J. Bangladesh Acad. Sci. 47(1); 1-20: June 2023 DOI: https://doi.org/10.3329/jbas.v47i1.66442

Journal of Bangladesh Academy of Sciences

Journal homepage: http://www.bas.org.bd/publications/jbas.html

Review Article

The chemistry of rhenium and manganese carbonyl complexes bearing heterocyclic thiolate ligands: Mono–, di–, tri–, and tetranuclear complexes

Md. Tuhinur Rahman Joy, Jagodish Chandra Sarker[1] and Shariff Enamul Kabir[1,*]

Department of Chemistry, Jashore University of Science and Technology, Jashore, Bangladesh

ARTICLE INFO

Article History

Received: 21 May 2023
Revised: 01 June 2023
Accepted: 11 June 2023

Keywords: Rhenium, Manganese, Carbonyls, Heterocyclic thiols, Polynuclear, Self-assembly, Mixed-metal clusters

ABSTRACT

This article provides an overview of the rich chemistry of rhenium and manganese decacarbonyls, $M_2(CO)_{10}$ (M = Re, Mn) and their acetonitrile derivatives $[M_2(CO)_8(NCMe)_2]$ as precursors for synthesis of new di–, tri– and tetranuclear complexes derived from a wide range of heterocyclic thiols such as pyridine-2-thiol, pyrimidine-2-thiol, tetrahydropyrimidine-2-thiol, 2-mercapto-1-methylimidazole, benzimidazole-2-thiol etc. A comparative study of the reactivities of these complexes with various mono– and bidentate ligands is also the subject of this review. In some instances, the structural aspects of the complexes are also discussed. The applications of these complexes as precursors for the synthesis of a wide variety of mixed-metal cluster complexes are highlighted.

Introduction

The chemistry of transition metal complexes bearing heterocyclic-thiolate ligands is of considerable interest because of their unique structural diversity (Deeming et al., 1988a; Umakoshi et al., 1990; Rose et al., 1994), important biological traits (Rosenfield et al., 1987; Castro et al., 1990; Kienitz et al., 1996; Liaw et al., 1998), and use as precursors for metallosulfide materials (Berardini et al., 1995; Rose et al., 1995; Cheng et al., 1996; Lee et al., 1997). Heterocyclic thiols such as pyridine-2-thiol and pyrimidine-2-thiol exist predominantly in the thiol and tautomeric thionate form (Chart 1).

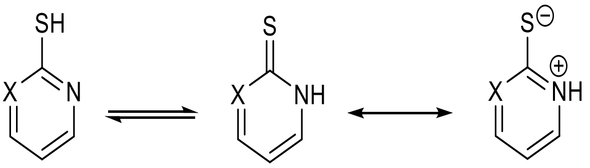


Chart 1. Major tautomers of pyridine-2-thiol (X = C) and pyrimidine -2-thiol (X = N).

Heterocyclic thiols are attractive ligands to synthetic inorganic and organometallic chemists as they are capable of coordinating to the metal centers in a wide variety of ways (Chart 2) due to the presence of both nitrogen and sulfur as potential electron-donating atoms which in turn is expected to influence the nature of the products formed (Deeming et al., 1988b).

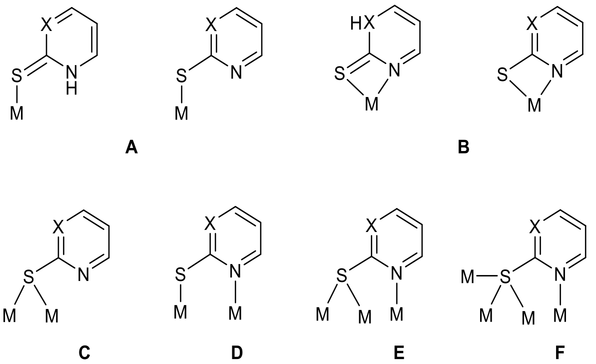


Chart 2. Coordination modes of pyridine-2-thiol (X = C) and pyrimidine -2-thiol (X = N).

The reactivity of heterocyclic thiols such as pyridine-2-thiol (Deeming et al. 1988b; Kabir et al., 2000), pyrimidine-2-thiol (Kabir et al., 2000), tetrahydropyrimidine-2-thiol (Ghosh et al., 2011),

---

[*] Corresponding author: <skabir_ju@yahoo.com>

[1] *Department of Chemistry, Jagannath University, Dhaka, Bangladesh*

2-mercapto-1-methylimidazole (Ghosh et al., 2009b), 2-mercapto-1-benzothiazole (Ghosh et al., 2010b), thiazole (Kabir et al., 2007; Azam et al., 1998a; Azam et al., 1998b), 4-methylthiazole (Azam et al., 1996), thiazolidine (Hanif et al., 1999), thiomorpholine (Hanif et al., 1999), benzothiazole and benzimidazole-2-thiol (Dilshad et al., 1999) with group 7 metal carbonyls have been investigated over the last three decades. It has been observed from these studies that the reactivity pattern of the heterocyclic thiols is not only determined by the structures of the thiols but also by the intrinsic reactivity of the metal carbonyls used.

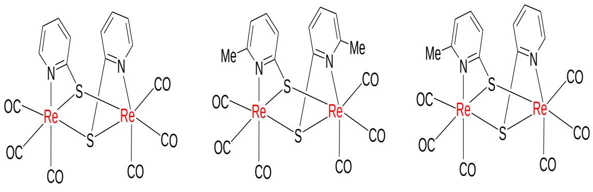
Manganese and rhenium carbonyls showed varied reactivity toward pyridine-2-thiol and pyrimidine-2-thiol; pyridine-2-thiol produces dimeric complexes, while pyrimidine-2-thiol forms tetrameric complexes (Deeming et al., 1988b; Kabir et al., 1996). Moreover, carbonyls of these two transition metals experienced different reactivity towards 2-mercapto-1-methylimidazole (five-membered heterocyclic thiol ligand), yielding di–, tri– and tetranuclear complexes (Ghosh et al., 2009b). In addition to exhibiting distinctive structural characteristics, the products isolated from these reactions also showed promise as potential precursors for synthesizing a wide range of mixed-metal complexes (Cockerton et al., 1991; Ghosh et al., 2009b).

The chemistry of mixed-metal clusters of low-valent transition metals has been of enduring interest due to their unique structural properties and various applications resulting from having disparate metals with different chemical properties in close proximity and also because of potential catalytic applications (Muetterties et al., 1977; Broussard et al., 1993; Braunstein et al., 1995; Adams et al., 1998a; Adams et al., 1998b; Quebatte et al., 2004; Gauther et al., 2004). In fact, they have also been used in homogeneous catalysis. Incorporating several metal types in clusters could provide synergistic benefits for catalytic conversion (Muetterties et al., 1977; Fusi et al., 1982; Broussard et al., 1993; Braunstein et al., 1995). The combining catalytic properties of several different metal centers are also provided by mixed-metal clusters, which contain non-equivalent binding sites and hence can be employed in homogeneous catalysis (Beuken et al., 1998; Kalck 1988; Braunstein et al., 1999).

In this review, we aim to summarize some exciting developments in low-valent transition metal carbonyl complexes bearing heterocyclic thiolate ligands, emphasizing their systematic synthesis, structural characterization, and reactivity with mono– and bidentate ligands. To make this article diverse and inclusive, we have also logically incorporated the synthesis and structural properties of mixed-metal cluster complexes of low-valent transition metals.

