DOI: 10.1002/ejic.200700089

Syntheses and Structures of Molybdenum, Tungsten, and Manganese Complexes of a Cyclic Thiourea, $[M(CO)_5(SC_3N_2Me_4)]$ (M = Mo, W) and $[\{CpMn(CO)_2\}_2(\mu\text{-}SC_3N_2Me_4)]$

Kazuya Saito,[a] Yasuro Kawano,*[a] and Mamoru Shimoi*[a]

Keywords: Imidazolinethiones / Manganese / Molybdenum / Thioureas / Tungsten

Photolysis of $[CpMn(CO)_3]$ in the presence of 1,3,4,5-tetramethylimidazoline-2-thione, $SC_3N_2Me_4$ (**1**), produced a thione-bridged dinuclear complex, $[\{CpMn(CO)_2\}_2(\mu\text{-}SC_3N_2Me_4)]$ (**2**). Compound **2** shows unprecedented geometry of the Mn–S–Mn framework, featuring a pyramidal sulfur atom and long Mn···Mn distance. Photoreaction of $[M(CO)_6]$ (M = Mo, W) with **1** afforded mononuclear complexes $[M(CO)_5(SC_3N_2Me_4)]$ [M = Mo (**3**), W (**4**)]. In compounds **2**–**4**, the C–S bond of the thione ligand is stretched on coordination because of the polarization of the metal–ligand linkage. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

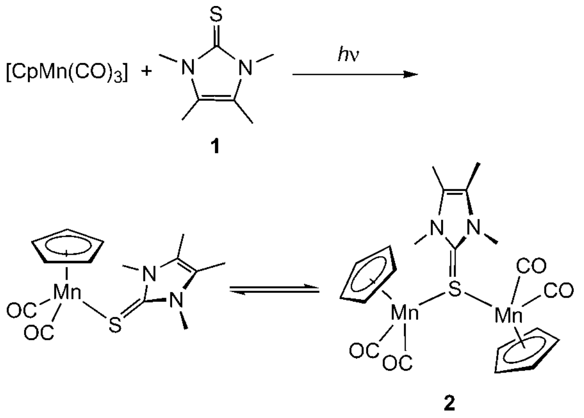
Introduction

N-Heterocyclic carbenes (NHC) have proved to be excellent ligands in transition-metal complexes.[1–4] NHCs also form various adducts with *p*-block element fragments to give compounds with a formula of $E–C(NR)_2(CR')_2$, where E = BX_3, AlX_3, GeI_2, $SnCl_2$, CH_2, S, Se, and so forth.[4,5] The sulfur adducts, imidazolinethiones (cyclic thioureas), are employed as precursors of NHCs.[6] They are also components of tris(mercaptoimidazolyl)hydroborate ligands, which attract considerable attention because of their face-capping character and strong electron-donating ability, and are applied to enzyme models.[7] It is thus increasingly important to better understand the coordinating ability of imidazolinethiones. However, few examples of their transition-metal complexes have been reported.[8–10] In this paper, we describe the reaction of 1,3,4,5-tetramethylimidazoline-2-thione (**1**)[6] with $[CpMn(CO)_3]$, which produces a dinuclear complex that involves a rare bridging thione ligand, $[\{CpMn(CO)_2\}_2(\mu\text{-}SC_3N_2Me_4)]$ (**2**). The syntheses and structures of molybdenum and tungsten derivatives, $[M(CO)_5(SC_3N_2Me_4)]$ [M = Mo (**3**), W (**4**)], are also reported here.

Results and Discussion

Synthesis of a Thione-Bridged Dinuclear Manganese Complex $[\{CpMn(CO)_2\}_2(\mu\text{-}SC_3N_2Me_4)]$ (2)

Irradiation of $[CpMn(CO)_3]$ with **1** in a 2:1 ratio produced a red solution. Its ^1H NMR spectrum exhibited three singlet resonances at δ = 1.11, 3.13, and 4.41 ppm, and their relative intensity was 6:6:5. This suggests formation of a mononuclear thione complex, $[CpMn(CO)_2(SC_3N_2Me_4)]$. However, cooling the solution afforded a small amount of $[\{CpMn(CO)_2\}_2(\mu\text{-}SC_3N_2Me_4)]$ (**2**) as red needles. Probably, the thione ligand is labile in solution, and a $[CpMn(CO)_2]$ fragment generated is reversibly coordinated to the sulfur atom of another molecule of $[CpMn(CO)_2(SC_3N_2Me_4)]$ to provide the dimer **2**, which precipitates on cooling [Equation (1)]. Indeed, when crystals of **2** were dissolved in [D_6]-benzene, the solution showed the ^1H NMR spectrum of the monomer.



