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Reactions of $M_2(CO)_9L$ (M = Re, Mn; L = CO, MeCN) with thioacetamide and thiobenzamide: Facile metal-mediated nitrogen-hydrogen bond activation and subsequent carbon-nitrogen or sulfur-sulfur bond formation

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ABSTRACT

Addition of thioacetamide or thiobenzamide to $\text{Re}_2(\text{CO})_{10}$ at room temperature in presence of Me_3NO gives low yields of the simple substitution products $\text{Re}_2(\text{CO})_9[\kappa^1-\text{S}=C(R)\text{NH}_2]$ (**1**, R = Me; **2**, R = Ph) in which the acyclic amides are bound through sulfur and occupy an equatorial site. In contrast, Me_3NO initiated reactions of $\text{Mn}_2(\text{CO})_{10}$ with the same amides lead to the isolation of hexacarbonyl complexes, $\text{Mn}_2(\text{CO})_6[\mu-\text{S}_2C(R)\text{NH}]_2$ (**3**, R = Me; **4**, R = Ph), crystallographic studies revealing a binuclear core in which $\text{Mn}(\text{CO})_3$ moieties are spanned by two RC(SS)NH ligands. When $\text{Mn}_2(\text{CO})_9(\text{NCMe})$ is used as the starting material only the mononuclear species $\text{Mn}(\text{CO})_4[\kappa^1:\eta^1-\text{RC}(S)\text{NHCO}]$ (**5**, R = Me; **6**, R = Ph) could be isolated. These contain a chelating RC(S)NHCO ligand formed as a result of coupling the deprotonated amides with CO. Crystallographic studies have been carried out on both complexes, a careful inspection of bond lengths and angles within the chelate ring suggesting that a zwitterionic acyl-thiolate resonance structure is most prevalent.

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1. Introduction

Reactions of $M_2(CO)_{10}$ (M = Re, Mn) with nitrogen and/or sulfur donor ligands such as thiols [1–3], dithiols [4], heterocyclic thiones or thiolactams [5–12], *N*-containing heterocycles [13–15], derivatives of thiourea [16,17], thioethers [18,19], thioketones [20] and elemental sulfur [21–23] have been thoroughly investigated. The first step in these reactions is generally the displacement of a carbonyl and coordination of the new ligand into an equatorial site. Once within the manifold of the binuclear center secondary rearrangements can then occur. A good example of this comes from the work of Adams and co-workers [17] who showed that reaction of Re₂(CO)₉(NCMe) with Et₂NC(S)NHAr (Ar = *p*-tolyl) proceeds in high yields at 68 °C to give Re₂(CO)₉{ κ^1 -SC(NEt₂)NHAr}, which in turn transforms cleanly into [Re(CO)₃{ μ -SC(*N*-*p*-tolyl)(NEt₂)]₂ at 97 °C as a result of N–H bond activation and carbonyl loss (Scheme 1).

To date no reports have documented the reactivity of $M_2(CO)_{10}$ (M = Mn, Re) with acyclic thioamides (RCSNH₂), simple molecules that possess both hard and soft donor sites. A literature survey on

the reactivity of metal carbonyls toward acyclic thioamides revealed only one example of such reactivity [24]. Thus the phosphinidine clusters, Fe₃(CO)₁₀(μ_3 -PR) (R = ^tBu, ⁱPr), react with thioacetamide to give the sulfido-capped carbene clusters, Fe₃(CO)₈{ η^1 -C(NH₂) Me}(μ_3 -S)(μ_3 -PR) (R = ^tBu, ⁱPr) as a result of carbon–sulfur bond scission at cluster surface [24] (Scheme 2). The facile nature of this carbon–sulfur bond scission supports the idea that this ligand system can in principle be used toward the synthesis of high nuclearity sulfido-capped clusters. With this in mind we have investigated the reactions of dirhenium and dimanganese carbonyls with thioacetamide and thiobenzamide. We find that not only do these dinuclear carbonyls behave differently toward thioamides, but also the isolated products varied when we use different carbonyl complexes of the same metal as starting material.

2. Experimental section

2.1. General data

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. Reagent grade solvents were dried using appropriate drying agents and distilled prior to use by standard methods. Thioacetamide (MeCSNH₂) and thiobenzamide (PhCSNH₂) were purchased from

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Scheme 1. N-H addition at a dirhenium center.