Reactivity of $[M_2(CO)_{10}]$ (M = Re, Mn) towards pyridine-2-thiol (pySH) and pyrimidine-2-thiol (pymSH): Synthesis of di– and tetranuclear square-type complexes

In 1988, Deeming et al. first reported the dinuclear hexhacarbonyl compound $[Re_2(\mu\text{-pyS})_2(CO)_6]$ (**1**) in almost quantitative yield (Deeming et al., 1988b) from the reaction of $[Re_2(CO)_{10}]$ with pyridine-2-thiol (pySH) in refluxing xylene. The corresponding 6-methylpyridine-2-thiolate analog $[Re_2(\mu\text{-MepyS})_{2\text{-}}(CO)_6]$ (**2**) was prepared following similar procedures but in lower yield. These dimers contain three fused four-membered rings. Importantly, they observed slow scrambling of $[Re_2(CO)_6(\mu\text{-pyS})_2]$ with the 6-methylsubstituted analog $[Re_2(CO)_6(\mu\text{-MepyS})_2]$, for which the X-ray structure is reported (Fig. 1), at ambient temperature giving an equilibrium involving $[Re_2(CO)_6(\mu\text{-pyS})(\mu\text{-MepyS})]$ (**3**) and suggested that the scrambling process occurred via the 16-electron mononuclear species $[Re(CO)_3(pyS)]$ or a related solvent-stabilized 18-electron species. After 8 years, in 1996, we reported the manganese analogs $[Mn_2(\mu\text{-pyS})_2(CO)_6]$ **(4)** and $[Mn_2(\mu\text{-MepyS})_2(CO)_6]$ (**5**) from the Me_3NO initiated reactions of $Mn_2(CO)_{10}$ with pyridine-2-thiol and 6-methylpyridine-2-thiol, respectively (Kabir et al., 1996).



1 2 3

Chart 3. Complexes derived from $[Re_2(CO)_{10}]$ reactions with pyS/MepyS.

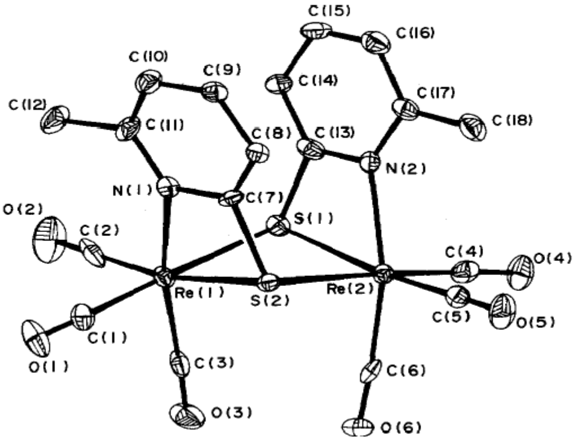
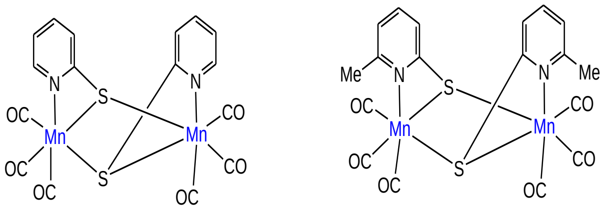


Fig. 1. The solid-state structure of $[Re_2(\mu\text{-MepyS})_2CO)_6]$ (2). Adapted from Kabir et al. 1996.

In these complexes, pyS and MepyS function as five electron donors and span the binuclear center by coordinating sulfur and nitrogen. From the X-ray determined structure of **4** (Fig. 2), it was apparent that it has a chiral structure with C_2 symmetry. The overall structure is very similar to that of its rhenium analog $[Re_2(\mu\text{-MepyS})_2(CO)_6]$ **(2)** (Deeming et al., 1988b). A four-membered chelate ring is formed when each pyS ligand connects two manganese centers through the sulfur atom and one manganese center through the nitrogen atom. Compound **5** is a dinuclear manganese complex that consists of three fused four-membered rings and auxiliary ligands (Fig. 2).



4 5

Chart 4. Complexes derived from the reaction of $[Mn_2(CO)_{10}]$ and pyS/MepyS.

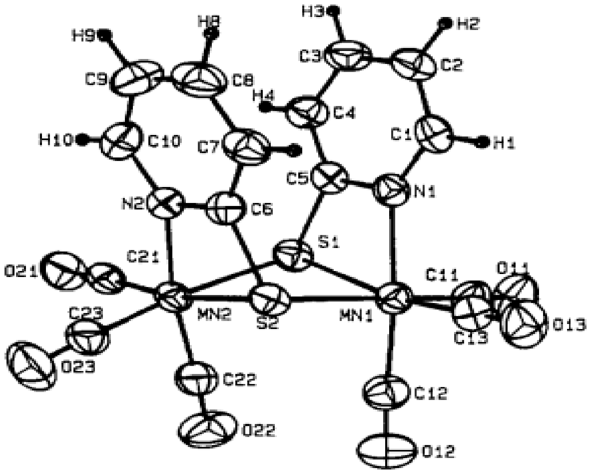
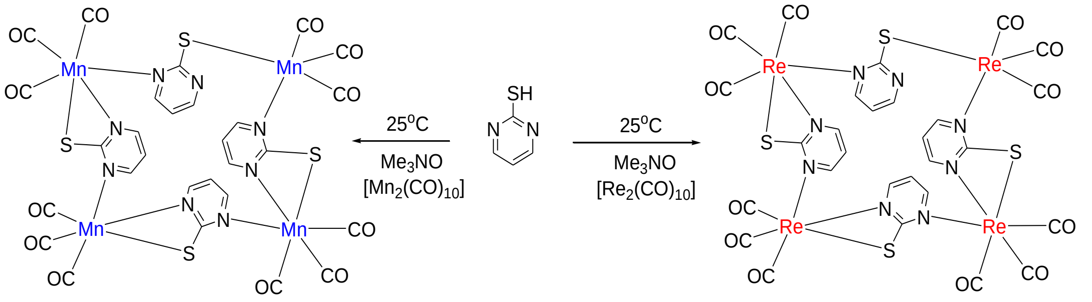


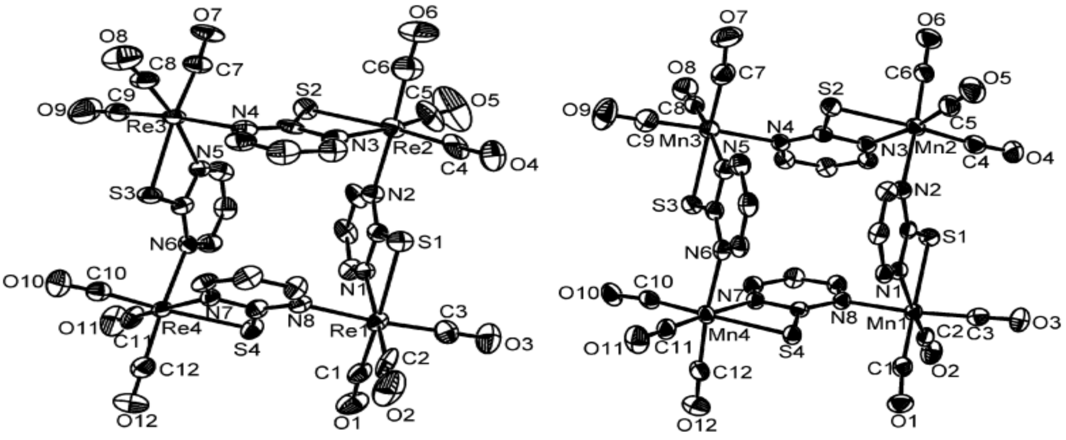
Fig. 2. The molecular structure of $[Mn_2(\mu\text{-pyS})_2(CO)_6]$ (4). Adapted from Kabir et al. 1996.