(1)

The molecular structure of **2** is displayed in Figure 1, and key geometrical parameters are given in Table 1. Two $[CpMn(CO)_2]$ moieties are bridged by the imidazolinethione ligand. The Mn(1)–S and Mn(2)–S bond lengths are 2.3343(15) and 2.3495(11) Å, respectively. These values are similar to those of $[Mn_2(\mu\text{-}SMe)_2(\mu\text{-}CO)(PMe_3)_2\text{-}$

---

[a] Department of Basic Science, Graduate School of Arts and Sciences, University of Tokyo,
Meguro-ku, Tokyo 153-8902, Japan
Fax: +813-5454-6567
E-mail: ckawano1@mail.ecc.u-tokyo.ac.jp
cshimoi@mail.ecc.u-tokyo.ac.jp

$(CO)_4$] (av. 2.331 Å).[11] Cationic dinuclear manganese thiolates, [{(MeCp)Mn$(CO)_2$}$_2$(μ-SR)][PF_6] (**5**, R = *i*Pr, *t*Bu; MeCp = η^5-MeC_5H_4), have substantially shorter Mn–S bonds [2.242(2)–2.267(1) Å].[12] The Mn–S bonds of "inidene" complexes, [{CpMn$(CO)_2$}$_2${μ-S(C_6H_4X)}][PF_6] (**6**, X = H, NO_2), are even shorter [2.177(3)–2.218(3) Å] because of their multiple bond character.[12,13]

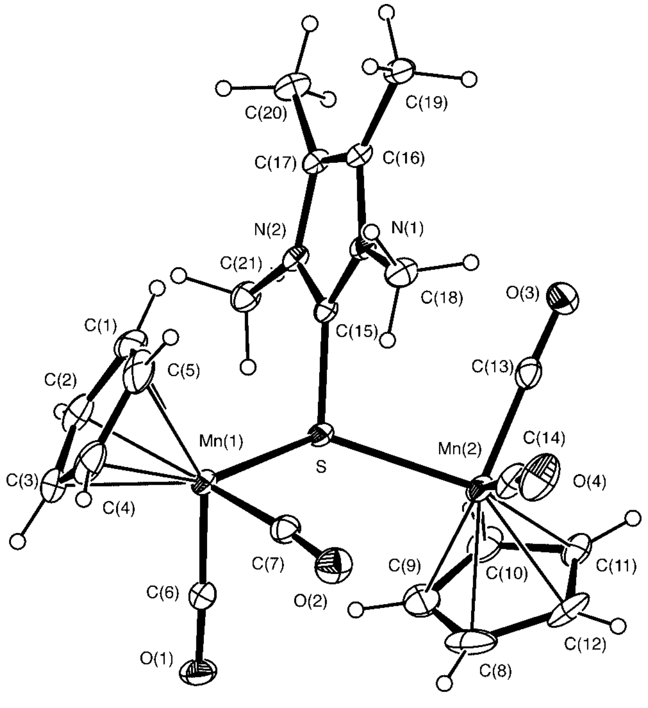


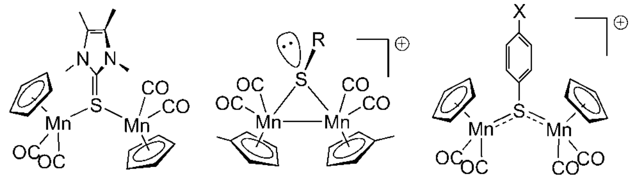
Figure 1. ORTEP drawing of [{CpMn$(CO)_2$}$_2$(μ-$SC_3N_2Me_4$)] (**2**) (30% thermal ellipsoids).

Table 1. Selected bond lengths [Å] and angles [°] for [{CpMn$(CO)_2$}$_2$(μ-S=$CN_2Me_2C_2Me_2$)] (**2**).

Bond lengths [Å]			
Mn(1)–S(1)	2.3343(15)	Mn(2)–S(1)	2.3495(11)
Mn(1)–C(6)	1.764(3)	Mn(1)–C(7)	1.773(3)
Mn(2)–C(13)	1.767(3)	Mn(2)–C(14)	1.779(3)
CNT(1)–Mn(1)[a]	1.785	CNT(2)–Mn(2)[a]	1.787
C(6)–O(1)	1.163(3)	C(7)–O(2)	1.158(4)
C(13)–O(3)	1.167(4)	C(14)–O(4)	1.159(4)
S(1)–C(15)	1.740(3)	C(15)–N(1)	1.348(3)
C(15)–N(2)	1.344(3)	C(16)–N(1)	1.389(3)
C(17)–N(2)	1.393(3)	C(16)–C(17)	1.357(4)
Bond angles [°]			
Mn(1)–S–Mn(2)	126.79(3)	C(15)–S–Mn(1)	110.05(10)
C(15)–S–Mn(2)	106.08(9)	CNT(1)–Mn(1)–S[a]	124.20
CNT(1)–Mn(1)–C(6)[a]	123.13	CNT(1)–Mn(1)–C(7)[a]	125.75
C(6)–Mn(1)–S	88.22(10)	C(7)–Mn(1)–S	96.13(10)
C(6)–Mn(1)–C(7)	88.85(13)	CNT(2)–Mn(2)–S[a]	117.68
CNT(2)–Mn(2)–C(13)[a]	124.16	CNT(2)–Mn(2)–C(14)[a]	123.38
C(13)–Mn(2)–S	94.56(10)	C(14)–Mn(2)–S	99.92(11)
C(13)–Mn(2)–C(14)	90.20(14)	N(1)–C(15)–S	129.4(2)
N(2)–C(15)–S	123.73(19)	N(2)–C(15)–N(1)	106.8(2)
C(15)–N(1)–C(16)	109.7(2)	C(15)–N(2)–C(17)	109.9(2)
C(17)–C(16)–N(1)	106.9(2)	C(16)–C(17)–N(2)	106.7(2)

[a] CNT: the centroid of the cyclopentadinyl ring.