Aldrich and used as received. $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ were purchased from Strem Chemicals Inc. and used without further purification. $Re_2(CO)_9(NCMe)$ and $Mn_2(CO)_9(NCMe)$ were prepared according to the literature methods [25]. Infrared spectra were recorded on a Shimadzu FTIR 8101 or Shimadzu IR Prestige 21 spectrophotometer. NMR spectra were recorded on a Varian 500 instrument. Elemental analyses were performed by BCSIR Laboratories, Dhaka.

2.2. Reaction of $Re_2(CO)_{10}$ with thioacetamide

A CH₂Cl₂ solution (25 mL) of Re₂(CO)₁₀ (100 mg, 0.153 mmol), MeCSNH₂ (12 mg, 0.160 mmol) and Me₃NO (12 mg, 0.160 mmol) was stirred at room temperature for 7 h. The solvent was removed by rotary evaporation under reduced pressure and the residue separated by TLC on silica gel. Elution with hexane/CH₂Cl₂ (7:3, v/v) developed five bands. The first and last bands were unreacted Re₂(CO)₁₀ (trace) and MeCSNH₂ (trace). The fourth band afforded Re₂(CO)₉{ κ^1 -S=C(Me)NH₂} (1) (15 mg, 14%) as colorless crystals after recrystallization from hexane/CH₂Cl₂ at 4 °C. The content of the other two bands were too small for characterization. Spectral data for 1: Anal. Calcd for C₁₁H₅NO₉Re₂S: C, 18.50; H, 0.71; N, 1.98. Found: C, 18.94; H, 0.76; N, 2.06%. IR (ν (CO), CH₂Cl₂): 2102 m, 2038 s, 1993 vs, 1958 s, 1911 s cm⁻¹. ¹H NMR (CDCl₃): δ 7.83 (br, s, 1H), 7.53 (br, s, 1H), 2.70 (s, 3H).

2.3. Reaction of $Re_2(CO)_9(NCMe)$ with thioacetamide

MeCSNH₂ (12 mg, 0.160 mmol) was added to a benzene solution (25 mL) of Re₂(CO)₉(NCMe) (100 mg, 0.150 mmol) and the mixture was then refluxed for 32 h. A similar chromatographic separation described as above gave **1** (12 mg, 11%) after recrystallization from hexane/CH₂Cl₂ at 4 °C.

2.4. Reaction of $Re_2(CO)_{10}$ with thiobenzamide

To a CH₂Cl₂ solution (25 mL) of Re₂(CO)₁₀ (100 mg, 0.153 mmol) was added PhCSNH₂ (22 mg, 0.160 mmol) and Me₃NO (12 mg, 0.160 mmol) and the mixture was stirred at room temperature for 5 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (7:3, v/v) developed one major and several minor bands. The major band afforded Re₂(CO)₉{ κ^1 -S=C(Ph)NH₂} (**2**) (16 mg, 14%)

as yellow crystals after recrystallization from hexane/CH₂Cl₂ at 4 °C. The content of the other minor bands were too small for characterization. Spectral data for **2**: Anal. Calcd for C₁₆H₇NO₉Re₂S: C, 24.98; H, 0.92; N, 1.82. Found: C, 25.36; H, 0.97; N, 1.87%. IR (ν (CO), CH₂Cl₂): 2107 w, 2037 s, 1994 s, 1934 m, 1915 s cm^{-1. 1}H NMR (CDCl₃): δ 7.95 (br, s, 1H), 7.89 (br, s, 1H), 7.77 (m, 2H), 7.59 (m, 1H), 7.46 (m, 2H).

2.5. Reaction of $Re_2(CO)_9(NCMe)$ with thiobenzamide

PhCSNH₂ (22 mg, 0.160 mmol) was added to a benzene solution (25 mL) of Re₂(CO)₉(NCMe) (100 mg, 0.150 mmol) and the mixture was then refluxed for 24 h. A similar chromatographic separation described as above gave **2** (11 mg, 10%) after recrystallization from hexane/CH₂Cl₂ at 4 °C.

