

Marquette University

e-Publications@Marquette

**Chemistry Faculty Research and Publications/Department of Chemistry**

***This paper is NOT THE PUBLISHED VERSION; but the author's final, peer-reviewed manuscript. The published version may be accessed by following the link in the citation below.***

*Journal of Chemical Crystallography*, Vol. 38, No. 8 (August 2009): 595-602. [DOI](#). This article is © Springer and permission has been granted for this version to appear in [e-Publications@Marquette](#). Springer does not grant permission for this article to be further copied/distributed or hosted elsewhere without the express permission from Springer.

## **Investigations of 2-Thiazoline-2-thiol as a Ligand: Synthesis and X-ray Structures of $[\text{Mn}_2(\text{CO})_7(\mu\text{-NS}_2\text{C}_3\text{H}_4)_2]$ and $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-NS}_2\text{C}_3\text{H}_4)]$**

**Shishir Ghosh**

Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh

**Faruque Ahmed**

Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh

**Rafique Al-Mamun**

Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh

**Daniel T. Haworth**

Department of Chemistry, Marquette University, Milwaukee, WI

**Sergey V. Lindeman**

Department of Chemistry, Marquette University, Milwaukee, WI

**Tasneem A. Siddiquee**

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI

**Dennis W. Bennett**

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI

**Shariff E. Kabir**

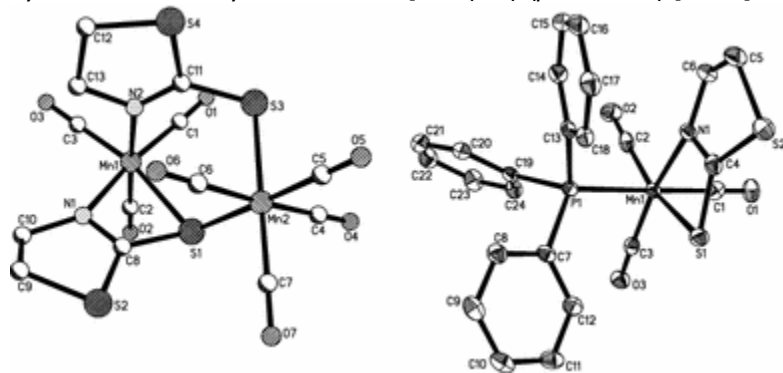
Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh

## Abstract

Treatment of  $\text{Mn}_2(\text{CO})_{10}$  with 2-thiazoline-2-thiol in the presence of  $\text{Me}_3\text{NO}$  at room temperature afforded the dimanganese complexes  $[\text{Mn}_2(\text{CO})_7(\mu\text{-NS}_2\text{C}_3\text{H}_4)_2]$  (**1**) and  $[\text{Mn}_2(\text{CO})_6(\mu\text{-NS}_2\text{C}_3\text{H}_4)_2]$  (**2**) in 51 and 34% yields, respectively. Compound **1** was quantitatively converted into **2** when reacted with one equiv of  $\text{Me}_3\text{NO}$ . Reaction of **1** with triphenylphosphine at room temperature furnished the mononuclear complex  $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-NS}_2\text{C}_3\text{H}_4)]$  (**3**) in 66% yield. All three new complexes have been characterized by elemental analyzes and spectroscopic data together with single crystal X-ray diffraction studies for **1** and **3**. Compound **1** crystallizes in the orthorhombic space group  $Pbcaw$  with  $a = 12.4147(2)$ ,  $b = 16.2416(3)$ ,  $c = 19.0841(4)$  Å,  $\beta = 90^\circ$ ,  $Z = 8$  and  $V = 3848.01(12)$  Å<sup>3</sup> and **3** crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 10.41730(10)$ ,  $b = 14.7710(2)$ ,  $c = 14.9209(2)$  Å,  $\beta = 91.1760(10)^\circ$ ,  $Z = 4$  and  $V = 2295.45(5)$  Å<sup>3</sup>.

## Graphical Abstract

Two new dimanganese complexes  $[\text{Mn}_2(\text{CO})_7(\mu\text{-NS}_2\text{C}_3\text{H}_4)_2]$  (**1**) and  $[\text{Mn}_2(\text{CO})_6(\mu\text{-NS}_2\text{C}_3\text{H}_4)_2]$  (**2**) were formed when  $[\text{Mn}_2(\text{CO})_{10}]$  was treated with 2-thiazoline-2-thiol in the presence of  $\text{Me}_3\text{NO}$ . Compound **2** reacts with  $\text{PPh}_3$  to give the monomeric complex  $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-NS}_2\text{C}_3\text{H}_4)]$ . The structures of **1** and **3** were established by crystallography. Shishir Ghosh, Faruque Ahmed, Rafique Al-Mamun, Daniel T. Haworth, Sergey V. Lindeman, Tasneem A. Siddiquee, Dennis W. Bennett, Shariff E. Kabir Investigations of 2-thiazoline-2-thiol as a ligand: Synthesis and X-ray structures of  $[\text{Mn}_2(\text{CO})_7(\mu\text{-NS}_2\text{C}_3\text{H}_4)_2]$  and  $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-NS}_2\text{C}_3\text{H}_4)]$ .



## Keywords

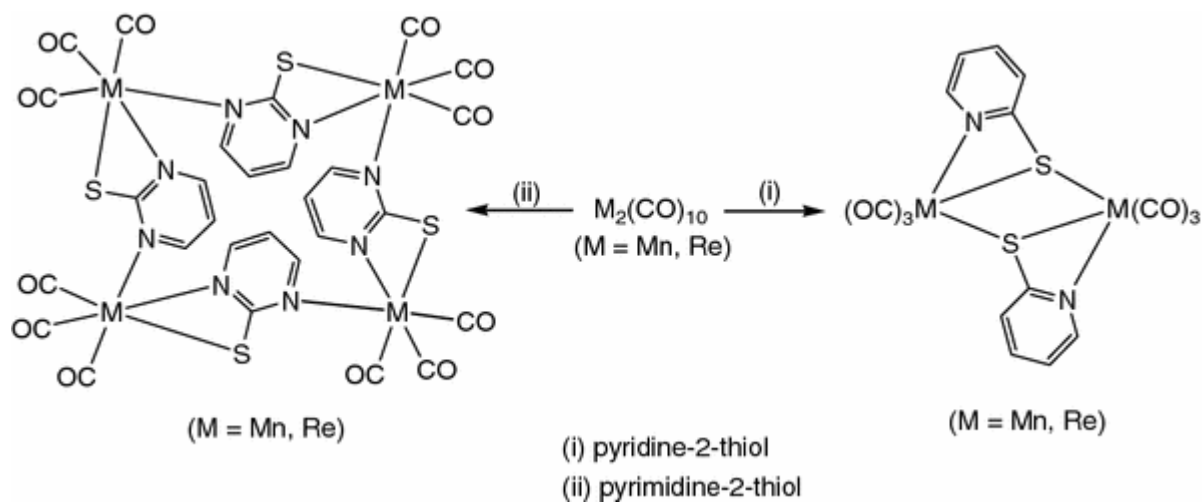
Manganese, Carbonyl, 2-Thiazoline-2-thiol, X-ray structures