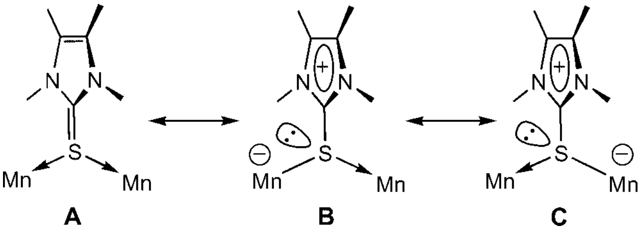
The bridging sulfur atom is pyramidalized. The sum of the bond angles around this atom is 343°, indicating the existence of a lone electron pair at the sulfur atom. The Mn(1)···Mn(2) interatomic distance is 4.1878(18) Å, and the Mn(1)–S–Mn(2) bond angle is 126.79(3)°. These indicate the absence of bonding interaction between the two metal atoms. Thus, the structure of **2** features a pyramidal sulfur atom and long Mn···Mn separation. This is an unprecedented geometry of the Mn–S–Mn framework (see Scheme 1). Thiolates **5** contain a pyramidal sulfur atom, but they have a Mn–Mn single bond.[12] The intermetallic bond length is 2.906(1) (R = *i*Pr) or 2.962(1) Å (R = *t*Bu). In contrast, the inidene complex **6** (X = NO_2) includes a planar sulfur atom and long Mn···Mn distance (4.032 and 4.046 Å; two independent molecules are present in the asymmetric unit).[12] Complex [Mn_2(μ-SMe)$_2$(μ-CO)$(PMe_3)_2(CO)_4$] has pyramidal sulfur atoms and a Mn–Mn single bond (2.581 Å).[11]



2 **5** (R = *i*Pr, *t*Bu) **6** (X = H, NO_2)

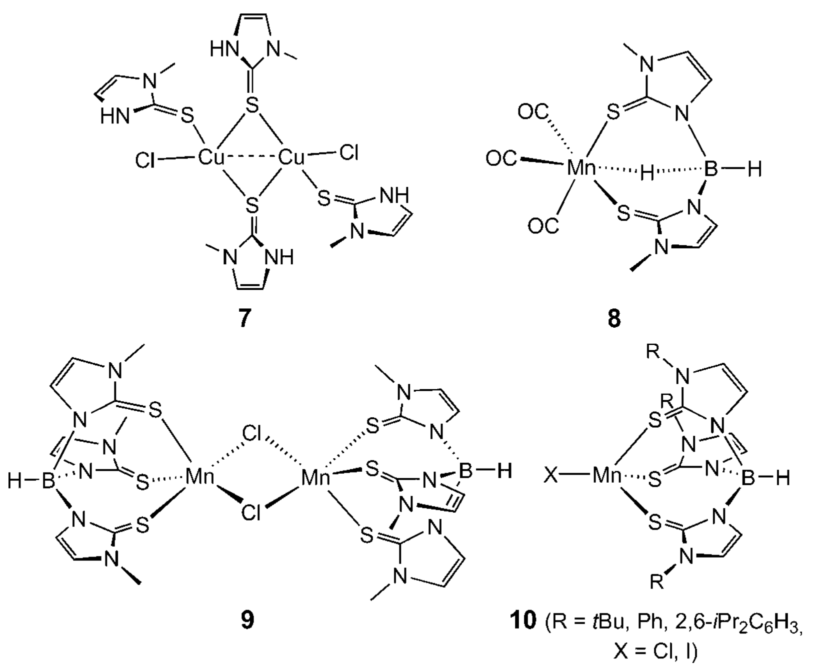
Scheme 1.

The C–S bond of the imidazolinethione ligand is stretched on coordination to the manganese atoms. The C(15)–S bond length is 1.740(3) Å, which is significantly longer than that of free **1**, 1.690(2) Å.[14] This is probably due to the pronounced polarization of the metal–ligand linkage (canonical structures **B** and **C**, Scheme 2), which is induced by the capability to take positive charge into the imidazole ring of the thione ligand. Through this polarization, the C–S moiety carries a single bond character. The imidazole ring is almost perpendicular with respect to the Mn–Mn vector. This is also consistent with the canonical structures **B** and **C**. If the sulfur–manganese interaction was composed of coordination of the lone electron pair on sp^2-sulfur (Scheme 2, **A**), the imidazole ring would be expected to be nearly parallel to the Mn–Mn vector.



Scheme 2.