2.6. Reaction of $Mn_2(CO)_{10}$ with thioacetamide

To a CH₂Cl₂ solution (25 mL) of Mn₂(CO)₁₀ (100 mg, 0.256 mmol) was added MeCSNH₂ (20 mg, 0.266 mmol) and Me₃NO (40 mg, 0.532 mmol) and the mixture was stirred at room temperature for 4 h. The solvent was removed by rotary evaporation under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (7:3, v/v) developed three bands. The faster moving band afforded $Mn_2(CO)_6{\mu-S_2C(Me)NH}_2$ (3) (11 mg, 9%) as orange crystals, while the slower moving band gave $Mn(CO)_{4}$ { κ^{1} : η^{1} -MeC(S)NHCO} (**5**) (3 mg, 2%) as yellow crystals after recrystallization from hexane/CH₂Cl₂ at 4 °C. The content of the other band was too small for characterization. Spectral data for 3: Anal. Calcd for C₁₀H₈Mn₂N₂O₆S₄: C, 24.49; H, 1.65; N, 5.71. Found: C, 25.14; H, 1.73; N, 5.76%. IR (v(CO), CH₂Cl₂): 2039 m, 2019 vs, 1993 vw, 1932 s cm⁻¹.¹H NMR (CDCl₃): δ 9.06 (br. s, 2H), 2.36 (s, 6H). Spectral data for 5: Anal. Calcd for C₇H₄MnNO₅S: C, 31.24; H, 1.50; N, 5.21. Found: C, 31.67; H, 1.56; N, 5.28%. IR (v(CO), CH₂Cl₂): 2085 m, 1997 vs, 1970 s, 1921 vw, 1657 w cm⁻¹. ¹H NMR (CDCl₃): δ 9.94 (br, s, 1H), 2.72 (s, 3H).

2.7. Reaction of $Mn_2(CO)_9(NCMe)$ with thioacetamide

MeCSNH₂ (20 mg, 0.266 mmol) was added to a CH₂Cl₂ solution (25 mL) of Mn₂(CO)₉(NCMe) (100 mg, 0.248 mmol) and the mixture was then stirred at room temperature for 4 h. A similar chromatographic separation described as above gave **5** (13 mg, 10%) after recrystallization from hexane/CH₂Cl₂ at 4 °C.



Scheme 2. C-S addition at a triiron center.

Table 1

Crystal and structural refinement data for $Mn_2(CO)_6{\mu-S_2C(Me)NH}_2$ (3), $Mn_2(CO)_6{\mu-S_2C(Ph)NH}_2$ (4), $Mn(CO)_4{\kappa^2-MeC(S)NHCO}$ (5) and $Mn(CO)_4{\kappa^2-PhC(S)NHCO}$ (6).

Compound	3	4	5	6
Empirical formula	C ₁₀ H ₈ Mn ₂ N ₂ O ₆ S ₄	C ₂₀ H ₁₂ Mn ₂ N ₂ O ₆ S ₄	C ₇ H ₄ MnNO ₅ S	C ₁₂ H ₆ MnNO ₅ S
Formula weight	490.30	614.44	269.11	331.18
Temperature (K)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P1bar	$P2_1/c$	P1bar	$P2_1/n$
Unit cell dimensions				
a (Å)	6.816(3)	11.447(3)	6.1474(9)	11.462(4)
b (Å)	7.568(4)	5.570(1)	6.887(1)	9.688(3)
<i>c</i> (Å)	8.556(4)	18.490(5)	12.697(2)	12.589(4)
α (°)	76.559(7)	90	90.830(2)	90
β(°)	80.583(7)	93.883(5)	90.979(2)	111.703(4)
$\gamma(^{\circ})$	76.338(7)	90	113.052(2)	1298.8(8)
Volume (Å ³)	414.4(3)	1176.2(5)	494.4(1)	90
Ζ	1	2	2	4
Density (calculated) (Mg/m ³)	1.965	1.735	1.808	1.694
Absorption coefficient (mm ⁻¹)	2.057	1.469	1.544	1.194
F(000)	244	616	268	664
Crystal size (mm ³)	$0.52 \times 0.26 \times 0.24$	$0.12 \times 0.04 \times 0.03$	$0.36\times0.36\times0.12$	$0.26\times0.20\times0.14$
heta range for data collection (°)	2.46-28.14	2.93-28.30	3.22-28.13	2.73-28.31
Index ranges	$-8 \le h \ge 9$	$-14 \le h \ge 14$	$-8 \le h \ge 8$	$-14 \leq h \geq 14$
	$-9 \le k \ge 9$	$-7 \le k \ge 7$	$-9 \le k \ge 8$	$-12 \leq k \geq 12$
	$-10 \le l \ge 11$	$-24 \le l \ge 24$	$-16 \le l \ge 16$	$-16 \le l \ge 16$
Reflections collected	3259	9456	4092	10,367
Independent reflections	1756 [$R(int) = 0.0269$]	2741 [$R(int) = 0.0478$]	2179 [$R(int) = 0.0190$]	2997 [$R(int) = 0.0616$]
Max. and min. transmission	0.6381 and 0.4144	0.9573 and 0.8434	0.8364 and 0.6064	0.8507 and 0.7466
Data/restraints/parameters	1756/0/109	2741/0/178	2179/0/153	2997/0/205
Goodness-of-fit on F ²	1.110	0.942	1.109	0.988
Final <i>R</i> indices $[F^2 > 2\sigma]$	$R_1 = 0.0383, wR_2 = 0.1034$	$R_1 = 0.0350, wR_2 = 0.0625$	$R_1 = 0.0250, wR_2 = 0.0671$	$R_1 = 0.0468, wR_2 = 0.1161$
R indices (all data)	$R_1 = 0.0438, wR_2 = 0.1082$	$R_1 = 0.0551, wR_2 = 0.0659$	$R_1 = 0.0261, wR_2 = 0.0675$	$R_1 = 0.0560, wR_2 = 0.1188$
Largest diff. peak and hole $(e^{A^{-3}})$	0.679 and -0.524	0.363 and -0.392	0.544 and -0.389	1.391 and -0.973

