer such as $Mn(SPh)(CO)_3$. Therefore, discussion of the reaction mechanism is left for future exploration. At present we would like to comment that this study is a paradigm for easy degradation of large clusters to small clusters by an oxidizing reagent, Me_3NO.

Figure 1 shows the molecular structures of **1** and the molecular structures of **2** and **3** are shown in Figures 2 and 3. As seen from Figure 1, the iron atom contained in the dppfe moiety of **1** lies on the twofold axis. The Mn · · · Mn distance 3.675(5) Å in **1** is longer than that of **3** (3.6206(7) Å). However, this distance is intermediate compared with those of the cubane-like tetramer, **2**; the cubane framework is composed from two long Mn · · · Mn distances (3.767(4) – 3.775(4) Å) and four short Mn · · · Mn distances (3.610(1) – 3.639(6) Å). The Mn—S bond length of **1** (2.392(7) Å) is close to those of **2** (2.355(7) – 2.415(6) Å) and **3** (2.391(1) –2.413(1) Å). The geometry around the manganese atom in **1** is significantly distorted from a regular octahedral arrangement (the S—Mn—S angle is 75.8(2)°). However, distortion from regular octahedral arrangement is lessened in **3**; the S—Mn—S angle is 81.71(3)° and 81.77(3)°. The S—Mn—S angles in **2** are classified into two types; eight S—Mn—S angles are around 80° (79.1(1) – 80.6(2)°) and four S—Mn—S angles are around 76° (76.0(2) – 76.4(2)°). This may be compared with two types of Mn · · · Mn distances in **2**. The Mn—C bond lengths (1.78(2) – 1.80(2) Å) *trans* to the Mn—S bonds are shorter than that (1.84(2) Å) *trans* to the Mn—P bond in **1**. A similar trend is observed in **3**, the Mn—C bond lenghts *trans* to the Mn—S bonds are in the range 1.808(4) –1.820(4) Å, while the Mn—C bond lengths *cis* to the Mn—S bond are in the range 1.858(3) – 1.869(3) Å. For **2**,

all Mn—C bonds are *trans* to Mn—S bonds. Coordination of dppfe to the manganese atoms does not bring essential structural change but significant distortion from the octahedral arrangement because of steric repulsion among the four phenyl groups in **1**.

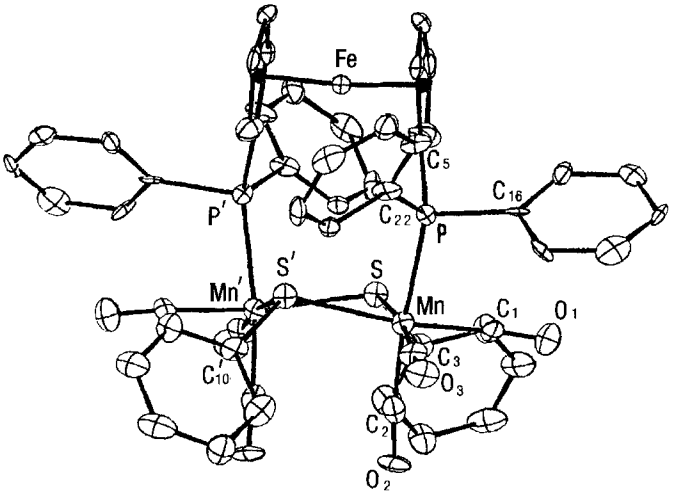

FIGURE 1 Molecular structure of $[Mn(CO)_3]_2(\mu\text{-}SPh)_2(\mu\text{-dppfe})$ (**1**).

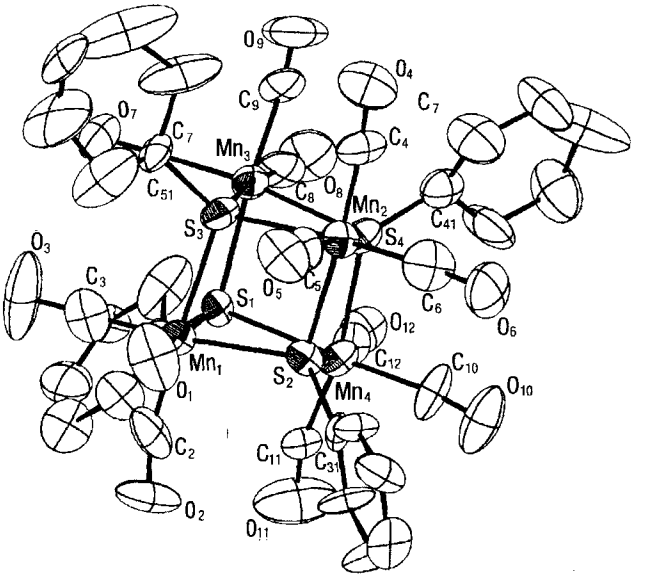

FIGURE 2 Molecular structure of $Mn_4(SPh)_4(CO)_{12}$ (**2**).

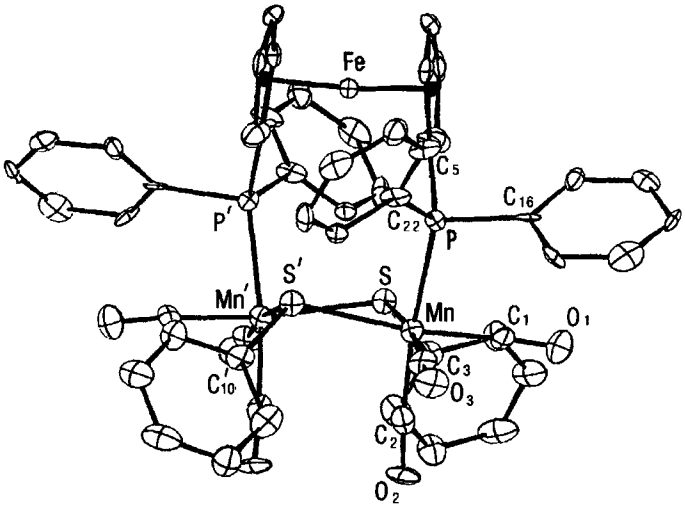

FIGURE 3 Molecular structure of $Mn_2(SPh)_2(CO)_8$ (**3**).

Cyclic voltammetric measurements were also made for these series of compounds expecting multi-redox processes as in Fe_4S_4 clusters;[1] however, only decomposition was observed during CV measurements.

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