In the last thirty years, quite a large number of tetranuclear square-type complexes have been reported mostly by Stang, Fujita, and their co-workers by applying the self-assembly phenomena (Stanget al., 1994a; Stang et al., 1995; Stang et al., 1996a; Stang et al., 1996b; Stang et al., 1994b; Fujita et al., 1990; Fujita et al., 1996). Most of these complexes are based on a square-planar metal coordination geometry. Kabir and our group has pioneered the synthesis of novel tetranuclear square-type complexes $[M_4(CO)_{12}(\mu\text{-pymS})_4]$ (**6**, M = Re; **7**, M = Mn) from trimethylamine-N-oxide initiated reactions of $M_2(CO)_{10}$ (M = Re, Mn) with pyrimidine-2-thiol (pymSH) (Kabir et al., 2009). The single crystal X-ray structures of **1** and **6** (Fig. 3) confirm that these molecules are tetranuclear; the four separate *fac*-$M(CO)_3$ units are held together by tridentate pyrimidine-2-thiolate ligands.

Two of the pyrimidine-2-thiolate ligands lie above and two below the M_4 plane. The coordination geometry of each metal atom is a distorted octahedron with a *cis*-arrangement of the pyrimidine-2-thiolate ligands. Each metal atom achieves an 18-electron configuration without any appreciable metal-metal interaction considering that each pyrimidine-2- thiolate ligand donates five electrons. Complexes **6** and **7** provide unusual examples of tetranuclear square-type structures bearing heterocyclic thiolate ligands and *fac*-$M(CO)_3$ fragments.



Scheme 1. Synthesis of square-type complexes $[Re_4(CO)_{12}(\mu\text{-pymS})_4]$(6) and $[Mn_4(CO)_{12}(\mu\text{-pymS})_4]$ (7).



(A) **(B)**

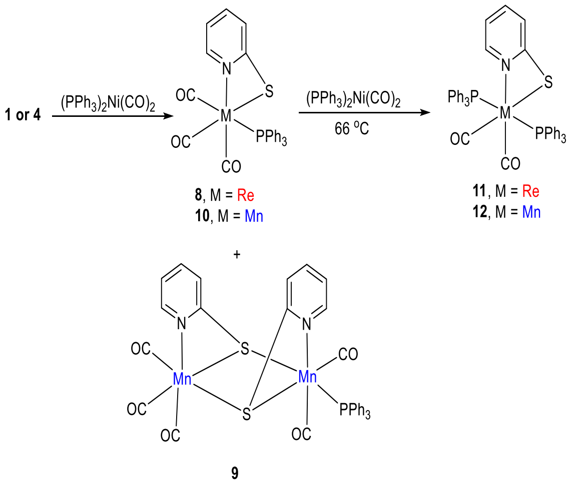
Fig. 3. Molecular structures of (A) $[Re_4(CO)_{12}(\mu\text{-pymS})_4]$ (6) and (B) $[Re_4(CO)_{12}(\mu\text{-pymS})_4]$ (7). Adapted from Kabir et al., 2009.

Reactivity of $[M_2(CO)_6(\mu\text{-pyS})_2]$ (1, M = Re; 4, M = Mn) towards mono–and bidentate ligands.

To explore whether the dinuclear complexes $[M_2(CO)_6(\mu\text{-pyS})_2]$ (**1**, M = Re; **4**, M = Mn) can form mixed-metal clusters when reacted with $(Ph_3P)_2Ni(CO)_2$, the reactions of **1** and **4** with the latter have been investigated. Treatment **4** with

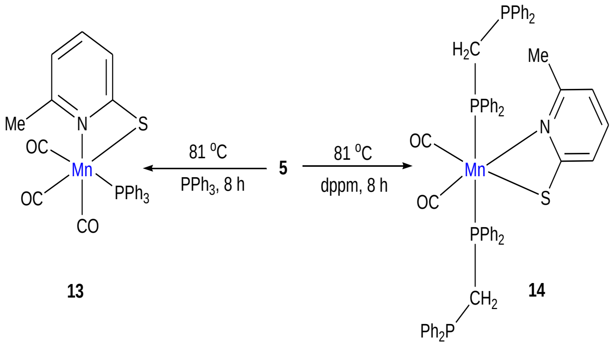
latter have been investigated. Treatment **4** with

$(Ph_3P)_2Ni(CO)_2$ at room temperature furnished the dinuclear complex $[Mn_2(CO)_5(PPh_3)(\mu\text{-pyS})_2]$ (**9**) and the mononuclear *fac*-$[Mn(CO)_3(PPh_3)(\kappa^2\text{-pyS})]$ (**10**), the former being the first example of a carbonyl-substituted product of **4** (Rahman et al., 2012). In contrast, **1** reacts with $(Ph_3P)_2Ni(CO)_2$ at ambient temperature to give mononuclear complex *fac*-$[Re(CO)_3(PPh_3)(\kappa^2\text{-pyS})]$ (**8**). Both **8** and **10** produce $[M(CO)_2(PPh_3)_2(\kappa^2\text{-pyS})]$ (**11**, M = Re; **12**, M = Mn) by CO substitution reaction when they are reacted further with $(Ph_3P)_2Ni(CO)_2$ at room temperature. Additionally, complex **9** reacts further with $(Ph_3P)_2Ni(CO_2)$ to produce **10** and **12**.



Scheme 2. Reactivity of $[M_2(CO)_6(\mu\text{-pyS})_2]$ (1, M = Re; 4, M = Mn) towards monodentate ligands.

Compound **5** reacts with PPh_3 and dppm [dppm = $Ph_2PCH_2PPh_2$ = bis(diphenylphosphino)methane] in refluxing cyclohexane to give $[Mn(MepyS)(PPh_3)(CO)_3]$ (**13**) and $[Mn(MepyS)(\eta^1\text{-dppm})_2(CO)_2]$ (**14**), respectively (Kabir et al., 1996), the latter containing a dangling dppm ligand. The NMR spectrum identified the η^1 mode of coordination of dppm in compound 14. The two $^2J_{PH}$ values (8 and 1.5 Hz) designate that the two phosphorus atoms in dppm are not equivalent; one is bonded to metal while the other is free from coordination.