2.8. Reaction of $Mn_2(CO)_{10}$ with thiobenzamide

A CH₂Cl₂ solution (25 mL) of Mn₂(CO)₁₀ (100 mg, 0.256 mmol), PhCSNH₂ (36 mg, 0.262 mmol) and Me₃NO (40 mg, 0.532 mmol) was stirred at room temperature for 8 h. The solvent was removed under reduced pressure and the residue chromatographed by TLC on silica gel. Elution with hexane/CH₂Cl₂ (7:3, v/v) developed three bands. The contents of the first two bands were too small for characterization while the third band yielded Mn₂(CO)₆{ μ -S₂C(Ph) NH₂ (**4**) (14 mg, 9%) as orange crystals after recrystallization from hexane/CH₂Cl₂ at 4 °C. Spectral data for **4**: Anal. Calcd for C₂₀H₁₂Mn₂N₂O₆S₄: C, 39.09; H, 1.97; N, 4.56. Found: C, 39.47; H, 2.06; N, 4.62%. IR (ν (CO), CH₂Cl₂): 2037 s, 2017 vs, 1937 s cm⁻¹. ¹H NMR (CDCl₃): δ 9.92 (br, s, 2H), 7.91 (d, *J* = 8 Hz, 4H), 7.61 (t, *J* = 8 Hz, 2H), 7.47 (t, *J* = 8 Hz, 4H).

2.9. Reaction of Mn₂(CO)₉(NCMe) with thiobenzamide

PhCSNH₂ (36 mg, 0.262 mmol) was added to a CH_2Cl_2 solution (25 mL) of $Mn_2(CO)_9(NCMe)$ (100 mg, 0.248 mmol) and the mixture was then stirred at room temperature for 18 h. The solvent was removed by rotary evaporation under reduced pressure and the residue separated by TLC on silica gel. Elution with hexane/CH₂Cl₂

(7:3, v/v) developed four bands. The fourth band gave $Mn(CO)_4{\kappa^1:\eta^1-PhC(S)NHCO}$ (**6**) (11 mg, 7%) as orange crystal after recrystallization from hexane/CH₂Cl₂ at 4 °C. The third band gave an oily substance which we were unable to characterize while the content of the first and second bands were too small for characterization. Spectral data for **6**: Anal. Calcd for C₁₂H₆MnNO₅S: C, 43.52; H, 1.83; N, 4.23. Found: C, 43.91; H, 1.88; N, 4.27%. IR (ν (CO), CH₂Cl₂): 2087 m, 1996 vs, 1970 m, 1935 m, 1662 vw cm⁻¹. ¹H NMR (CDCl₃): δ 9.92 (br, s, 1H), 7.91 (d, *J* = 8 Hz, 2H), 7.61 (t, *J* = 8 Hz, 1H), 7.47 (t, *J* = 8 Hz, 2H).