Creighton and co-workers have reported the reaction of an imidazolinethione with $CuCl_2$. During the reaction, Cu^{II} is reduced to afford a dimeric Cu^{I} complex **7** (Scheme 3), which contains bridging imidazolinethione ligands and a short Cu–Cu contact [2.914(1) Å].[15]



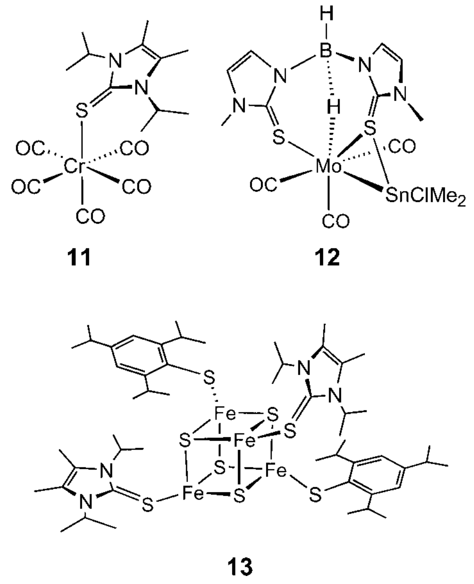
Scheme 3.

Several manganese complexes containing a bis- or tris(mercaptoimidazolyl)hydroborate ligand have been reported (**8**–**10**, Scheme 3).[16,17] The crystal structures of **9** and **10** were determined, and it was shown that they had Mn–S bond lengths of 2.435(3)–2.569(8) Å and S–C bond lengths of 1.707(2)–1.721(2) Å.[17] Compound **2** has a shorter Mn–S bond and a longer C–S bond than **9** and **10**. Hence, the thione ligand polarizes very strongly in **2**, probably because the charge separation concentrates in one imidazolinethione unit.

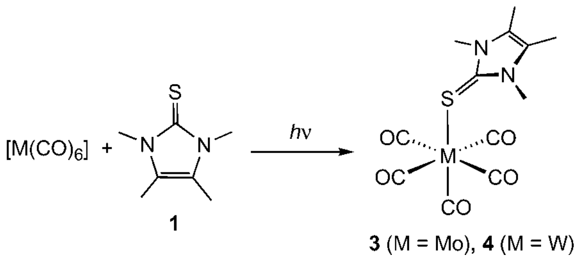
Synthesis of Group 6 Metal Complexes [M(CO)$_5$(SC$_3$N$_2$Me$_4$)] [M = Mo (3), W (4)]

Group 6 metal complexes of chalcogenoimidazolines have been synthesized by Kuhn and co-workers. Thione, selone, and tellone, E=C(N*i*Pr)$_2$(CMe)$_2$ (E = S, Se, Te), react with [M(CO)$_6$] or [M(CO)$_5$(thf)] to produce the corresponding mononuclear chalcogenoimidazoline complexes.[8] Chromium derivatives [Cr(CO)$_5${E=C(N*i*Pr)$_2$(CMe)$_2$}] (**11**, E = S, Se, Scheme 4) were crystallographically characterized. However, with regard to tetramethylimidazoline derivatives, only the tellone complex [W(CO)$_5${TeC$_3$N$_2$Me$_4$}] has been documented.[8] Does the use of sterically less demanding **1** influence the number of metal fragments in the product, as observed in the formation of **2**? To clarify this point, we carried out the reaction of **1** with [M(CO)$_6$] (M = Mo, W) under photolytic conditions.

Photoreactions of [M(CO)$_6$] with **1** proceeded smoothly and gave yellow solutions, from which the thione complexes [M(CO)$_5$(SC$_3$N$_2$Me$_4$)] [M = Mo (**3**), W (**4**)] were isolated as analytically pure crystals [76% for **3** and 33% for **4**, Equation (2)]. No evidence for the formation of dimeric species was obtained.



Scheme 4.



(2)

Figures 2 and 3 display the crystal structures of compounds **3** and **4**. The important bond lengths and angles are listed in Tables 2 and 3. Although the molecular structures of **3** and **4** are quite similar, the two compounds are not isomorphous. Crystals of **3** contain two crystallographically independent molecules in the asymmetric unit. However, their structures are essentially the same. The two molecules of **3** are associated through π-stacking of the imidazole rings. The separation between the five-membered rings is 3.3–3.6 Å. In **3** and **4**, the [M(CO)$_5$] unit is coordinated to the cyclic thione ligand through a M–S dative bond to form an octahedral geometry. As a whole, their structures are akin to Kuhn's complex **11**.[8] They also resemble that of a methyleneimidazoline complex, [Mo(CO)$_5$(CH$_2$=C$_3$N$_2$Me$_4$)],[18] whose ligand, an ylidic olefine, is isoelectronic with **1**. The M–S bond lengths are 2.6084(11) Å and 2.6113(11) Å in **3**, and 2.6146(14) Å in **4**. In compound **12** (Scheme 4), one thione unit of the bis(mercaptoimidazolyl)dihydroborate bridges the molybdenum center and tin atom with a long Mo–S bond length of 2.631(3) Å. The interatomic distance between the molybdenum and sulfur of the other ("terminal") thione moiety is 2.51(2) Å.[19]

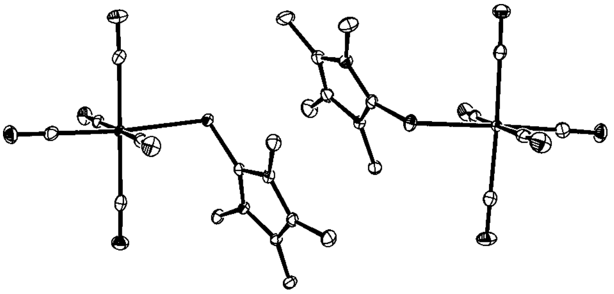


Figure 2. ORTEP drawing of [Mo(CO)$_5$(SC$_3$N$_2$Me$_4$)] (**3**) (50% thermal ellipsoids). Hydrogen atoms have been omitted for clarity.