## Introduction

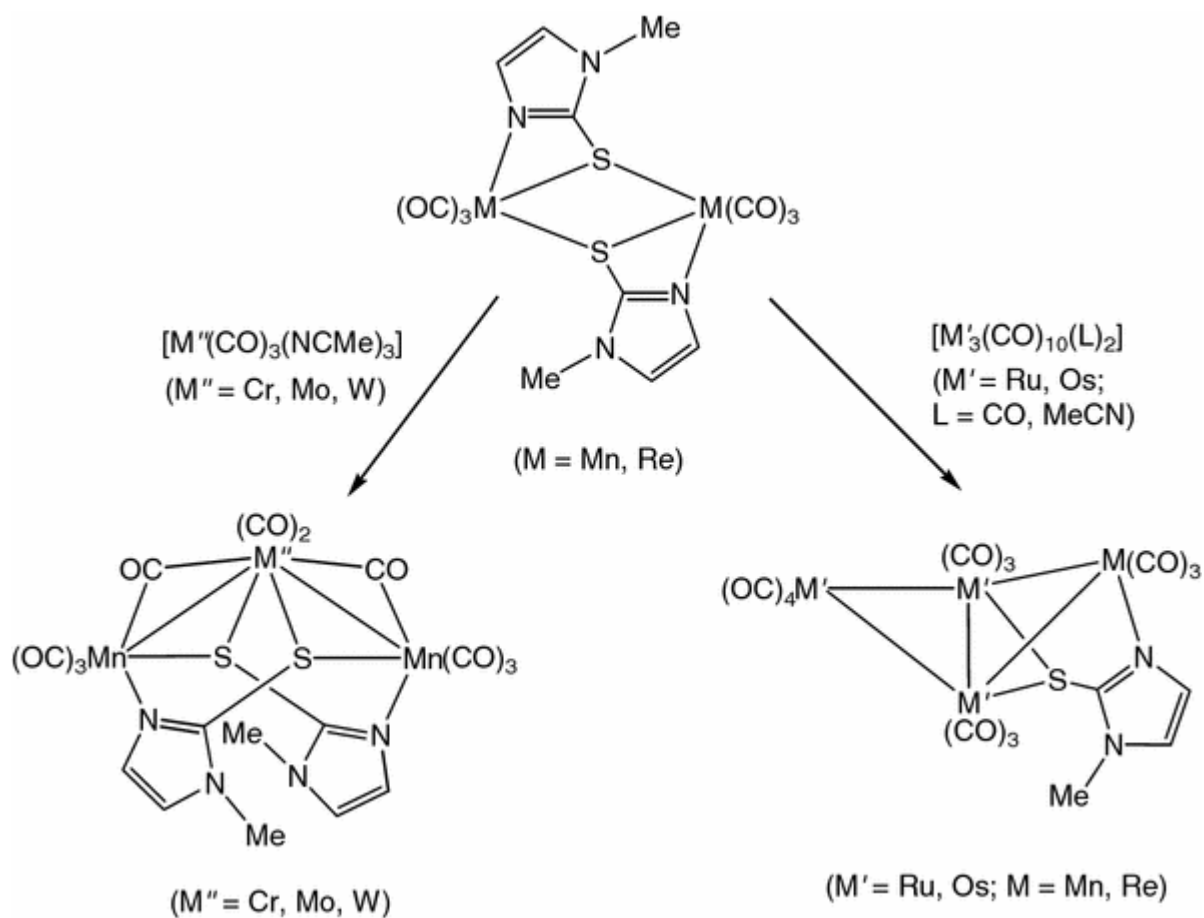
The study of the reactivity of nitrogen and sulfur containing small heterocyclic organic molecules towards transition metal carbonyl clusters has attracted considerable interest because such ligands frequently stabilizes the metal cluster framework by serving as chelating or bridging ligands<sup>1,2,3,4,5</sup> and also due to their potential applicability in modeling hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) processes.<sup>1,2,3,4,5,6,7</sup> These reactions are usually accompanied by C–H, N–H, S–H and C–N bonds activation of the heterocyclic ligand and markedly influenced by the structure of the heterocycle as well as the reaction conditions and starting complexes. We have previously investigated the reactions of pyridine-2-thiol,<sup>8</sup> pyrimidine-2-thiol,<sup>8</sup> thiazole,<sup>9,10</sup> 4-methylthiazole,<sup>11</sup> thiazolidine,<sup>7</sup> thiomorpholine,<sup>7</sup> benzothiazole,<sup>6</sup> and benzimidazole-2-thiol<sup>6</sup> with osmium and ruthenium carbonyl clusters and observed that the type of products obtained in these reactions are

remarkably influenced by the intrinsic reactivity of the metal carbonyl clusters, the heterocyclic ligands and the reaction conditions.

The reactions of heterocyclic thiols with group seven metal carbonyls are also influenced by the structure of the heterocyclic ligands as well as by the intrinsic reactivity of the metal carbonyls. For example, pyridine-2-thiol<sup>12,13</sup> reacts with  $M_2(CO)_{10}$  ( $M = Mn, Re$ ) to give the dimeric complex  $[M_2(CO)_6(\mu-NSC_5H_4)_2]$  ( $M = Mn, Re$ ), whereas, pyrimidine-2-thiol<sup>14</sup> affords the tetrameric complex  $[M_4(CO)_{12}(\mu-SN_2C_4H_3)_4]$  ( $M = Mn, Re$ ) exclusively (Scheme 1). We have recently shown that the five-membered heterocyclic thiol 2-mercapto-1-methylimidazole reacts with  $Mn_2(CO)_{10}$  to give the dimer  $[Mn_2(CO)_6(\mu-N_2SC_4H_5)_2]$ , while with  $Re_2(CO)_{10}$  the di-, tri- and tetramer products:  $[Re_2(CO)_6(\mu-N_2SC_4H_5)_2]$ ,  $[Re_3(CO)_8(\mu-CO)(\mu^3-SN_2C_4H_5)_2(\mu-H)]$  and  $[Re_4(CO)_{12}(\mu-SN_2C_4H_5)_4]$  were obtained.<sup>15</sup> The products isolated from these reactions not only show unique structural features, but also prove to be useful precursors for the synthesis of a wide variety of mixed-metal complexes.<sup>14,15,16,17</sup> For example, the trimetallic mixed-metal complexes of the general formula  $[MMn_2(CO)_8(\mu-CO)_2(\mu^3-SN_2C_4H_5)_2]$ <sup>15</sup> ( $M = Cr, Mo, W$ ) were obtained from the reaction between  $[M(CO)_3(NCMe)_3]$  ( $M = Cr, Mo, W$ ) and the dimanganese complex  $[Mn_2(CO)_6(\mu-NSC_4H_5)_2]$  in which the three metal atoms are linked by two  $M-Mn$  bonds, two  $\mu^3-N_2SC_4H_5$  ligands and two  $\mu-CO$  groups, whereas,  $[M'_3(CO)_{10}(L)_2]$  ( $M' = Ru, Os$ ;  $L = CO, MeCN$ ) and  $[M_2(CO)_6(\mu-N_2SC_4H_5)_2]$  ( $M = Mn, Re$ ) furnished the tetranuclear mixed-metal butterfly clusters of the general formula  $[M'_3M(CO)_{13}(\mu^3-SN_2C_4H_5)]$ <sup>17</sup> ( $M' = Ru, Os$ ;  $M = Mn, Re$ ) in which the single atom occupies a wingtip position (Scheme 2).