2.10. X-ray structure determinations

Single crystals of **3–6** suitable for X-ray diffraction were obtained by recrystallization from hexane/CH₂Cl₂ at 4 °C and mounted on Nylon fibers with a mineral oil, and diffraction data were collected at low temperatures (see Table 1) on a Bruker SMART APEX CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å). Data reduction and integration were carried out with SAINT+ and absorption corrections were applied using the program SADABS [26]. Structures were solved by direct methods (**4–6**) or Patterson synthesis (**3**) and developed using alternating cycles of leastsquares refinement and difference-Fourier synthesis. All non-



Scheme 3. Synthesis of dirhenium thioamide complexes.



Scheme 4. Formation of S₂C(R)=NH ligands at the dimanganese center.

hydrogen atoms were refined anisotropically. The SHELXTL PLUS V6.10 program package was used for structure solution and refinement [27]. The details of the data collection and structure refinement are given in Table 1.

3. Results and discussion

3.1. Reactions of $Re_2(CO)_9L$ (L = CO, MeCN) with thioamides

Treatment of either Re₂(CO)₉(NCMe) at 80 °C or Re₂(CO)₁₀ in presence of Me₃NO at ambient temperature with thioacetamide and thiobenzamide afforded low yields of the simple substitution complexes Re₂(CO)₉{ κ^1 -S=C(R)NH₂} (**1**, R = Me; **2**, =Ph) as the only isolable products (Scheme 3). In an attempt to prepare analogous disubstituted species, similar reactions between Re₂(C-O)₈(NCMe)₂ and RCSNH₂ were carried out however this led only to decomposition.

Complexes **1–2** are easily characterized by spectroscopic methods. The IR spectrum of both show five absorption bands within the range from 2107 to 1911 $\rm cm^{-1}$ characteristic of an



Fig. 1. Molecular structure of $Mn_2(CO)_6\{\mu-S_2C(Me)NH\}_2$ (3) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles(°): Mn(1)-N(1) 2.068(3), Mn(1A)-S(2) 2.409(1), Mn(1)-S(2) 2.355(1), S(1)-S(2) 2.079(2), C(5)-S(1) 1.732(4), C(5)-N(1) 1.311(5), C(1)-Mn(1)-N(1) 174.8(2), C(3)-Mn(1)-N(1) 91.7(2), C(2)-Mn(1)-C(3) 89.2(2), C(2)-Mn(1)-S(2) 175.4(1), S(2)-Mn(1)-S(2) 83.33(5), Mn(1)-S(2)-Mn(1) 96.67(5), N(1)-Mn(1)-S(2) 84.48(9), N(1)-Mn(1)-S(2) 85.50(9), S(1)-S(2)-Mn(1) 100.38(5), S(1)-S(2)-Mn(1) 107.92(6).



Fig. 2. Molecular structure of $Mn_2(CO)_6[\mu-S_2C(Ph)NH]_2$ (**4**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles(°): Mn(1)-N(1) 2.043(2), Mn(1)-S(1) 2.3605(8), Mn(1)-S(1A) 2.4043(8), S(1)-S(2) 2.0803(9), C(4)-S(2) 1.742(2), C(4)-N(1) 1.298(3), C(2)-Mn(1)-N(1) 176.4(1), C(3)-Mn(1)-N(1) 94.31(9), C(1)-Mn(1)-C(3) 93.3(1), C(3)-Mn(1)-S(1) 175.22(8), S(1)-Mn(1)-S(1A) 83.42(3), Mn(1)-S(1)-Mn(1A) 96.58(3), N(1)-Mn(1)-S(1) 83.77(6), N(1)-Mn(1) 98.43(3), S(2)-S(1)-Mn(1A) 109.67(3).

Re₂(CO)₉L framework. The ¹H NMR spectrum of **1** consists of two broad and one sharp singlet at δ 7.83, 7.53 and 2.70 in a 1:1:3 ratio, while **2** shows two broad singlets at δ 7.95 and 7.89 together with multiplets at δ 7.77, 7.59 and 7.46 in 1:1:2:1:2 indicating the formation of simple substitution products. The observation of two inequivalent amine protons in both instances suggests that rotation about the carbon–nitrogen bond is hindered as a result of some double-bond character. Characterization of **1** was confirmed by a poor quality crystal structure which showed that thioacetamide was coordinated to the binuclear center through the sulfur atom at an equatorial site.