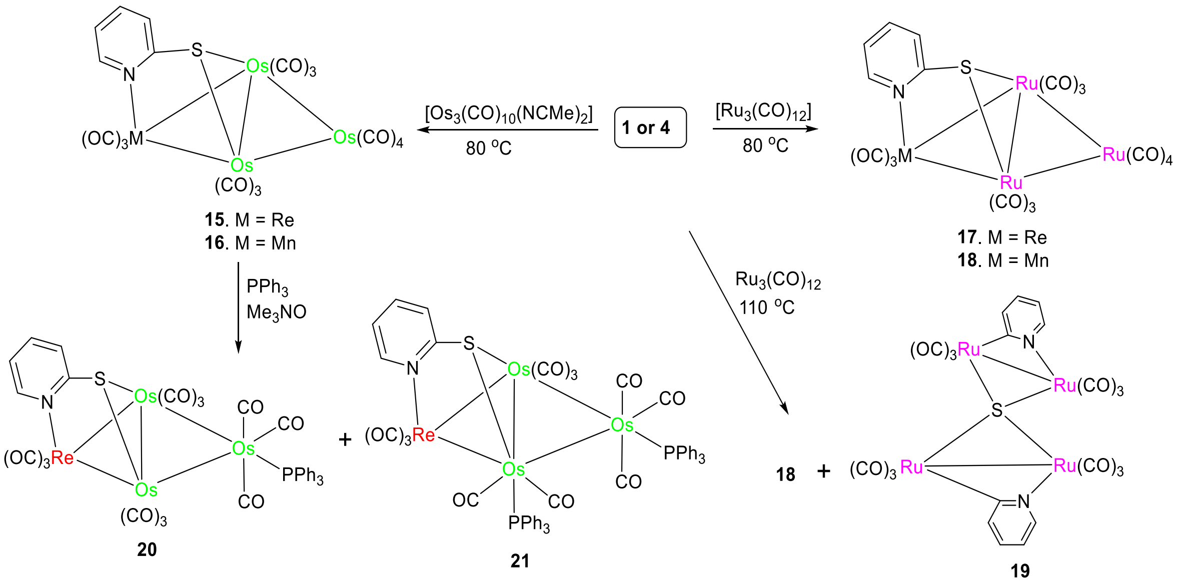
Scheme 3. Reactivity of $[Mn_2(\mu\text{-MepyS})_2(CO)_6]$ (5) towards mono– and bidentate ligands.

Formation of mixed-metal clusters: Reactivity of complexes 1 and 4 towards $[M_3(CO)_{10}(L)_2]$ (M = Fe, Os, Ru; L = CO, NCMe)

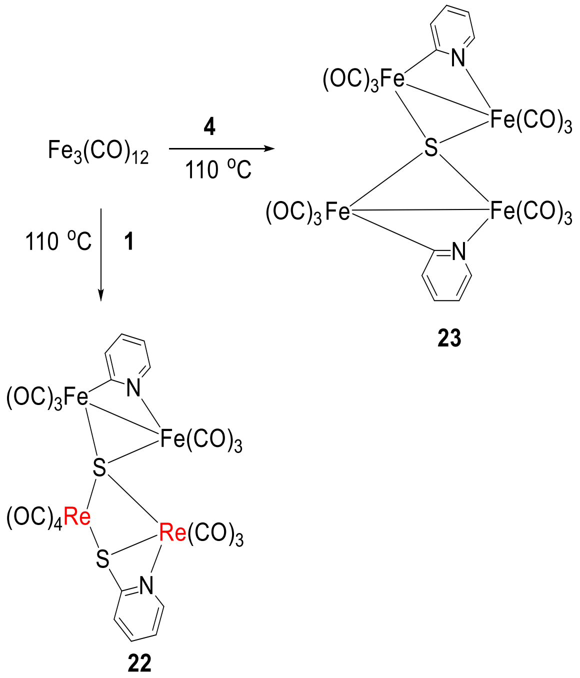
The reactions of **1** and **4** with group 8 metal carbonyl clusters have yet to be explored systematically, but the reaction of **1** towards $Ru_3(CO)_{12}$ has received some attention (Cockerton et al., 1991). Heating **1** with $Ru_3(CO)_{12}$ in toluene at 138 °C affords a series of Re–Ru mixed-metal clusters with varying nuclearity like $ReRu_3$, Re_3Ru, and Re_2Ru_2 groups which are formally built up by the combination of the 16-electron mononuclear species $Re(pyS)(CO)_n$ and $Ru(CO)_n$ (n = 2, 3 or 4) units. In contrast, reactions of $[M_2(CO)_6(\mu\text{-pyS})_2]$ (**1**, M = Re; **4**, M = Mn) with $[Os_3(CO)_{10}(NCMe)_2]$ in refluxing benzene at 80 °C furnish the mixed-metal clusters $[MOs_3(CO)_{13}(\mu_3\text{-pyS})]$ (**15**, M = Re; **16**, M = Mn) (Ghosh et al., 2010a). Similar reaction between **1** and $Ru_3(CO)_{12}$ at 80 °C produces $[ReRu_3(CO)_{13}(\mu_3\text{-pyS})]$ (**17**), whereas at 110 °C the tetraruthenium cluster $[Ru_4(CO)_{12}(\mu\text{-py})_2(\mu_4\text{-S})]$ (**18**) has been obtained as the only product (Scheme 4). Thus, the products obtained from reaction **1** with $Ru_3(CO)_{12}$ are temperature dependent. Compound 18 comprises two $Ru_2(CO)_6(\mu\text{-py})$units linked by a quadruply bridging sulfur ligand. The solid-state structure shows that the 2-pyridyl ligands, formed by cleavage of the C–S bond of the coordinated pyS ligand, span across two different Ru–Ru edges. Compound $[Mn_2(CO)_6(\mu\text{-pyS})_2]$ (**4**) reacts with $Ru_3(CO)_{12}$ to afford $[MnRu_3(CO)_{13}(\mu_3\text{-pyS})]$ (**19**) as the sole product. Introduction of PPh_3 to 15 in the presence of Me_3NO yields both the rnono– and bis(phosphine) substituted products $[ReOs_3(CO)_{12}(PPh_3)(\mu_3\text{-pyS})]$ (**20**) and $[ReOs_3(CO)_{11}(PPh_3)_2(\mu_3\text{-pyS})]$ (**21**), respectively (Scheme 4).

They then examined the reactions of **1** and **4** with $Fe_3(CO)_{12}$ at 110 °C, from which two completely different products have been isolated; the Fe_2Re_2 mixed-metal sulfido cluster $[Fe_2Re_2(CO)_{13}(\mu\text{-py})(\mu\text{-pyS})(\mu_4\text{-S})]$ (**22**) and the tetrairon cluster $[Fe_4(CO)_{12}(\mu\text{-py})_2(\mu_4\text{-S})]$ (**23**) (Scheme 5), respectively. All the mixed-metal clusters have been structurally characterized.

To see whether the manganese dimer $[Mn_2(CO)_6(pyS)_2]$ (**4**) can act as a precursor for the synthesis of Mo–Mn mixed metal complexes, Begum et al. investigated the reaction of $[Mn_2(CO)_6(pyS)_2]$**(4)** with $[CpMo(CO)_3]_2$. Thus boiling a toluene solution of the dimer **4** at 110 °C yields the Mo–Mn mixed metal complex $[CpMoMn(CO)_3(\mu\text{-CO})(\mu\text{-}\eta^2\text{-pyS})(\mu\text{-}\eta^1\text{-pyS})]$, the



Scheme 4. Formation of mixed-metal clusters from the reactions of $[M_2(CO)_6(\mu\text{-}pyS)_2]$ (M = Re, Mn) with $[M_3(CO)_{10}(L)_2]$ (M = Os, Ru; L = CO, NCMe).