Scheme 1



**Scheme 2**

However, the reactivity of all these heterocyclic thiols so far studied is aromatic. In order to investigate the difference in reactivity and product distribution in the absence of aromaticity within the heterocyclic ring, we examined the reactivity of 2-thiazoline-2-thiol towards  $Mn_2(CO)_{10}$  and the results of this study are reported in the present paper.

## Experimental

All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. Reagent-grade solvents were dried by standard procedures and were distilled from appropriate drying agents prior to use. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Bruker DPX 400 instrument. Mass spectra were recorded on a Varian Mat 312 mass spectrometer. Elemental analyzes were performed by BCSIR Laboratories, Dhaka.  $Mn_2(CO)_{10}$  was purchased from Strem Chemical Inc. and used without further purification. 2-Thiazoline-2-thiol was purchased from Aldrich and used as received.

## Reaction of $\text{Mn}_2(\text{CO})_{10}$ with 2-Thiazoline-2-thiol in the Presence of $\text{Me}_3\text{NO}$

A  $\text{CH}_2\text{Cl}_2$  solution (40 mL) of  $\text{Mn}_2(\text{CO})_{10}$  (401 mg, 1.03 mmol), 2-thiazoline-2-thiol (245 mg, 2.06 mmol) and  $\text{Me}_3\text{NO}$  (155 mg, 2.07 mmol) was stirred at room temperature for 48 h. The solvent was removed in vacuo and the residue chromatographed by TLC on silica gel. Elution with hexane/acetone (7:3, v/v) developed two bands. The faster moving band gave  $[\text{Mn}_2(\text{CO})_7(\mu\text{-NS}_2\text{C}_3\text{H}_4)_2]$  (**1**) (283 mg, 51%) as yellow crystals, while the slower moving band afforded  $[\text{Mn}_2(\text{CO})_6(\mu\text{-NS}_2\text{C}_3\text{H}_4)_2]$  (**2**) (179 mg, 34%) as orange crystals after recrystallization from hexane/ $\text{CH}_2\text{Cl}_2$  at 4 °C. Spectral data for **1**: Anal. Calcd. for  $\text{C}_{13}\text{H}_8\text{Mn}_2\text{N}_2\text{O}_7\text{S}_4$ : C, 28.79; H, 1.49; N, 5.17. Found: C, 28.95; H, 1.63; N, 5.28%. IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_2\text{Cl}_2$ ): 2,089 m, 2,038 s, 2,029 vs, 2,018 vs, 2,008 vs, 1,964 s, 1,941 vs, 1,924 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.32 (s, 1H), 4.13 (s, 1H), 3.96 (s, 1H), 3.74 (s, 2H), 3.47 (s, 1H), 3.33 (s, 2H); mass spectrum:  $m/z$  542 ( $\text{M}^+$ ), 514 ( $\text{M}^+ - \text{CO}$ ), 486 ( $\text{M}^+ - 2\text{CO}$ ), 458 ( $\text{M}^+ - 3\text{CO}$ ), 430 ( $\text{M}^+ - 4\text{CO}$ ), 402 ( $\text{M}^+ - 5\text{CO}$ ), 374 ( $\text{M}^+ - 6\text{CO}$ ), 346 ( $\text{M}^+ - 7\text{CO}$ ). Spectral data for **2**: Anal. Calcd. for  $\text{C}_{12}\text{H}_8\text{Mn}_2\text{N}_2\text{O}_6\text{S}_4$ : C, 28.02; H, 1.57; N, 5.45. Found: C, 28.25; H, 1.63; N, 5.59%. IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_2\text{Cl}_2$ ): 2,089 w, 2,039 s, 2,020 vs, 1,939 vs (br)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.81 (s, 4H), 3.38 (s, 4H); mass spectrum:  $m/z$  514 ( $\text{M}^+$ ), 486 ( $\text{M}^+ - \text{CO}$ ), 458 ( $\text{M}^+ - 2\text{CO}$ ), 430 ( $\text{M}^+ - 3\text{CO}$ ), 402 ( $\text{M}^+ - 4\text{CO}$ ), 374 ( $\text{M}^+ - 5\text{CO}$ ), 346 ( $\text{M}^+ - 6\text{CO}$ ).

### Conversion of **1** into **2**

To a  $\text{CH}_2\text{Cl}_2$  solution (20 mL) of **1** (50 mg, 0.092 mmol) was added  $\text{Me}_3\text{NO}$  (7 mg, 0.093 mmol) and the mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/acetone (7:3, v/v) developed only one band, which gave **2** (42 mg, 89%) as orange crystals after recrystallization from hexane/ $\text{CH}_2\text{Cl}_2$  at 4 °C.

### Reaction of **2** with triphenylphosphine ( $\text{PPh}_3$ )

$\text{PPh}_3$  (102 mg, 0.389 mmol) was added to a  $\text{CH}_2\text{Cl}_2$  solution (30 mL) of **2** (100 mg, 0.195 mmol) and the mixture was stirred at room temperature for 72 h. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with hexane/acetone (1:1, v/v) developed one major and several minor bands. The major band gave **3** (134 mg, 66%) as yellow crystals after recrystallization from hexane/ $\text{CH}_2\text{Cl}_2$  at 4 °C while the content of the minor bands were too small for characterization. Spectral data for **3**: Anal. Calcd. for  $\text{C}_{24}\text{H}_{19}\text{MnNO}_3\text{PS}_2$ : C, 55.49; H, 3.69; N, 2.69. Found: C, 55.76; H, 3.75; N, 2.82%. IR ( $\nu_{\text{CO}}$ ,  $\text{CH}_2\text{Cl}_2$ ): 2,022 vs, 1,941 s, 1,907 s  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.60 (br. s, 6H), 7.38 (br. s, 9H), 3.39 (s, 1H), 3.25 (s, 1H), 2.99 (s, 1H), 2.48 (s, 1H);  $^{31}\text{P}\{-^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  59.0 (s); mass spectrum:  $m/z$  519 ( $\text{M}^+$ ), 491 ( $\text{M}^+ - \text{CO}$ ), 463 ( $\text{M}^+ - 2\text{CO}$ ), 435 ( $\text{M}^+ - 3\text{CO}$ ).