3.2. Reactions of $Mn_2(CO)_{10}$ with thioamides

Reactions of $Mn_2(CO)_{10}$ with thioacetamide and thiobenzamide proceed in a quite different manner to that observed for at the dirhenium center leading instead to the formation at room temperature of low yields of $Mn_2(CO)_6{\mu-S_2C(R)NH}_2$ (**3**, R = Me; **4**, R = Ph) (Scheme 4). These species result from a series of



5, R = Me; 6, R = Ph

Scheme 5. N-H addition and CO insertion of thioamides at a dimanganese center.



Fig. 3. Molecular structure of $Mn(CO)_4 \{x^2-MeC(S)NHCO\}$ (**5**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and $angles(^\circ)$: Mn(1)-C(1) 1.827(2), Mn(1)-C(2) 1.859(2), Mn(1)-C(3) 1.850(2), Mn(1)-C(4) 1.868(2), Mn(1)-C(5) 2.022(2), Mn(1)-S(1) 2.3440(5), C(6)-S(1) 1.6704(16), C(6)-N(1) 1.330(2), C(5)-N(1) 1.438(2), C(5)-O(5) 1.2322(19), C(5)-Mn(1)-S(1) 84.00(4), C(2)-Mn(1)-S(1) 92.40(6), C(1)-Mn(1)-C(5) 88.87(7), C(1)-Mn(1)-C(2) 94.84(7), C(1)-Mn(1)-C(3) 18.27(5), C(3)-Mn(1)-C(4) 176.17(7), Mn(1)-S(1) 27(5), C(3)-Mn(1)-C(4) 176.17(7), Mn(1)-S(1) 28.82(6), N(1)-C(6)-S(1) 12.00(1), Mn(1)-C(5)-O(5) 130.4(1), N(1)-C(5)-O(5) 114.4(1).

transformations including activation of one N–H bond, carbon– sulfur bond scission and sulfur–sulfur bond formation.

Characterization was initially made on the basis of analytical and spectroscopic data. The IR spectra of both display three carbonyl absorptions suggesting a *facial* arrangement of these ligands. The ¹H NMR spectrum of **3** shows only two resonances, a broad singlet at δ 9.06 and a sharp singlet at δ 2.36 in 1:3 ratio, while that of **4** shows four resonances, a broad singlet at δ 9.92, a doublet at δ 7.91 (J = 8 Hz) and two triplets at δ 7.61 and 7.47 (J = 8 Hz) in 1:2:1:2 intensity ratio. This clearly indicates that nitrogen—hydrogen bond activation has taken place. The precise molecular structure could not be surmised from these spectroscopic data, so we performed single crystal X-ray diffraction



Fig. 4. Molecular structure of $Mn(CO)_4[\kappa^2-PhC(S)NHCO\}$ (**6**) with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles(°): Mn(1)-C(1) 1.860(3), Mn(1)-C(2) 1.850(3), Mn(1)-C(3) 1.851(3), Mn(1)-C(4) 1.817(3), Mn(1)-C(5) 2.006(3), Mn(1)-S(1) 2.340(1), C(6)-S(1) 1.682(3), C(6)-N(1) 1.330(3), C(5)-N(1) 1.430(4), C(5)-O(5) 1.230(3), C(5)-Mn(1)-S(1) 83.52(8), C(3)-Mn(1)-C(1) 95.49(9), C(4)-Mn(1)-C(2) 175.6(1), Mn(1)-C(4) 99.56(9), N(1)-C(6)-S(1) 118.3(2), Mn(1)-C(5)-O(5) 128.8(2), N(1)-C(5)-O(5) 114.9(2).



Chart. 1. Proposed resonace structures of SC(R)NHC(O) ligands.