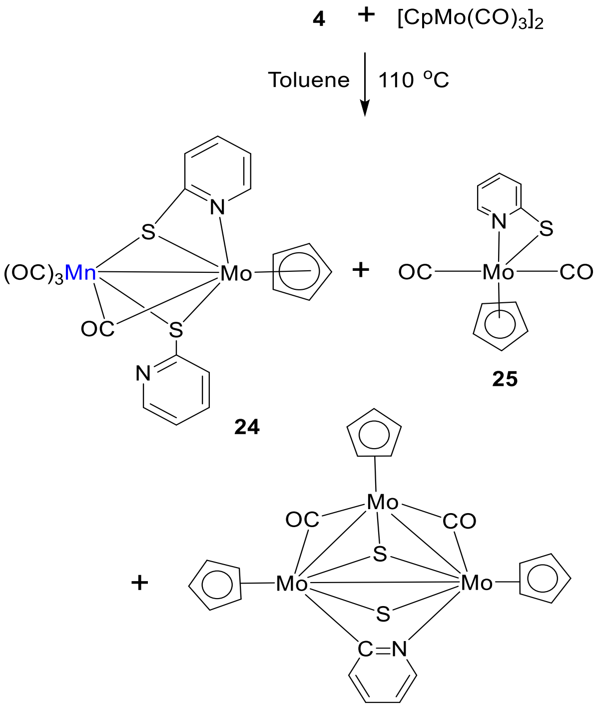


Scheme 5. Reactivity of $[M_2(CO)_6(\mu\text{-}pyS)_2]$ (M = Re, Mn) towards $Fe_3(CO)_{12}$.

unsaturated trimolybdenum cluster $[Cp_3Mo_3(\mu\text{-}CO)_2(\mu\text{-}S)(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}NC_5H_4)]$ (**26**) and the mononuclear molybdenum complex $[CpMo(\mu\text{-}CO)_2)(\eta^2\text{-}pyS)]$ (Begum et al., 2005). Diffraction studies have determined the structures of all three compounds. Complex **24** represents an unusual example of a Mo–Mn heterodinuclear complex containing a μ-η^2-pyridine-2-thiolato, a μ-η^1-pyridine-2- thiolato, and a cyclopentadienyl ligand. The 46-electron cluster **26** is a rare example of a 46-electron trimolybdenum cluster bearing three cyclopentadienyl ligands, an orthometalated pyridyl ligands, a capping sulfide, a bridging sulfido, and two semi bridging ligands. The facile cleavage of the sulfur–carbon bond illustrated by the formation of **26** is reminiscent of numerous literature examples (Neumann et al., 1988).

Reactivity of tetranuclear complexes $[M_4(CO)_{12}(\mu\text{-}pymS)_4]$ (6, M = Re; 7, M = Mn) towards mono– and bidentate ligands

Kabir and co-workers reported that the reactions of $[M_4(CO)_{12}(\mu\text{-}pymS)_4]$ (**6**, M = Re; **7**, M = Mn) with donor ligands result in breaking the square-type skeleton to produce mononuclear species containing either mono– or bidentate pyrimidine-2-thiolate ligands (Kabir et al., 2009; Rahman et al., 2012). In those articles, they showed that a 2-electron donor ligand, PPh$_3$ reacts with **7** to produce [Mn(CO)$_3$(PPh$_3$)(κ^2-pymS)] (**27**) in which the pyrimidindne-2-thiolate ligand binds in a bidentate fashion while the bidentate N-donor diamines react with **6** and **7** to furnish [M(CO)$_3$ (κ^2-L)(κ^1-pymS)] (**28–31**) (M = Re, Mn; L = 2,2′-bipyridine, 1,10-phenanthroline) in which the pyrimidine-2-thiolate coordinates in a monodentate fashion via sulfur. Depending on the nature of the metals and diphosphines, complexes with various stoichiometries and pyrimidine-2-thiolate binding modes can be produced using diphosphines. With dppm and dppe, **6** affords [Re(CO)$_2$(κ^1-pymS)(κ^2-dppm)] (**32**) and [Re(CO)$_2$(κ^2-pymS)(κ^1-dppe)$_2$] (**33**), respectively, whereas **7** gives [Mn(CO)$_2$(κ^2-pymS)(κ^1-dppm)$_2$] (**34**) and [Mn(CO)$_2$(κ^2-pyS)(κ^2-dppe)] (**35**) under similar experimental conditions (Chart 5).



Scheme 6. Reactivity of [Mn$_2$(CO)$_6$(μ-pyS)$_2$] towards (CpMo(CO)$_3$)$_2$.

They also reported that the reaction of [Mn$_4$(CO)$_{12}$(μ-pymS)$_4$] (**7**) and (PPh$_3$)$_2$Ni(CO)$_2$ follows a similar route to that of **4** yielding the dinuclear complex [Mn$_2$(CO)$_5$(μ-pymS)$_2$(PPh$_3$)] (**36)** and the mononuclear *fac*-[Mn(CO)$_3$(κ^2-pymS)(PPh$_3$)] (**27**) and [Mn(CO)$_2$ (κ^2-pymS)(PPh$_3$)$_2$] (**37**) (Scheme 7).

Instead of producing any dinuclear compounds, the reaction of [Re$_4$(CO)$_{12}$(μ-pymS)$_4$] **(6)** with (PPh$_3$)$_2$ Ni (CO)$_2$ at room temperature gives the monophosphine substituted compound *fac*-[Re(CO)$_3$(κ^2-pymS) (PPh$_3$)] (**38**) as the sole product.When compound **27** is treated with PPh$_3$ at a high temperature (100 °C), compound **37** is also produced. An analogous reaction of **6** with triphenylphosphine at 110 °C affords [Re(CO)$_2$ (κ^2-pymS)(PPh$_3$)$_2$] (**39**).

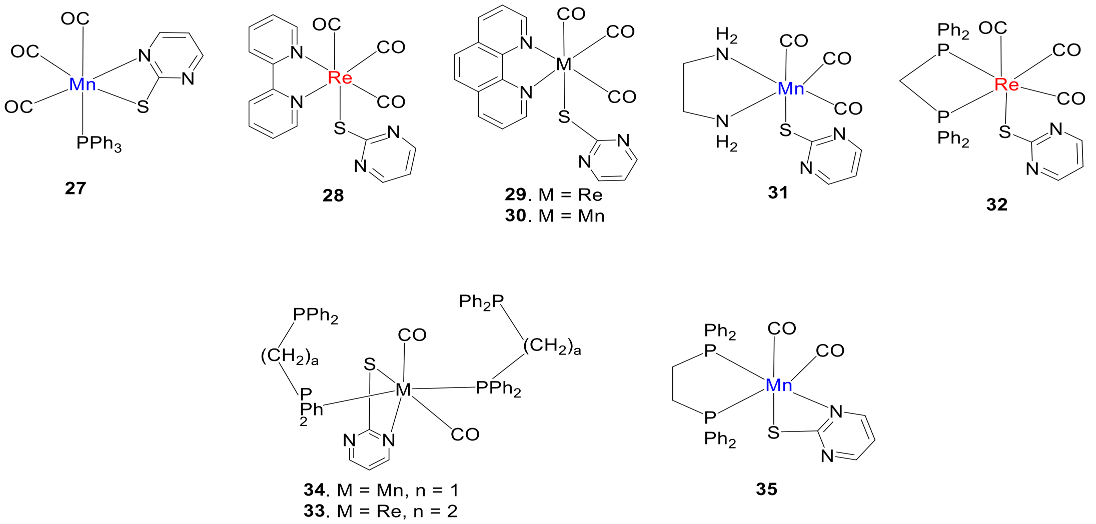
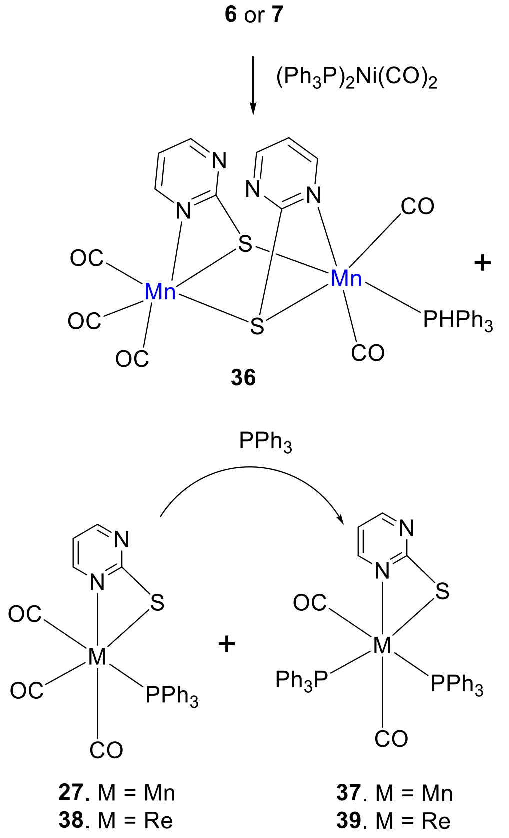