### X-ray Crystallography

Single crystals were mounted on fibers and diffraction data were collected at low temperature (see Table [1](#)) on a Bruker AXS SMART APEX CCD diffractometers using  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Data collection, indexing and initial cell refinements were all done using SMART<sup>18</sup> software. Data reduction was accomplished with SAINT<sup>19</sup> software and the SADABS program<sup>20</sup> was used to apply

empirical absorption corrections. The structures were solved by direct methods<sup>21</sup> and refined by full-matrix least-squares.<sup>22</sup> All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model. Scattering factors were taken from International Tables for X-ray Crystallography.<sup>23</sup> Additional details of data collection and structure refinement are given in Table 1.

**Table 1.** Crystal and structural refinement data for **1** and **3**

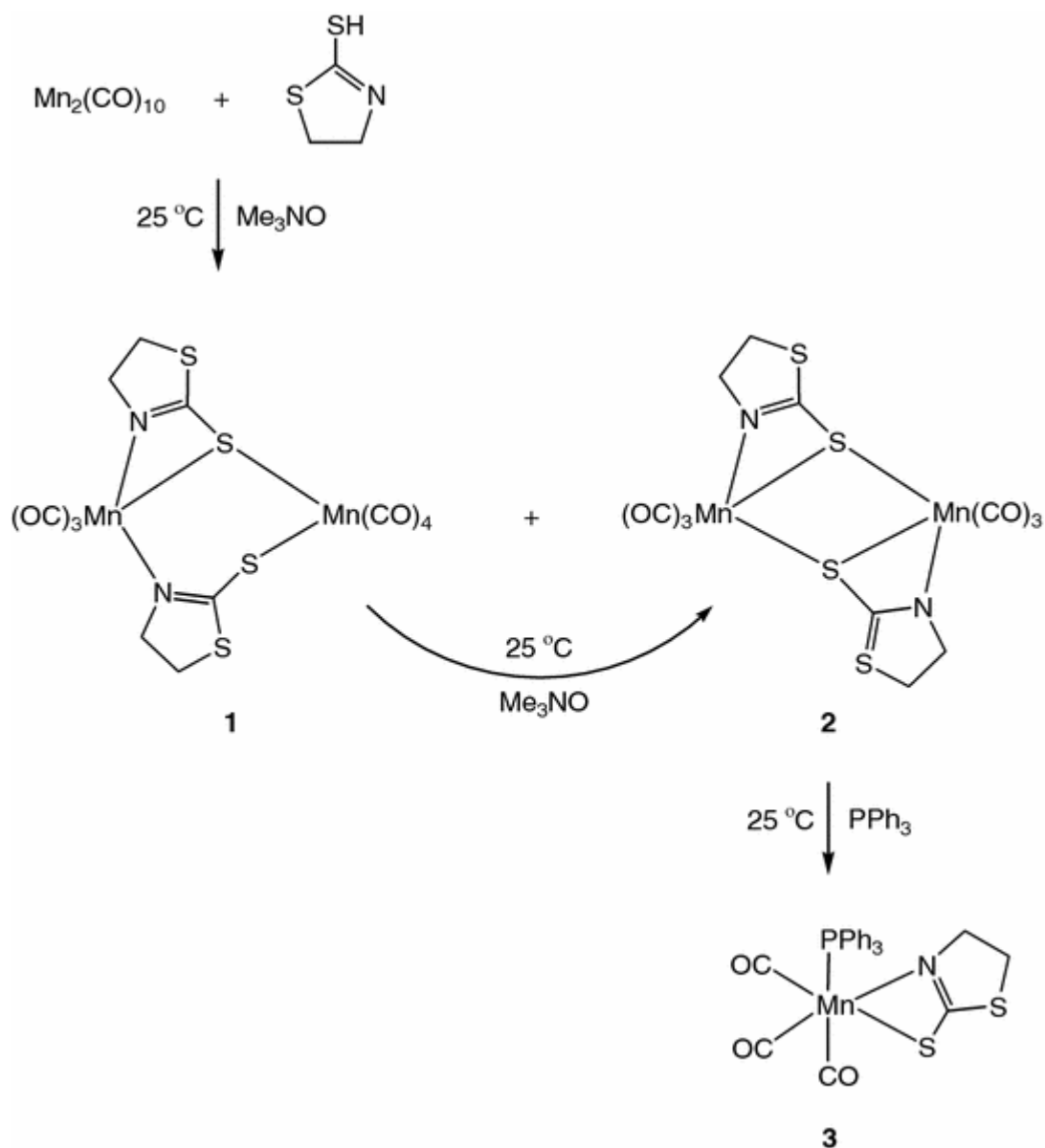
	<b>1</b>	<b>3</b>
Empirical formula	C <sub>13</sub> H <sub>8</sub> N <sub>2</sub> S <sub>4</sub> O <sub>7</sub> Mn <sub>2</sub>	C <sub>24</sub> H <sub>19</sub> NS <sub>2</sub> O <sub>3</sub> PMn
CCDC deposit no.	621648	694817
Formula weight	542.33	519.43
Crystal system	Orthorhombic	Monoclinic
Space group	<i>P bca</i>	<i>P 2<sub>1</sub>/n</i>
Unit cell dimensions		
<i>a</i> (Å)	12.4147(2)	10.41730(10)
<i>b</i> (Å)	16.2416(3)	14.7710(2)
<i>c</i> (Å)	19.0841(4)	14.9209(2)
$\alpha$ (°)	90	90
$\beta$ (°)	90	91.1760(10)
$\gamma$ (°)	90	90
Volume (Å <sup>3</sup> )	3848.01(12)	2295.45(5)
Z	8	4
Density (calculated) (Mg/m <sup>3</sup> )	1.872	1.503
Absorption coefficient (mm <sup>-1</sup> )	15.120	7.262
<i>F</i> (000)	2160	1064
Crystal size (mm <sup>3</sup> )	0.44 × 0.09 × 0.08	0.27 × 0.19 × 0.11
$\vartheta$ range for data collection (°)	5.05–61.46	4.21–68.08
Index ranges	0 ≤ <i>h</i> ≤ 14	-12 ≤ <i>h</i> ≤ 12

	<b>1</b>	<b>3</b>
	$0 \leq k \leq 18$	$0 \leq k \leq 17$
	$0 \leq l \leq 21$	$0 \leq l \leq 17$
Reflections collected	32056	19048
Independent reflections	2955 [ $R(\text{int}) = 0.0292$ ]	4052 [ $R(\text{int}) = 0.0199$ ]
Completeness to $\vartheta = 67.10^\circ$	99.2%	96.7%
Max. and min. transmission	0.3776 and 0.0576	0.5022 and 0.2445
Data/restraints/parameters	2955/0/285	4052/0/289
Goodness-of-fit on $F^2$	1.029	1.027
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0227$ , $wR_2 = 0.0526$	$R_1 = 0.0300$ , $wR_2 = 0.0753$
$R$ indices (all data)	$R_1 = 0.0245$ , $wR_2 = 0.0535$	$R_1 = 0.0313$ , $wR_2 = 0.0760$
Largest diff. peak and hole ( $\text{e}\text{\AA}^{-3}$ )	0.326 and $-0.261$	0.702 and $-0.274$