analysis for both the results of which are shown in Figs. 1 and 2. Both consist of a dimanganese framework in which Mn(CO)₃ units are spanned by two S₂C(R)NH ligands; one sulfur atom bridging the two metal atoms and the nitrogen binding in a monodentate fashion to give a five-membered chelate ring. Both species are centrosymmetric and the coordination geometry around each manganese center is best described as a distorted octahedron. The manganese-nitrogen [2.068(3) Å in 3 and 2.043(2) Å in 4] and manganese-sulfur [2.4087(13), 2.3554(13) Å in **3** and 2.3605(8), 2.4043(8) Å in 4] distances are similar to those reported for related complexes [6-11,22,23]. The carbon-nitrogen bond lengths [1.311(5) Å in **3** and 1.298(3) Å in **4**] are again close to those found in imines, while carbon—sulfur [1.732(4) Å in **3** and 1.742(2) Å in **4**] and sulfur-sulfur [2.0793(15) Å in 3 and 2.0803(9) Å in 5] bond distances in these ligands are similar to the corresponding single bond distances [22,23]. The molecular structures of 3-4 are very similar to that of the dianion $[Mn_2(CO)_6(\mu-SCS_3)_2]^{2-}$ [22,23]. In order to gain some insight concerning the source of sulfur we carried out the same reactions in presence of elemental sulfur but this surprisingly lead to a decrease in the yield of both 3 and 4. We did observe a slight but significant improvement in yields when the thioamides were used in 5-fold excess.

3.3. Reactions of Mn₂(CO)₉(NCMe) with thioamides

In contrast to the dirhenium chemistry discussed earlier in which Re₂(CO)₉(MeCN) and mixtures of Re₂(CO)₁₀/Me₃NO lead to the same products, reactions of both thioacetamide and thiobenzamide with Mn₂(CO)₉(NCMe) in dichloromethane lead only to the isolation in low yields of Mn(CO)₄{ κ^1 : η^1 -RC(S)NHCO} (**5**, R = Me; **6**, R = Ph) (Scheme 5). Complex **5** was also obtained in low (3%) yield from the reaction with Mn₂(CO)₁₀ but **6** was only isolated from this reaction.

We have carried out single crystal X-ray diffraction analysis for 5 and 6, the results of which are summarized in Figs. 3 and 4, respectively. Both consist of a single manganese atom coordinated by four carbonyls and a chelating RC(S)NHCO ligand. The coordination geometry at manganese can be best described as a distorted octahedron evident from the small chelate angle $[84.00(4)^{\circ}]$ in 5 and 83.52(8)° in 6]. In both, the manganese-carbonyl bonds trans to sulfur are slightly shorter (ca. 0.03–0.04 Å) than all others possibly due to the lack of competition for back-donation from manganese. Both the carbon-nitrogen [1.330(2) Å in 5 and 1.330(3) Å in 6] and carbon-sulfur [1.670(2) Å in 5 and 1.682(3) Å in 6] bonds within the amide are intermediate between single and double bond distances. This leads us to consider two resonance hydrids for these chelate rings (Chart 1) and as in the case of **1–2** it is the zwitterionic resonance structure that dominates. It is noteworthy that in 6 the phenyl ring lies approximately in the plane of the chelate suggests some extra overlap between the two π -ring systems in this case. The structures of **5–6** are very similar to that of $Mn(CO)_4(\kappa^1:\eta^1-$ SCNHC₃H₆NCO) isolated as a minor product from the reaction between Mn₂(CO)₉(NCMe) and tetrahydropyrimidine-2-thiol [8] under similar conditions.

4. Summary

In summary, we have shown that dinuclear Group 7 carbonyls react with both thioacetamide and thiobenzamide to afford three different types of low yielding products. With rhenium these were the simple substitution products $\text{Re}_2(\text{CO})_9\{\kappa^1-S=C(R)\text{NH}_2\}$ (1–2). In contrast with manganese such simple substitution products could not be isolated and the reaction product was found to depend strongly upon the nature of the starting carbonyl complex. Thus with $\text{Mn}_2(\text{CO})_{10}$ binuclear complexes $\text{Mn}_2(\text{CO})_6\{\mu-S_2C(R)\text{NH}\}_2$ (3–4) were either the sole or major product, however with $\text{Mn}_2(\text{CO})_9(\text{MeCN})$ only mononuclear species $\text{Mn}(\text{CO})_4\{\kappa^1:\eta^1-\text{RC}(S)$ NHCO} (5–6) could be isolated. Dinuclear 3–4 result formally from further insertion of sulfur into the metal–thiolate interaction followed by dimerisation, while mononuclear 5–6 are a consequence of the amide reacting with CO.

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Appendix A. Supplementary material

CCDC 919633 for **3**, 919634 for **4**, 919635 for **5**, and 919636 for **6** 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.