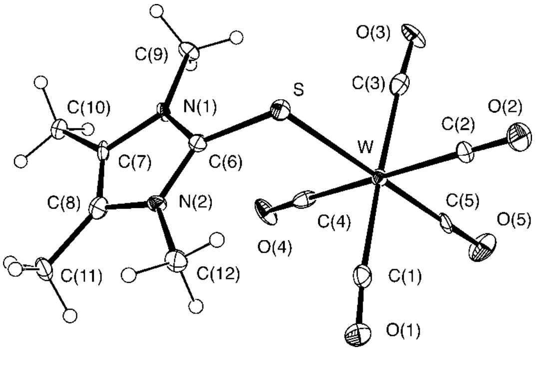


Figure 3. ORTEP drawing of [W(CO)$_5$(SC$_3$N$_2$Me$_4$)] (**4**) (50% thermal ellipsoids).

The imidazolinethione ligand is connected to the central metal, directing the face of the heterocycle to the [M(CO)$_5$] fragment. This is in sharp contrast to a chromium–thioacetone complex [Cr(CO)$_5$(S=CMe$_2$)][20] and a mercury derivative [HgCl$_2$(SC$_3$N$_2$H$_4$)$_2$],[21] in which the thione ligand directs the edge of the molecular plane to the metal. Such geometry of **3** and **4** suggests sp^3 hybridization of the sulfur atom caused by the greatly polarized M–S–C linkage (canonical structure **E**, Scheme 5). Indeed, the M–S–C bond angles are 108.31(7) and 109.40(7)° in **3**, and 103.29(16)° in **4**, which are close to the tetrahedral angle. As expected, the C=S bond is elongated. The C–S interatomic distances are 1.719(2) and 1.717(2) in **3** and 1.731(5) Å in **4** [that of free **1** is 1.690(2) Å].[14] Such phenomena are also found in **11**

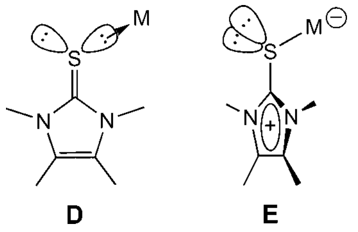
Table 2. Selected bond lengths [Å] and angles [°] for [Mo(CO)$_5$(S=C$_3$N$_2$Me$_4$)] (**3**).

Bond lengths [Å]			
Molecule A			
Mo(1)–S(1)	2.6084(11)	Mo(1)–C(1)	2.071(2)
Mo(1)–C(2)	2.026(2)	Mo(1)–C(3)	2.044(2)
Mo(1)–C(4)	2.072(2)	Mo(1)–C(5)	1.971(2)
C(1)–O(1)	1.132(3)	C(2)–O(2)	1.141(3)
C(3)–O(3)	1.141(3)	C(4)–O(4)	1.128(3)
C(5)–O(5)	1.148(3)	S(1)–C(6)	1.719(2)
C(6)–N(1)	1.355(2)	C(6)–N(2)	1.348(2)
C(7)–N(1)	1.397(2)	C(8)–N(2)	1.389(2)
C(7)–C(8)	1.353(2)		
Molecule B			
Mo(2)–S(2)	2.6113(11)	Mo(2)–C(13)	2.066(2)
Mo(2)–C(14)	2.050(2)	Mo(2)–C(15)	2.037(2)
Mo(2)–C(16)	2.062(2)	Mo(2)–C(17)	1.971(2)
C(13)–O(6)	1.139(3)	C(14)–O(7)	1.139(3)
C(15)–O(8)	1.143(3)	C(16)–O(9)	1.134(3)
C(17)–O(10)	1.150(3)	S(2)–C(18)	1.717(2)
C(18)–N(3)	1.349(2)	C(18)–N(4)	1.351(2)
C(19)–N(3)	1.399(2)	C(20)–N(4)	1.389(2)
C(19)–C(20)	1.352(3)		
Bond angles [°]			
Molecule A			
C(1)–Mo(1)–S(1)	85.34(7)	C(2)–Mo(1)–S(1)	91.61(6)
C(3)–Mo(1)–S(1)	94.20(7)	C(4)–Mo(1)–S(1)	90.58(6)
C(5)–Mo(1)–S(1)	174.83(5)	C(6)–S(1)–Mo(1)	108.31(7)
N(1)–C(6)–S(1)	126.04(14)	N(2)–C(6)–S(1)	127.50(13)
N(1)–C(6)–N(2)	106.21(15)	C(6)–N(1)–C(7)	109.82(15)
C(6)–N(2)–C(8)	110.24(15)	C(8)–C(7)–N(1)	106.70(16)
C(7)–C(8)–N(2)	107.03(15)		
Molecule B			
C(13)–Mo(2)–S(2)	86.10(7)	C(14)–Mo(2)–S(2)	89.10(7)
C(15)–Mo(2)–S(2)	96.60(6)	C(16)–Mo(2)–S(2)	88.27(7)
C(17)–Mo(2)–S(2)	175.09(5)	C(18)–S(2)–Mo(2)	109.40(7)
N(3)–C(18)–S(2)	128.29(14)	N(4)–C(18)–S(2)	125.50(14)
N(3)–C(18)–N(4)	106.07(16)	C(18)–N(3)–C(19)	109.95(16)
C(18)–N(4)–C(20)	110.36(15)	C(20)–C(19)–N(3)	106.78(17)
C(19)–C(20)–N(4)	106.83(17)		