Chart 5. Products of the reactions of 6 or 7 with mono– and bidentate ligands



Scheme 7. Reactivity of square-type complexes $[M_4(CO)_{12}(\mu\text{-pymS})_4]$ (6, M = Re; 7, M = Mn) towards $(PPh_3)_2Ni(CO)_2$.

Reactivity of tetranuclear square-type complexes 6 or 7 towards $[M_3(CO)_{10}(L)_2]$ (M = Fe, Os, Ru; L = CO, NCMe)

Kabir and co-workers have detailed the reactivity **6** and **7** towards $[M_3(CO)_{10}(L)_2]$ (M = Fe, Os, Ru; L = CO, NCMe). Heating the tetrameric complexes **6** and **7** with $[Os_3(CO)_{10}(NCMe)_2]$ furnish butterfly mixed-metal clusters $[MOs_3(CO)_{13}(\mu_3\text{-}\kappa^2\text{-pymS})]$ (**40**, M = Re; **41**, M = Mn) in which the pyrimidine-2-thiolate ligand covers a triangular Os2M face, while the group **7** metal is located at the wing-tip. $Ru_3(CO)_{12}$ undergoes carbon-sulfur bond cleavage, resulting in the formation of tetranuclear clusters $[MRu_3(CO)_{14}(\mu_4\text{-}S)(\mu\text{-}\kappa^1\text{:}\eta^1\text{-pym})]$ (**42**, M = Re; **43**, M = Mn) (Chart 6). The heterocyclic ring and the extruded sulfur are present in **42** and **43** (Kabir et al., 2009).

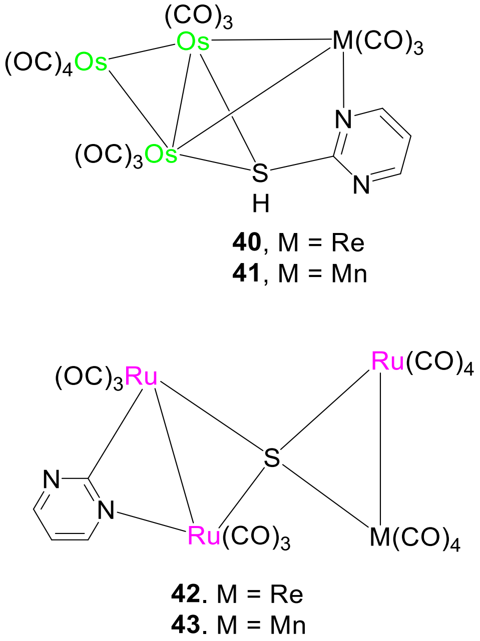
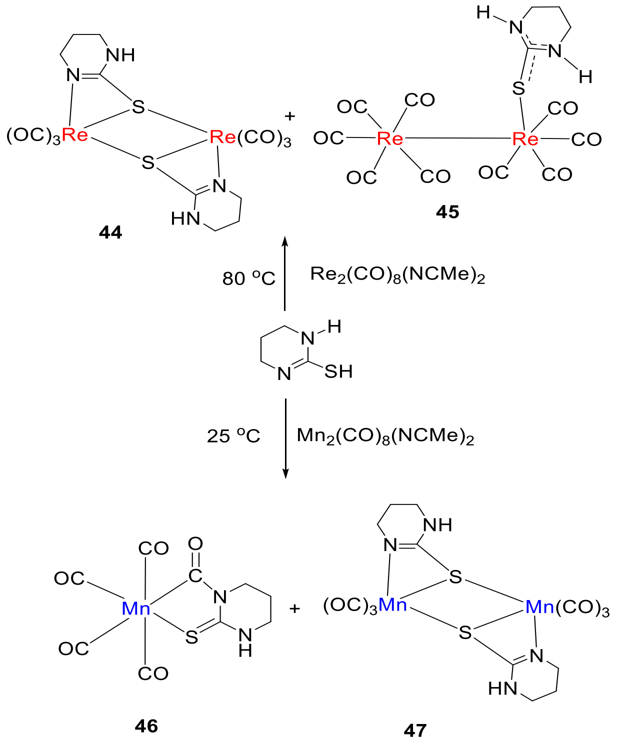


Chart 6. Products of the reactions of $[M_4(CO)_{12}(\mu\text{-pymS})_4]$ (6, M = Re; 7, M = Mn) with $[Os_3(CO)_{10}(NCMe)_2]$.

Reactions of $[M_2(CO)_{10}]$ (M = Re, Mn) with tetrahydropyrimidine-2-thiol (thpymSH)