- References
- [1] H. Egold, D. Schwarze, U. Flörke, J. Chem. Soc. Dalton Trans. (1999) 3203.
- [2] P.M. Treichejl, H. Morris, F.G.A. Stone, J. Chem. Soc. (1963) 720.
- [3] A.G. Osborne, F.G.A. Stone, J. Chem. Soc. (A) (1966) 1143.
- [4] N. Begum, M.I. Hyder, S.E. Kabir, G.M.G. Hossain, E. Nordlander, D. Rokhsana, E. Rosenberg, Inorg. Chem. 44 (2005) 9887.
 [5] A.J. Deeming, M. Karim, P.A. Bates, M.B. Hursthouse, Polyhedron 7 (1988)
- [5] A.J. Deening, M. Kalini, F.A. Bates, M.B. Hulshlouse, Polyhedroll 7 (1988) 1401.
- [6] S.E. Kabir, M.M. Karim, K. Kundu, S.M.B. Ullah, K.I. Hardcastle, J. Organomet. Chem. 517 (1996) 155.
- [7] S.E. Kabir, J. Alam, S. Ghosh, K. Kundu, G. Hogarth, D.A. Tocher, G.M.G. Hossain, H.W. Roesky, J. Chem. Soc. Dalton Trans. (2009) 4458.
- [8] S. Ghosh, F.K. Camellia, K. Fatema, M.I. Hossain, M.R. Al-Mamun, G.M.G. Hossain, G. Hogarth, S.E. Kabir, J. Organomet. Chem. 696 (2011) 2935.
- [9] S. Ghosh, S.E. Kabir, S. Pervin, G.M.G. Hossain, D.T. Haworth, S.V. Lindeman, T.A. Siddiquee, D.W. Bennett, H.W. Roesky, Z. Anorg. Allg. Chem. 635 (2009) 76.
- [10] S. Ghosh, F. Ahmed, R. Al-Mamun, D.T. Haworth, S.V. Lindeman, T.A. Siddiquee, D.W. Bennett, S.E. Kabir, J. Chem. Crystallogr. 39 (2009) 595.
- [11] S. Ghosh, M.S.A. Mia, E. Begum, G.M.G. Hossain, S.E. Kabir, Inorg. Chim. Acta 384 (2012) 76.
- [12] S. Ghosh, K.N. Khanam, M.K. Hossain, G.M.G. Hossain, D.T. Haworth, S.V. Lindeman, G. Hogarth, S.E. Kabir, J. Organomet. Chem. 695 (2010) 1146.
- [13] P.O. Nubel, S.R. Wilson, T.L. Brown, Organometallics 2 (1983) 515.
- [14] D.R. Gard, T.L. Brown, Organometallics 1 (1982) 1143.
- [15] S.E. Kabir, F. Ahmed, A. Das, M.R. Hassan, D.T. Haworth, S.V. Lindeman, G.M.G. Hossain, T.A. Siddiquee, D.W. Bennett, J. Organomet. Chem. 692 (2007) 4337.
- [16] K.A. Azam, M.M. Hossain, M.B. Hursthouse, S.E. Kabir, M.M. Karim, K.M.A. Malik, J. Organomet. Chem. 544 (1997) 23.
- [17] R.D. Adams, M. Huang, J.H. Yamamoto, L. Zhang, Chem. Ber. 129 (1996) 137.
- [18] R.D. Adams, J.A. Belinski, J. Schierlmann, J. Am. Chem. Soc. 113 (1991) 9004.
- [19] R.D. Adams, S.B. Falloon, Organometallics 14 (1995) 1748.
- [20] H. Alper, Inorg. Chem. 15 (1976) 962.
- [21] T.S.A. Hor, B. Wagner, W. Beck, Organometallics 9 (1990) 2183.
- [22] H. Alper, F. Sibtain, F.W.B. Einstein, A.C. Willis, Organometallics 4 (1985) 604.
 [23] K.-C. Huang, Y.-C. Tsai, G.-H. Lee, S.-M. Peng, M. Shieh, Inorg. Chem. 36 (1997)
- 4421.
- [24] B. Eber, G. Huttner, W. Imhof, J. Organomet. Chem. 402 (1991) 221.
- [25] U. Koelle, J. Organomet. Chem. 155 (1978) 53.
- [26] SMART and SAINT+ Software for CCDC Diffractometers, Version 6.1, Bruker, AXS, Madison, WI, 2000.
- [27] G.M. Sheldrick, SHELXTL PLUS, Version 6.1, Bruker AXS, Madison, WI, 2000.