Table 3. Selected bond lengths [Å] and angles [°] for [W(CO)$_5$(S=C$_3$N$_2$Me$_4$)] (**4**).

Bond lengths [Å]			
W(1)–S(1)	2.6146(14)	W(1)–C(1)	2.040(4)
C(1)–O(1)	1.145(6)	C(2)–O(2)	1.151(6)
C(3)–O(3)	1.151(6)	C(4)–O(4)	1.160(6)
C(5)–O(5)	1.166(5)	S(1)–C(6)	1.731(5)
C(6)–N(1)	1.353(5)	C(6)–N(2)	1.351(6)
C(7)–N(1)	1.390(5)	C(8)–N(2)	1.377(6)
C(7)–C(8)	1.341(6)		
Bond angles [°]			
C(1)–W(1)–S(1)	90.77(12)	C(2)–W(1)–S(1)	90.82(14)
C(3)–W(1)–S(1)	90.02(12)	C(4)–W(1)–S(1)	91.22(15)
C(5)–W(1)–S(1)	178.00(13)	C(6)–S(1)–W(1)	103.51(15)
N(1)–C(6)–S(1)	125.9(4)	N(2)–C(6)–S(1)	127.5(3)
N(2)–C(6)–N(1)	106.6(4)	C(6)–N(1)–C(7)	109.5(4)
C(6)–N(2)–C(8)	109.1(3)	C(8)–C(7)–N(1)	106.5(4)
C(7)–C(8)–N(2)	108.3(4)		

[the C–S bond length is 1.737(5) Å][8] and a rhodium complex [RhCl(cod)($SC_3N_2Me_4$)] [1.725(2) Å].[9] An iron–sulfur cluster **13** includes two imidazolinethione ligands, whose C–S bond lengths are 1.689(14) and 1.719(16), respectively.[10]



Scheme 5.

The strong donating ability of the thione ligand leads to enhancement of back-donation to the *trans* carbonyl ligand. The bond lengths between the metal and *trans*-carbonyl carbon atoms are 1.969(2) and 1.967(2) Å for **3**, and 1.966(5) Å for **4**. These are substantially shorter than the metal–*cis*-carbonyl bonds. The averages of the separations between the metal and *cis* carbonyls are 2.05 and 2.04 Å for **3** and **4**, respectively. In fact, the infrared spectra of **3** and **4** showed carbonyl stretching bands that are low-frequency shifted relative to [M(CO)$_6$].

Experimental Section

All manipulations were carried out under high vacuum or dry nitrogen. Reagent-grade hexane, THF, and toluene were distilled under nitrogen from sodium-benzophenone ketyl just before use. [D$_6$]benzene was dried with potassium mirrors before use and transferred into NMR tubes under vacuum. $SC_3N_2Me_4$ (**1**) was prepared according to the literature.[6] [Mo(CO)$_6$] (Strem), [W(CO)$_6$] (Aldrich), and [CpMn(CO)$_3$] (Strem) were used as purchased. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL α-500 spectrometer. IR spectra were recorded with a JASCO FTIR-350 spectrometer. Mass spectra were measured with a JEOL JMS-S600H spectrometer.

Syntheses of [{CpMn(CO)$_2$}$_2$(μ-$SC_3N_2Me_4$)] (2): A solution of [CpMn(CO)$_3$] (80 mg, 0.040 mmol) and **1** (31 mg, 0.020 mg) in hexane (4 mL) and THF (1 mL) mixture was irradiated with a 450-W medium-pressure Hg arc lamp for 1 h. Removal of volatiles, extraction of the residue with toluene, and cooling of the extract afforded **2** as red needles in small amounts. ^{1}H NMR (500 MHz, [D$_6$]benzene): δ = 1.11 (s, 6 H, CMe), 3.13 (s, 6 H, NMe), 4.41 (br., 5 H) ppm. This spectrum is consistent with a mononuclear complex, [CpMn(CO)$_2$($SC_3N_2Me_4$)].