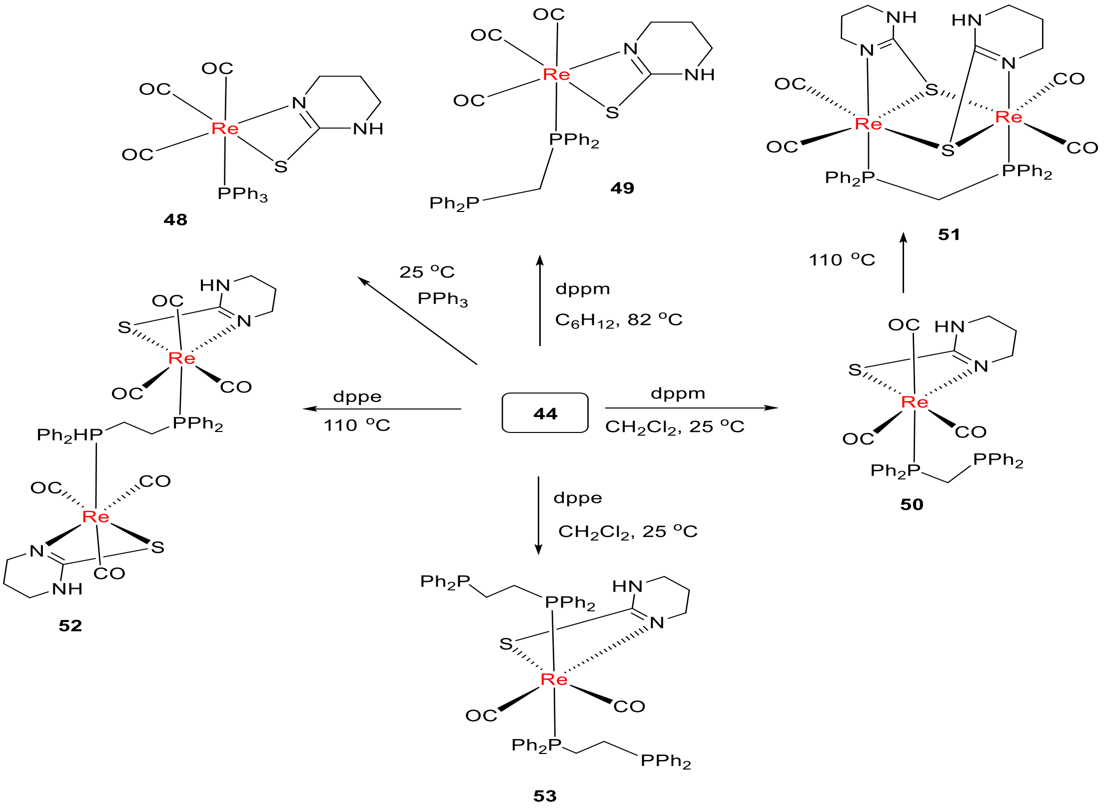
The reactivity of $[Re_2(CO)_{10}]$ towards tetrahydropyrimidine-2-thiol (thpymSH) follows a different and unique path. Two dirhenium complexes $[Re_2(CO)_6(\mu\text{-thpymS})_2]$ (**44**) and eq-$Re_2(CO)_9\{\kappa^1\text{-}(S)\text{-}SN_2C_4H_8\}$ (**45**) (Scheme 8) have been obtained from the reactions of thpymSH with $[Re_2(CO)_8(NCMe)_2]$or $[Re_2(CO)_{10}]$ (Ahmad et al., 2013). Compound **44** proves to be an excellent precursor to a range of mono– and polymetallic complexes acting as a source of “$Re(CO)_3$(thpymS)”. On the other hand, reaction of $[Mn_2(CO)_9(NCMe)]$ with thpymSH at 25 °C affords the mono– and dinuclear complexes $[Mn(CO)_4(\kappa^1\text{:}\eta^1\text{-}SCNH\text{-}C_3H_6\,NCO)]$ (**46**) and $[Mn_2(CO)_6(\mu\text{-thpymS})_2]$ (**47**), respectively (Ghosh et al., 2011). Carbon–nitrogen coupling is observed in compound 46, resulting in the formation of $\kappa^1\text{:}\eta^1\text{-}SCNHC_3H_6NCO$ ligand, while compound 47 adopts a centrosymmetric structure (Scheme 8).



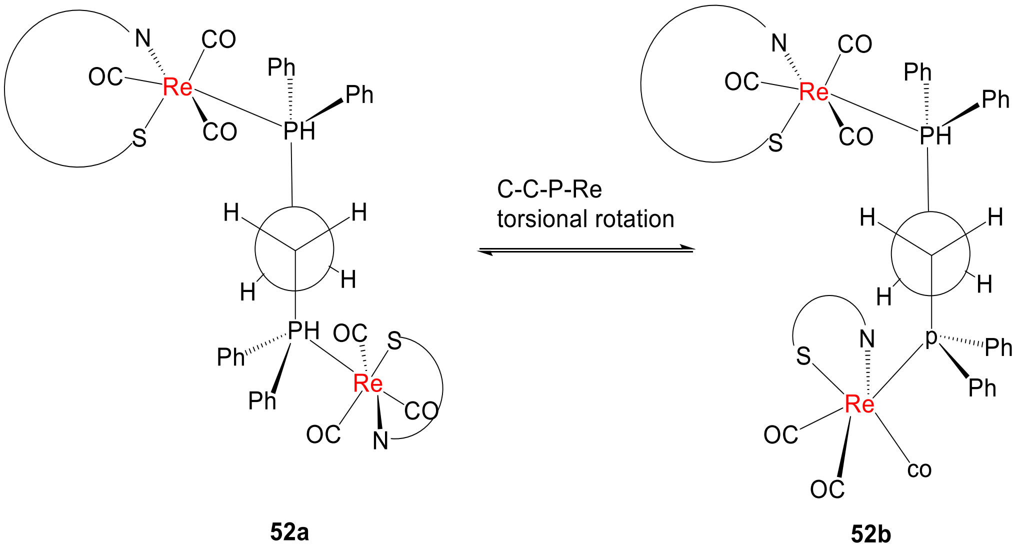
Scheme 8. Reactivity of [M$_2$(CO)$_8$(NCMe)$_2$] (M = Re, Mn) towards thpymSH.

Reactivity of [Re$_2$(CO)$_6$(μ-thpymS)$_2$] towards mono– and bidentate ligands.

The dimer [Re$_2$(CO)$_6$(μ-thpymS)$_2$] (**44**) shows moderate reactivity towards mono– and diphosphines. The reactions of **44** with PPh$_3$ and dppm yield the mononuclear complexes *fac*-Re(CO)$_3$(PPh$_3$)(κ^2-thpymS) (**48**) and *fac*-Re(CO)$_3$-(κ^1-dppm)(κ^2-thpymS) (**49**), respectively (Ahmad et al., 2013). The solid-state structure determination shows that in **48**, the pyrimidine-2-thiolate ligand binds in a chelating fashion. Rigid dppm reacts with **44** to give [Re(CO)$_3$(κ^1-dppm)(κ^2-thpymS)] (**50**) resulting from phosphine-promoted scission of the dithiolate bridges (Moni et al., 2018). When **50** is heated in toluene at 110 °C, CO is lost, and dinuclear [Re$_2$(CO)$_4$(μ-dppm)(μ,κ^2-thpymS)$_2$] (**51**) is formed (Scheme 9), which has two thiolates and one dppm ligand bridging Re–Re bond. On the other hand, the reaction of **44** with more flexible dppe at room temperature affords [Re(CO)$_3$(κ^2-thpymS)$_2$(μ,κ^1,κ^1-dppe) (**52**) where each phosphine center is



Scheme 9. Products of the reaction of [Re$_2$(CO)$_6$(μ-thpymS)$_2$] towards mono– and bidentate ligands.



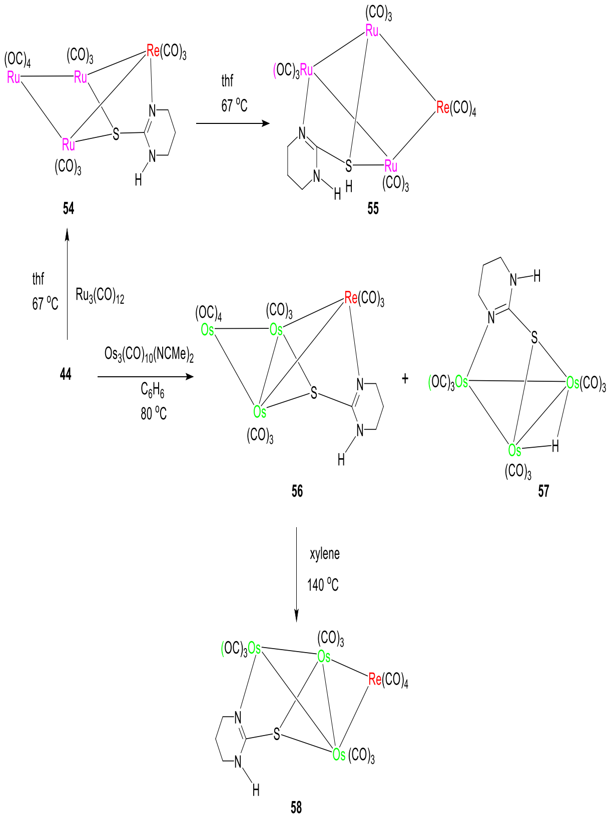
Scheme 10. Two configurational isomers (52a and 52b) of complex 52.

bonded to a d^6-ML_5 rhenium moiety. Two different configurational isomers (**52a** and **52b**) of complex **52** have been isolated (Scheme 10), and their solid-state structures have been crystallographically determined. The orientation of the two [$Re(CO)_3(\kappa^2$-thpymS)] moieties at the anti-staggered Newman projection involving the P–C–C–P backbone of the dppe ligand accounts for the majority of the differences between the stereoisomeric products. Both stereoisomers remain distinct in solution at room temperature, but after being heated at 363 K for one hour, they combine to form a 1:1 combination. In toluene at 383 K, complex **44** reacts with dppe to furnish [$Re(CO)_2(\kappa^1$-dppe$)_2(\kappa^2$-thpymS)] (**53**) containing two dangling dppe ligands (Scheme 10).