<sup>a</sup>Details in common: X-radiation, Cu-K $\alpha$  ( $\lambda = 1.54178\text{\AA}$ ), temperature (K) 100(2), refinement method: full-matrix least-squares on  $F^2$

## Results and Discussion

The reaction of  $\text{Mn}_2(\text{CO})_{10}$  with 2-thiazoline-2-thiol in the presence of  $\text{Me}_3\text{NO}$  at room temperature, followed by usual workup and chromatographic separation, afforded two dimanganese complexes,  $[\text{Mn}_2(\text{CO})_7(\mu\text{-NS}_2\text{C}_3\text{H}_4)_2]$  (**1**) and  $[\text{Mn}_2(\text{CO})_6(\mu\text{-NS}_2\text{C}_3\text{H}_4)_2]$  (**2**) in 51 and 34% yields, respectively. Compound **1** converted into **2** in 89% yield when a  $\text{CH}_2\text{Cl}_2$  solution of the former was treated with equivalent amount of  $\text{Me}_3\text{NO}$  (Scheme 3). These new compounds were characterized by elemental analysis, IR,  $^1\text{H}$  NMR and mass spectral data together with single crystal X-ray diffraction studies for **1**.

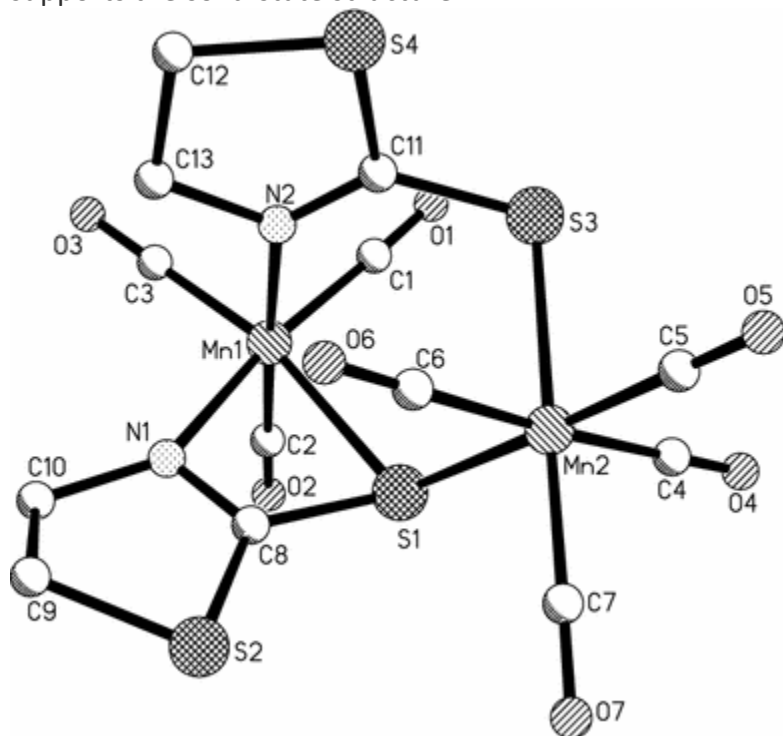


**Scheme 3**

An ORTEP diagram of the molecular structure of **1** is depicted in Fig. [1](#) and selected bond lengths and angles are listed in Table [2](#). The structure of compound **1** is analogous to the 2-mercapto-1-methylimidazole analog  $[\text{Mn}_2(\text{CO})_7(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$  previously reported.<sup>15</sup> The molecule consists of a dinuclear framework of two manganese atoms ligated by seven carbonyl and two 2-thiazoline-2-thiolato ligands. The seven carbonyl ligands are all terminal: three of which are bonded to Mn(1) and four to Mn(2) such that the molecule contains one  $\text{Mn}(\text{CO})_3$  and one  $\text{Mn}(\text{CO})_4$  groups which are linked by two bridging 2-thiazoline-2-thiolato ligands. The coordination modes of the heterocyclic ligands in the molecule are different. One bridges the two manganese centers through the exo-sulfur atom, while forming a four-membered chelate ring by coordinating through the nitrogen atom. The N–Mn–S angle within the chelate ring is  $68.12(5)^\circ$  which is very close to that observed in  $[\text{Mn}_2(\text{CO})_7(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$   $\{69.1(2)^\circ\}$ . Other bridges the two manganese centers using the nitrogen and the exo-



sulfur atoms that are coordinated to different metal centers. Thus one heterocyclic ligand acts as a five electron donor whereas the other donates three electrons to the metal centers. The coordination geometry around each manganese center can be rationalized as a distorted octahedron which is evident from the short S(1)–Mn(2)–S(3) and N(1)–Mn(1)–S(1) angles {88.40(2) and 68.12(5)°}. The *trans* angles about the manganese centers range from 167.49(7)° to 178.27(7)°. The Mn–S bond distances ranging from 2.3771(6)–2.4495(6) Å can be regarded as Mn–S single bonds. The av. Mn–C and av. Mn–N bond distances in **1** {1.831(2) and 2.060(18) Å} are similar to those observed in [Mn<sub>2</sub>(CO)<sub>7</sub>(μ-SN<sub>2</sub>C<sub>4</sub>H<sub>5</sub>)<sub>2</sub>] {1.811(9) and 2.057(8) Å}. The geometries of the heterocyclic ligands do not seem to be substantially distorted by coordinating to the metal centers. The Mn···Mn distance of 4.175(1) Å is clearly a non-bonding distance and according to the electron counting procedures, each manganese atom achieves an 18-electron configuration without a metal–metal bond. The spectroscopic data of compound **1** are consistent with the solid-state structure. The infrared spectrum in the carbonyl stretching region shows absorption bands above 1,900 cm<sup>-1</sup> indicating that all carbonyl groups are terminal. The <sup>1</sup>H NMR spectrum displays two sets of resonances: four singlets at δ 4.32, 4.13, 3.96 and 3.47 (each integrating to 1H) and two singlets at δ 3.74 and 3.33 (each integrating to 2H). However, from this study it is not possible to assign these resonances to the particular thiol moieties unambiguously. We assume that the four singlets appear due to the hydrogen atoms of one 2-thiazoline-2-thiolato ligand while the doublets appear for the hydrogen atoms of the other 2-thiazoline-2-thiolato ligand. The FAB mass spectrum exhibits the parent molecular ion peak at *m/z* 542 and peaks due to the sequential loss of seven CO ligands which supports the solid-state structure.