Syntheses of [Mo(CO)$_5$($SC_3N_2Me_4$)] (3): A dichloromethane solution of [Mo(CO)$_6$] (85 mg, 0.32 mmol) and **1** (46 mg, 0.30 mmol) was irradiated at 8 °C for 1 h with stirring using a 450-W medium pressure Hg lamp. The resulting yellow solution was concentrated to about 1 mL and diluted with hexane (4 mL). Cooling the solution to –25 °C provided **2** (90 mg, 0.23 mmol, 76%) as yellow-gray crystals. ^{1}H NMR (500 MHz, [D$_6$]benzene): δ = 1.09 (s, 6 H, CMe), 2.92 (s, 6 H, NMe) ppm. ^{13}C NMR (125 MHz, [D$_6$]benzene): δ = 7.96 (CMe), 31.9 (NMe), 122.6 (ring-C), 158.6 (C=S), 206.5, 213.7 (CO) ppm. IR (Nujol mull): $\tilde{\nu}$ = ν(CO) 2066, 1987, 1912, 1872 cm^{-1}. MS (70 eV): *m/z* (%) = 393 ([M$^+$]), 156 ([$SC_3N_2Me_4^+$]). $C_{12}H_{12}MoN_2O_5S$ (392.24): calcd. C 36.75, H 3.08, N 7.14; found C 36.59, H 3.10, N 6.96.

Syntheses of [W(CO)$_5$($SC_3N_2Me_4$)] (4): The synthesis of **4** was conducted in a similar manner to that of **3**. The yield of yellow crystals

Table 4. Crystal data for compounds **2**, **3**, and **4**.

	2	3	4
Empirical formula	$C_{21}H_{22}Mn_2N_2O_4S$	$C_{12}H_{12}MoN_2O_5S$	$C_{12}H_{12}N_2O_5SW$
Formula mass	508.35	408.24	480.15
Crystal color	red	yellow-gray	yellow
Temperature [K]	153(2)	153(2)	153(2)
Wavelength	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a [Å]	8.945(5)	10.827(6)	20.494(9)
b [Å]	9.911(6)	11.281(6)	6.474(4)
c [Å]	13.650(7)	14.582(6)	24.651(11)
α [°]	107.69(2)	111.07(2)	90
β [°]	92.521(19)	99.989(19)	112.932(14)
γ [°]	109.35(2)	106.31(2)	90
V [Å^3]	1073.6(10)	1518.4(13)	3012(2)
Z	2	4	8
D_{calcd} [Mg m^{-3}]	1.573	1.786	1.588
Abs. coeff. [mm^{-1}]	1.303	1.031	5.872
F(000)	520	806	1368
Crystal size [mm]	0.25 × 0.20 × 0.08	0.60 × 0.40 × 0.30	0.50 × 0.15 × 0.10
θ range [°]	3.12–27.46	3.08–27.47	3.30–27.48
Index ranges	$-11 \le h \le 11$, $-12 \le k \le 12$, $-17 \le l \le 15$	$0 \le h \le 14$, $-14 \le k \le 13$, $-18 \le l \le 18$	$0 \le h \le 26$, $0 \le k \le 8$, $-31 \le l \le 29$
Independent reflections	10625	6874	3434
No. of parameters	275	387	194
Gof on F^2	1.086	1.138	1.066
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0414$, $wR_2 = 0.1194$	$R_1 = 0.0253$, $wR_2 = 0.0941$	$R_1 = 0.0357$, $wR_2 = 0.1170$
R indices (all data)	$R_1 = 0.0540$, $wR_2 = 0.1371$	$R_1 = 0.0271$, $wR_2 = 0.0999$	$R_1 = 0.0366$, $wR_2 = 0.1206$
Largest diff. peak and hole [e Å^{-3}]	0.883 and –0.616	0.487 and –1.535	1.520 and –2.902

of **4** was 33 %. ^{1}H NMR (500 MHz, [D$_6$]benzene): δ = 1.00 (s, 6 H, CMe), 2.91 (s, 6 H, NMe) ppm. ^{13}C NMR (125 MHz, [D$_6$]benzene): δ = 7.91 (CMe), 31.8 (NMe), 123.0 (ring-C), 157.3 (C=S), 199.6, 201.6 (CO) ppm. IR (Nujol mull): $\tilde{\nu}$ = ν(CO) 2064, 1980, 1899, 1864 cm^{-1}. MS (70 eV): *m*/*z* (%) = 480 ([M$^+$]), 156 ([SC$_3$N$_2$Me$_4$$^+$]). $C_{12}H_{12}N_2O_5SW$ (480.14): calcd. C 30.02, H 2.51, N 5.83; found C 30.20, H 2.71, N 5.59.

X-ray Crystal Structure Determination: Crystals of **2**, **3**, and **4** (Table 4) were grown by cooling their solutions. Intensity data were collected with a Rigaku RAPID imaging plate diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was carried out at –120 °C. Crystal data, data collection parameters, and convergence results are listed in Table 4.

Numerical absorption corrections were applied on the crystal shapes. The structures of all complexes were solved by the direct method and refined on F^2. All non-hydrogen atoms were located and refined applying anisotropic temperature factors. Coordinates of hydrogen atoms were idealized with the use of riding models. Calculations were performed using the program package SHELX 97.[22]

CCDC-634432 (for **2**), -634433 (for **3**), and -634434 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Acknowledgments

This work was financially supported by the Japanese Ministry of Education, Science, Sports, and Culture (Grant-in Aid for Special Project Research, number 15036215).