**Fig. 1.** X-ray structure of [Mn<sub>2</sub>(CO)<sub>7</sub>(μ-NS<sub>2</sub>C<sub>3</sub>H<sub>4</sub>)<sub>2</sub>] (**1**) showing the atom labeling scheme used. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level

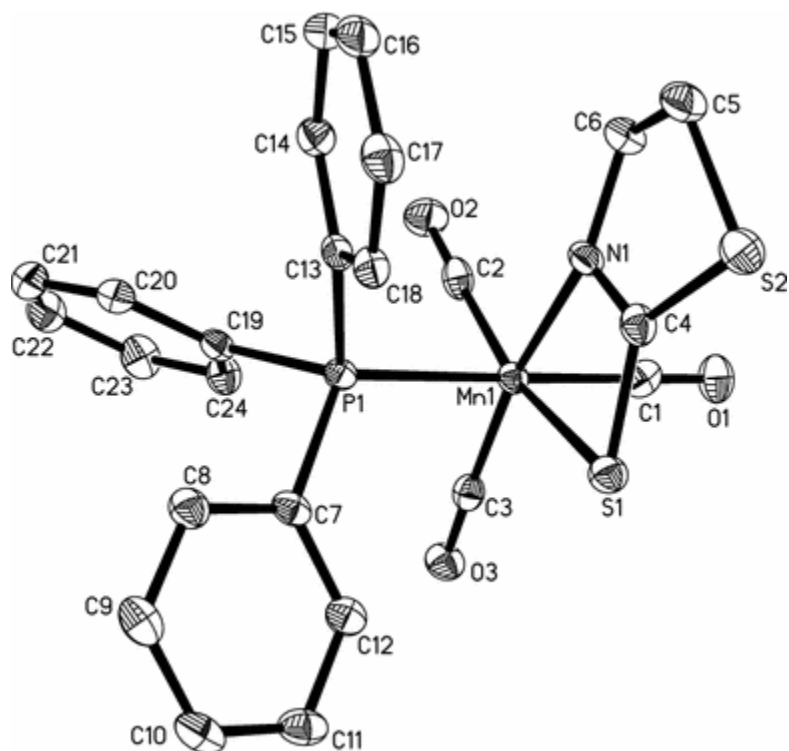
**Table 2** Selected bond distances (Å) and angles (°) for **1**

Bond distances (Å)			
Mn(1)–C(3)	1.800(2)	S(4)–C(11)	1.754(2)
Mn(1)–C(2)	1.815(2)	S(4)–C(12)	1.814(3)
Mn(1)–C(1)	1.819(2)	O(1)–C(1)	1.149(3)
Mn(1)–N(1)	2.0519(18)	O(2)–C(2)	1.144(3)
Mn(1)–N(2)	2.0681(18)	O(3)–C(3)	1.151(3)
Mn(1)–S(1)	2.4495(6)	O(4)–C(4)	1.126(3)
Mn(2)–C(7)	1.819(2)	O(5)–C(5)	1.140(3)
Mn(2)–C(5)	1.823(2)	O(6)–C(6)	1.138(3)
Mn(2)–C(6)	1.860(2)	O(7)–C(7)	1.145(3)
Mn(2)–C(4)	1.882(3)	N(1)–C(8)	1.281(3)
Mn(2)–S(1)	2.3771(6)	N(1)–C(10)	1.474(3)
Mn(2)–S(3)	2.4243(6)	N(2)–C(11)	1.292(3)
S(1)–C(8)	1.749(2)	N(2)–C(13)	1.483(3)
S(2)–C(8)	1.750(2)	C(9)–C(10)	1.531(4)
S(2)–C(9)	1.835(3)	C(12)–C(13)	1.523(3)
S(3)–C(11)	1.742(2)		
Bond angles (°)			
C(3)–Mn(1)–C(2)	88.56(10)	C(8)–S(1)–Mn(2)	109.89(7)
C(3)–Mn(1)–C(1)	89.25(10)	C(8)–S(1)–Mn(1)	75.87(8)
C(2)–Mn(1)–C(1)	88.81(10)	Mn(2)–S(1)–Mn(1)	119.76(2)
C(3)–Mn(1)–N(1)	100.23(9)	C(8)–S(2)–C(9)	88.75(11)
C(2)–Mn(1)–N(1)	93.75(8)	C(11)–S(3)–Mn(2)	100.37(7)
C(1)–Mn(1)–N(1)	170.23(9)	C(11)–S(4)–C(12)	91.63(11)

C(3)–Mn(1)–N(2)	94.11(9)	C(8)–N(1)–C(10)	113.22(19)
C(2)–Mn(1)–N(2)	177.31(9)	C(8)–N(1)–Mn(1)	102.27(14)
C(1)–Mn(1)–N(2)	91.62(8)	C(10)–N(1)–Mn(1)	144.38(15)
N(1)–Mn(1)–N(2)	85.39(7)	C(11)–N(2)–C(13)	112.65(18)
C(3)–Mn(1)–S(1)	167.49(7)	C(11)–N(2)–Mn(1)	128.32(15)
C(2)–Mn(1)–S(1)	87.74(7)	C(13)–N(2)–Mn(1)	119.02(14)
C(1)–Mn(1)–S(1)	102.61(7)	O(1)–C(1)–Mn(1)	175.0(2)
N(1)–Mn(1)–S(1)	68.12(5)	O(2)–C(2)–Mn(1)	177.7(2)
N(2)–Mn(1)–S(1)	89.57(5)	O(3)–C(3)–Mn(1)	176.6(2)
C(7)–Mn(2)–C(5)	91.51(10)	O(5)–C(5)–Mn(2)	179.5(2)
C(7)–Mn(2)–C(6)	91.56(10)	O(4)–C(4)–Mn(2)	176.7(2)
C(5)–Mn(2)–C(6)	88.52(10)	O(6)–C(6)–Mn(2)	178.8(2)
C(7)–Mn(2)–C(4)	92.29(10)	O(7)–C(7)–Mn(2)	179.5(2)
C(5)–Mn(2)–C(4)	92.47(10)	N(1)–C(8)–S(1)	113.18(17)
C(6)–Mn(2)–C(4)	176.00(10)	N(1)–C(8)–S(2)	117.66(17)
C(7)–Mn(2)–S(1)	90.18(7)	S(1)–C(8)–S(2)	129.05(13)
C(5)–Mn(2)–S(1)	178.27(7)	C(10)–C(9)–S(2)	105.60(17)
C(6)–Mn(2)–S(1)	91.81(7)	N(1)–C(10)–C(9)	107.27(19)
C(4)–Mn(2)–S(1)	87.09(7)	N(2)–C(11)–S(3)	127.51(17)
C(7)–Mn(2)–S(3)	177.46(7)	N(2)–C(11)–S(4)	116.76(17)
C(5)–Mn(2)–S(3)	89.90(7)	S(3)–C(11)–S(4)	115.66(13)
C(6)–Mn(2)–S(3)	90.59(7)	C(13)–C(12)–S(4)	105.75(16)
C(4)–Mn(2)–S(3)	85.54(7)	N(2)–C(13)–C(12)	111.03(19)
S(1)–Mn(2)–S(3)	88.40(2)		