---

[1] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

[2] D. Bourissou, O. Guerret, F. P. Gabba, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.

[3] C. J. Carmalt, A. H. Cowley, *Adv. Inorg. Chem.* **2000**, *50*, 1–32.

[4] W. A. Herrmann, C. Koecher, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187.

[5] For example: a) N. Kuhn, H. Bohnen, J. Kreutzberg, D. Bläser, R. Boese, *J. Chem. Soc., Chem. Commun.* **1993**, 1136–1137; b) W. A. Hermann, C. Köcher, L. J. Goossen, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 1627–1636; c) M. D. Francis, D. E. Hibbs, M. B. Hursthouse, C. Jones, N. A. Smithies, *J. Chem. Soc., Dalton Trans.* **1998**, 3249–3254; d) A. J. Arduengo III, H. V. R. Dias, J. C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* **1992**, *114*, 9724–9725; e) X.-W. Li, J. Su, G. H. Robinson, *Chem. Commun.* **1996**, 2683–2684; f) A. J. Arduengo III, H. V. R. Dias, J. C. Calabrese, F. Davidson, *Inorg. Chem.* **1993**, *32*, 1541–1542; g) N. Kuhn, T. Kratz, D. Bläser, R. Boese, *Chem. Ber.* **1995**, *128*, 245–250; h) A. Schäfer, M. Weidenbrush, W. Saak, S. Pohl, *J. Chem. Soc., Chem. Commun.* **1995**, 1157–1158; i) N. Kuhn, G. Henkel, T. Kratz, J. Kreutzberg, R. Boese, A. H. Maulitz, *Chem. Ber.* **1993**, *126*, 2041–2045.

[6] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561–562.

[7] a) J. Reglinski, M. Garner, I. D. Cassidy, P. A. Slavin, M. D. Spicer, D. R. Armstrong, *J. Chem. Soc., Dalton Trans.* **1999**, 2119–2126; b) M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer, A. R. Kennedy, *Chem. Commun.* **1996**, 1975–1976; c) I. R. Crossley, A. F. Hill, E. R. Humphrey, M. K. Smith, *Organometallics* **2006**, *25*, 2242–2247; d) M. M. Ibrahim, J. Seebacher, G. Steinfeld, H. Vahrenkamp, *Inorg. Chem.* **2005**, *44*, 8531–8538.

[8] N. Kuhn, R. Fawzi, T. Kratz, M. Steimann, *Phosphorus Sulfur Silicon* **1996**, *108*, 107–119.

[9] A. Neveling, G. R. Julius, S. Cronje, C. Esterhuysen, H. G. Raubenheimer, *Dalton Trans.* **2005**, 181–192.

[10] M. Harmjanz, C. Junghans, U. A. Opitz, B. Bahlmann, S. Pohl, *Z. Naturforsch., B: Chem. Sci.* **1996**, *51*, 1040–1048.

[11] L. J. Lyons, M. H. Tegen, K. J. Haller, D. H. Evans, P. M. Treichel, *Organometallics* **1988**, *7*, 357–365.

[12] P. Lau, H. Braunwarth, G. Huttner, D. Günauer, K. Evertz, W. Imhof, C. Emmerich, L. Zsolnai, *Organometallics* **1991**, *10*, 3861–3873.

[13] H. Braunwarth, G. Huttner, L. Zsolnai, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 698–699.

[14] N. Kuhn, J. Fahl, R. Fawzi, M. Steimann, *Z. Kristallogr. - New Cryst. Struct.* **1998**, *213*, 434.

[15] J. R. Creighton, D. J. Gardiner, A. C. Gorvin, C. Gutterridge, A. R. W. Jackson, E. S. Raper, P. M. A. Sherwood, *Inorg. Chim. Acta* **1985**, *103*, 195–205.

[16] P. J. Bailey, A. Dawson, C. McCormack, S. A. Moggach, I. D. H. Oswald, S. Parsons, D. W. H. Rankin, A. Turner, *Inorg. Chem.* **2005**, *44*, 8884–8898.

[17] S. Senda, Y. Ohki, T. Hirayama, D. Toda, J. L. Chen, T. Matsumoto, H. Kawaguchi, K. Tatsumi, *Inorg. Chem.* **2006**, *45*, 9914–9925.

[18] N. Kuhn, H. Bohnen, D. Bläser, R. Boese, *Chem. Ber.* **1994**, *127*, 1405–1407.

[19] M. R. St.-J. Foreman, A. F. Hill, M. K. Smith, N. Tshabang, *Organometallics* **2005**, *24*, 5224–5226.

[20] B. A. Karchar, R. A. Jacobson, *J. Organomet. Chem.* **1977**, *132*, 387–393.

[21] G. Pavlović, Z. Popović, Ž. Soldin, D. Matković-Čalogović, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2000**, *56*, 61–63.

[22] a) G. M. Sheldrick, *SHELXS-97*, University of Göttingen, **1997**; b) G. M. Sheldrick, *SHELXL-97*, University of Göttingen, **1997**.

Received: January 24, 2007