Compound **2** is straightforwardly characterized by comparison of the spectroscopic data with those of the structurally characterized similar dimanganese complexes  $[\text{Mn}_2(\text{CO})_6(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$ ,<sup>15</sup>  $[\text{Mn}_2(\text{CO})_6(\mu\text{-SNC}_5\text{H}_4)_2]$ <sup>12</sup> and  $[\text{Mn}_2(\text{CO})_6(\mu\text{-SN}(\text{Me})\text{C}_5\text{H}_3)_2]$ .<sup>12</sup> The infrared spectrum of **2** in the carbonyl stretching region is very similar to those observed for  $[\text{Mn}_2(\text{CO})_6(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$ ,<sup>15</sup>  $[\text{Mn}_2(\text{CO})_6(\mu\text{-SNC}_5\text{H}_4)_2]$ <sup>12</sup> and  $[\text{Mn}_2(\text{CO})_6(\mu\text{-SN}(\text{Me})\text{C}_5\text{H}_3)_2]$ ,<sup>12</sup> indicating that they are isostructural. The FAB mass spectrum shows the parent molecular ion peak at  $m/z$  514 and peaks due to successive loss of six CO ligands. The  $^1\text{H}$  NMR spectrum displays two equal intensity singlets at  $\delta$  3.81 and 3.38 as expected for the two equivalent 2-thiazoline-2-thiolato ligands<sup>12,15</sup> which are also consistent with the proposed structure.

Treatment of complex **2** with  $\text{PPh}_3$  at room temperature gave the monomeric complex *fac*- $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-NS}_2\text{C}_3\text{H}_4)]$  (**3**) in 66% yield (Scheme 3). The infrared spectrum shows three strong  $\nu\text{CO}$  absorption bands [ $\text{CH}_2\text{Cl}_2$ : 2,022 vs, 1,941 s, 1,907 s  $\text{cm}^{-1}$ ] which support the facial configuration of **3**.<sup>12,24</sup> The FAB mass spectrum exhibits a parent molecular ion peak at  $m/z$  519 together with fragmentation peaks due to stepwise loss of three CO ligands. An ORTEP diagram of the molecular structure of **3** is shown in Fig. 2 and selected bond angles and distances are collected in Table 3. The molecule contains a single manganese atom with three carbonyl groups, a chelating 2-thiazoline-2-thiolato ligand and a triphenylphosphine ligand. The coordination geometry around manganese atom is a distorted octahedron with three carbonyl groups arranged in a facial fashion. The main distortion of the ideal octahedral geometry is due to the short bite angle of the chelating 2-thiazoline-2-thiolato ligand {68.29(5) $^\circ$ }. Within the molecule, the coordinated nitrogen and sulfur atom of the chelating ligand and the carbon atoms of the two CO ligands {C(2) and C(3)} constitute the best equatorial plane around the metal center with small deviation from planarity. The manganese atom is located in this plane and the  $\text{PPh}_3$  ligand occupies an axial site with respect to this plane. The *trans* angles about the metal center range from 162.82(7) $^\circ$  to 178.30(6) $^\circ$ . Compound **3** is structurally similar to *fac*- $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-SN}_2\text{C}_4\text{H}_3)]$ <sup>14</sup> obtained from the reaction between  $[\text{M}_4(\text{CO})_{12}(\mu\text{-SN}_2\text{C}_4\text{H}_3)_4]$  and triphenylphosphine. The Mn–N, Mn–S and av. Mn–C bond distances in **3** {2.0493(16), 2.4434(6) and 1.819(2) Å} are similar to those observed *fac*- $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-SN}_2\text{C}_4\text{H}_3)]$ <sup>14</sup> and related complexes found in literature.<sup>12,14,15,17</sup> In addition to usual aromatic resonances for the phenyl protons of the  $\text{PPh}_3$  ligand, the aliphatic region of the  $^1\text{H}$  NMR spectrum displays four singlets at  $\delta$  3.39, 3.25, 2.99 and 2.48 while the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum displays a singlet at  $\delta$  59.0 for the phosphorus atom of the  $\text{PPh}_3$  ligand which is consistent with the solid-state structure.



**Fig. 2.** X-ray structure of  $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-NS}_2\text{C}_3\text{H}_4)]$  (**3**) showing the atom labeling scheme used. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level

**Table 3.** Selected bond distances (Å) and angles (°) for **3**

Bond distances (Å)			
Mn(1)–C(3)	1.803(2)	P(1)–C(13)	1.8257(19)
Mn(1)–C(2)	1.809(2)	P(1)–C(7)	1.836(2)
Mn(1)–C(1)	1.845(2)	P(1)–C(19)	1.8418(19)
Mn(1)–N(1)	2.0493(16)	O(1)–C(1)	1.130(2)
Mn(1)–P(1)	2.3383(5)	O(2)–C(2)	1.141(3)
Mn(1)–S(1)	2.4434(6)	O(3)–C(3)	1.155(2)
Mn(1)–C(4)	2.620(2)	N(1)–C(4)	1.293(3)
S(1)–C(4)	1.713(2)	N(1)–C(6)	1.462(2)
S(2)–C(4)	1.756(2)	C(5)–C(6)	1.533(3)
S(2)–C(5)	1.836(2)		
Bond angles (°)			

C(3)–Mn(1)–C(2)	95.31(9)	C(4)–S(2)–C(5)	89.09(10)
C(3)–Mn(1)–C(1)	89.55(9)	C(13)–P(1)–C(7)	105.41(9)
C(2)–Mn(1)–C(1)	91.18(9)	C(13)–P(1)–C(19)	103.27(9)
C(3)–Mn(1)–N(1)	169.65(8)	C(7)–P(1)–C(19)	101.19(8)
C(2)–Mn(1)–N(1)	94.75(8)	C(13)–P(1)–Mn(1)	110.14(6)
C(1)–Mn(1)–N(1)	87.84(8)	C(7)–P(1)–Mn(1)	118.43(7)
C(3)–Mn(1)–P(1)	92.00(6)	C(19)–P(1)–Mn(1)	116.76(6)
C(2)–Mn(1)–P(1)	89.36(6)	C(4)–N(1)–C(6)	113.89(17)
C(1)–Mn(1)–P(1)	178.30(6)	C(4)–N(1)–Mn(1)	100.81(13)
N(1)–Mn(1)–P(1)	90.51(5)	C(6)–N(1)–Mn(1)	142.91(14)
C(3)–Mn(1)–S(1)	101.76(6)	O(1)–C(1)–Mn(1)	177.53(18)
C(2)–Mn(1)–S(1)	162.82(7)	O(2)–C(2)–Mn(1)	178.26(19)
C(1)–Mn(1)–S(1)	90.87(6)	O(3)–C(3)–Mn(1)	177.75(17)
N(1)–Mn(1)–S(1)	68.29(5)	N(1)–C(4)–S(1)	114.78(16)
P(1)–Mn(1)–S(1)	88.145(19)	N(1)–C(4)–S(2)	116.91(15)
C(2)–Mn(1)–C(4)	123.75(8)	S(1)–C(4)–S(2)	128.24(13)
C(1)–Mn(1)–C(4)	87.36(7)	N(1)–C(4)–Mn(1)	50.19(10)
N(1)–Mn(1)–C(4)	28.99(7)	S(1)–C(4)–Mn(1)	64.74(7)
P(1)–Mn(1)–C(4)	91.00(4)	S(2)–C(4)–Mn(1)	165.60(12)
S(1)–Mn(1)–C(4)	39.36(5)	C(6)–C(5)–S(2)	105.80(14)
C(4)–S(1)–Mn(1)	75.90(7)	N(1)–C(6)–C(5)	107.90(17)

## Supplementary Material

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number 621648 (space group *Pbca*) and 694817 (space group *P2<sub>1</sub>/n*). Copies of this information can be obtained free of

charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.ac.uk>).

## Notes

## Acknowledgment

Financial support of this work by the University Grants Commission of Bangladesh is gratefully acknowledged and FA acknowledges the National University of Bangladesh for a study leave.

## References

- <sup>1</sup>Brodie AM, Holden HD, Lewis J, Tailor MJ (1986) *J Chem Soc Dalton Trans* 633. doi: [10.1039/dt9860000633](https://doi.org/10.1039/dt9860000633)
- <sup>2</sup>Au YK, Cheung KK, Wong WT (1995) *Inorg Chim Acta* 228:267. doi: [10.1016/0020-1693\(94\)04184-W](https://doi.org/10.1016/0020-1693(94)04184-W)
- <sup>3</sup>Au YK, Cheung KK, Wong WT (1986) *J Chem Soc Dalton Trans* 633
- <sup>4</sup>Deeming AJ, Hardcastle KI, Karim M (1992) *Inorg Chem* 31:4792. doi: [10.1021/ic00049a015](https://doi.org/10.1021/ic00049a015)
- <sup>5</sup>Jeannin S, Jeannin Y, Lavigne G (1978) *Inorg Chem* 17:2103. doi: [10.1021/ic50186a014](https://doi.org/10.1021/ic50186a014)
- <sup>6</sup>Dilshad R, Hanif KM, Hursthouse MB, Kabir SE, Malik KMA, Rosenberg E (1999) *J Organomet Chem* 588:100. doi: [10.1016/S0022-328X\(99\)00201-6](https://doi.org/10.1016/S0022-328X(99)00201-6)
- <sup>7</sup>Hanif KM, Hursthouse MB, Kabir SE, Malik KMA, Rosenberg E (1999) *J Organomet Chem* 580:60. doi: [10.1016/S0022-328X\(98\)01090-0](https://doi.org/10.1016/S0022-328X(98)01090-0)
- <sup>8</sup>Kabir SE, Malik KMA, Molla E, Mottalib MA (2000) *J Organomet Chem* 616:157. doi: [10.1016/S0022-328X\(00\)00696-3](https://doi.org/10.1016/S0022-328X(00)00696-3)
- <sup>9</sup>Azam KA, Hursthouse MB, Kabir SE, Malik KMA, Tesmer M, Vahrenkamp H (1998) *Inorg Chem Commun* 1:402. doi: [10.1016/S1387-7003\(98\)00110-5](https://doi.org/10.1016/S1387-7003(98)00110-5)
- <sup>10</sup>Azam KA, Hussain SA, Kabir SE, Rahman MM, Hursthouse MB, Malik KMA, Rosenberg E (1998) *J Organomet Chem* 559:81. doi: [10.1016/S0022-328X\(98\)00416-1](https://doi.org/10.1016/S0022-328X(98)00416-1)
- <sup>11</sup>Azam KA, Dilshad R, Kabir SE, Khatoun K, Nessa L, Rahman MM, Rosenberg E, Hursthouse MB, Malik KMA, Deeming AJ (1996) *J Chem Soc, Dalton Trans* 1731
- <sup>12</sup>Kabir SE, Karim MM, Kundu K, Ullah SMB, Hardcastle KI (1996) *J Organomet Chem* 517:155. doi: [10.1016/0022-328X\(96\)06187-6](https://doi.org/10.1016/0022-328X(96)06187-6)
- <sup>13</sup>Deeming AJ, Karim M, Bates PA, Hursthouse MB (1988) *Polyhedron* 7:1401. doi: [10.1016/S0277-5387\(00\)80393-9](https://doi.org/10.1016/S0277-5387(00)80393-9)
- <sup>14</sup>Kabir SE, Alam J, Ghosh S, Kundu K, Hogarth G, Hossain GMG, Roesky HW (submitted) *J Chem Soc Dalton Trans*
- <sup>15</sup>Ghosh S, Kabir SE, Pervin S, Hossain GMG, Haworth DT, Lindeman SV, Siddiquee TA, Bennett DW, Roesky HW (2009) *Z Anorg Allg Chem* 635:76
- <sup>16</sup>Cockerton B, Deeming AJ, Karim M, Hardcastle KI (1991) *J Chem Soc Dalton Trans* 431. doi: [10.1039/dt9910000431](https://doi.org/10.1039/dt9910000431)
- <sup>17</sup>Kabir SE, Raha AK, Pervin S, Ghosh S, Hossain GMG, Haworth DT, Lindeman SV, Siddiquee TA, Bennett DW, Roesky HW, Salassa L (in press) *J Chem Soc Dalton Trans*
- <sup>18</sup>Version SMART 5.628 (2003) Bruker AXS, Inc.: Madison, WI
- <sup>19</sup>Version SAINT 6.36 (2002) Bruker AXS, Inc.: Madison, WI
- <sup>20</sup>Sheldrick G (2003) *SADABS* Version 2.10; University of Göttingen
- <sup>21</sup>Program XS from SHELXTL package (2001) V. 6.12, Bruker AXS, Inc.: Madison, WI
- <sup>22</sup>Program XL from SHELXTL package (2001) V. 6.12, Bruker AXS, Inc.: Madison, WI
- <sup>23</sup>Wilson AJC (ed) (1992) *International tables for X-ray crystallography, volume C*; Kynoch, Academic Publishers: Dordrecht, Tables 6.1.1.4 (pp 500–502) and 4.2.6.8 (pp 219–222)

24Singleton E, Moelwyn-Hughes JT, Gardner AWB (1970) J Organomet Chem 21:449. doi: [10.1016/S0022-328X\(00\)83647-5](https://doi.org/10.1016/S0022-328X(00)83647-5)