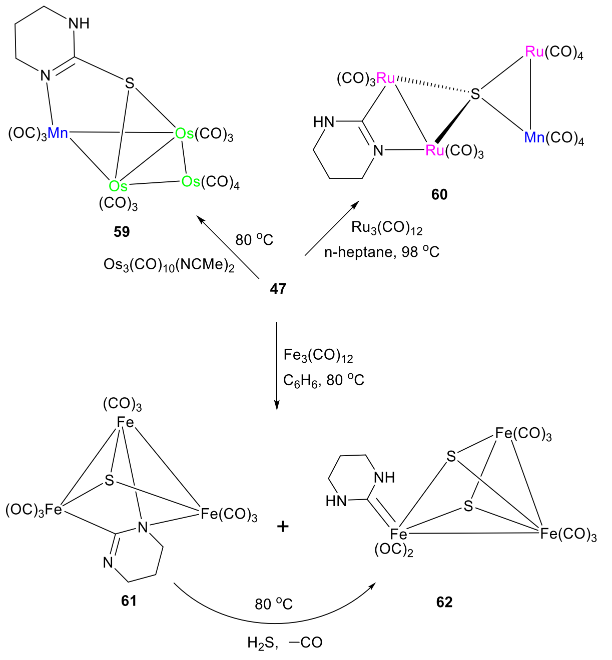
Reactivity of [$M_2(CO)_6(\mu$-thpymS$)_2$] (M = Re, Mn) towards [$M_3(CO)_{10}(L)_2$] (M = Fe, Os, Ru; L = CO, NCMe)

The reaction of **44** with $Ru_3(CO)_{12}$ in refluxing THF results tetranuclear butterfly complexes $ReRu_3(CO)_{13}(\mu_3$-thpymS) (**54**, **55**) where the capping pyrimidine-2-thiolate ligand is positioned differently on the cluster surface (Ahmad et al., 2013) (Scheme 11). The Ru_3 face is covered by the tetrahydro pyrimidine-2-thiolate in the thermodynamic isomer **55**, whereas the $ReRu_2$ face is covered in the kinetic isomer **54**. In refluxing benzene, a similar reaction with [$Os_3(CO)_{10}$-$(NCMe)_2$] yields mostly the $ReOs_3$ cluster [$ReOs_3(CO)_{13}(\mu_3$-thpymS)] (**56**), together with trace quantities of [$(\mu$-H$)Os_3(CO)_9(\mu_3$-thpymS)] (**57**) due to rhenium loss. Cluster **56** is stable in boiling toluene, although it progressively transforms into isomeric **58** in xylene at 140 °C, albeit with low yields. Only minor differences in the cluster core shape may be seen in the isomeric **54** and **55** crystal structures.

Reaction of **47** with [$Os_3(CO)_{10}(NCMe)_2$] in refluxing benzene furnishes the MnOs mixed-metal cluster [$MnOs_3(CO)_{13}(\mu_3$-thpymS)] (**59**) which has a butterfly-shaped skeleton made up of four metal atoms whereas $Ru_3(CO)_{12}$ at 110 °C produces the mixed Mn–Ru cluster [$MnRu_3$-$(CO)_{14}(\mu_4$-S$)(\kappa^1$:η^1-thpym)] (**60**) (Ghosh et al., 2011). In contrast, reaction of **47** with $Fe_3(CO)_{12}$ at 80 °C affords two triiron clusters [$Fe_3(CO)_9(\mu_3$-S$)(\mu_3$-κ^1:η^1-$C_4H_6N_2$)] (**61**) and [$Fe_3(CO)_8(\mu_3$-S$)_2$-$(\eta^1$-$C_4H_8N_2$)] (**62**). The former is also formed from the direct reaction of thpymSH with $Fe_3(CO)_{12}$, and it reacts with H_2S to produce **62** (Scheme 12).



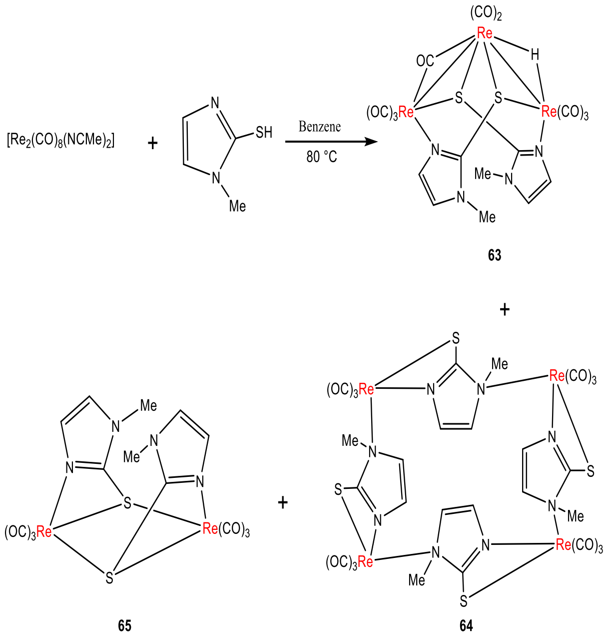
Scheme 11. Schematic representation of the reactions of $[Re_2(CO)_6(\mu\text{-thpymS})_2]$ (44) with $[Os_3(CO)_{10}(NCMe)_2]$ and $Ru_3(CO)_{12}$.



Scheme 12. Reaction of $[Mn_2(CO)_6(\mu\text{-thpymS})_2]$ (47) with group 8 trimetallic clusters

Reactivity of $[M_2(CO)_{10}]$ (M = Re, Mn) towards 2-mercapto-1-methylimidazole: Formation of di–, tri–, and tetranuclear compounds

The neutral heterocyclic thiolate ligand 2-mercapto-1-methylimidazole can also coordinate to transition metals both in the thiol and tautomeric thione form (-NH-C=S ↔ -N=C-SH). This thiol has attracted considerable attention due to its biomedical significance and use as medicinal substances (Katiyar et al., 2003). An unprecedented reaction took place when $[Re_2(CO)_8(NCMe)_2]$ was reacted with 2-mercapto-1-methylimidazole at 80 °C affording a mixture of di-, tri-, and tetrarhenium complexes $[Re_3(CO)_8(\mu\text{-}CO)(\mu_3\text{-}SN_2C_4H_5)_2(\mu\text{-}H)]$ (**63**), $[Re_4(CO)_{12}(\mu\text{-}SN_2C_4H_5)_4]$ (**64**), and $[Re_2(CO)_6(\mu\text{-}SN_2C_4H_5)_2]$ (**65**) (Ghosh et al., 2009b) (Scheme 13).



Scheme 13. Reaction of $[Re_2(CO)_8(NCMe)_2]$ with 2-mercapto-1-methylimidazole.

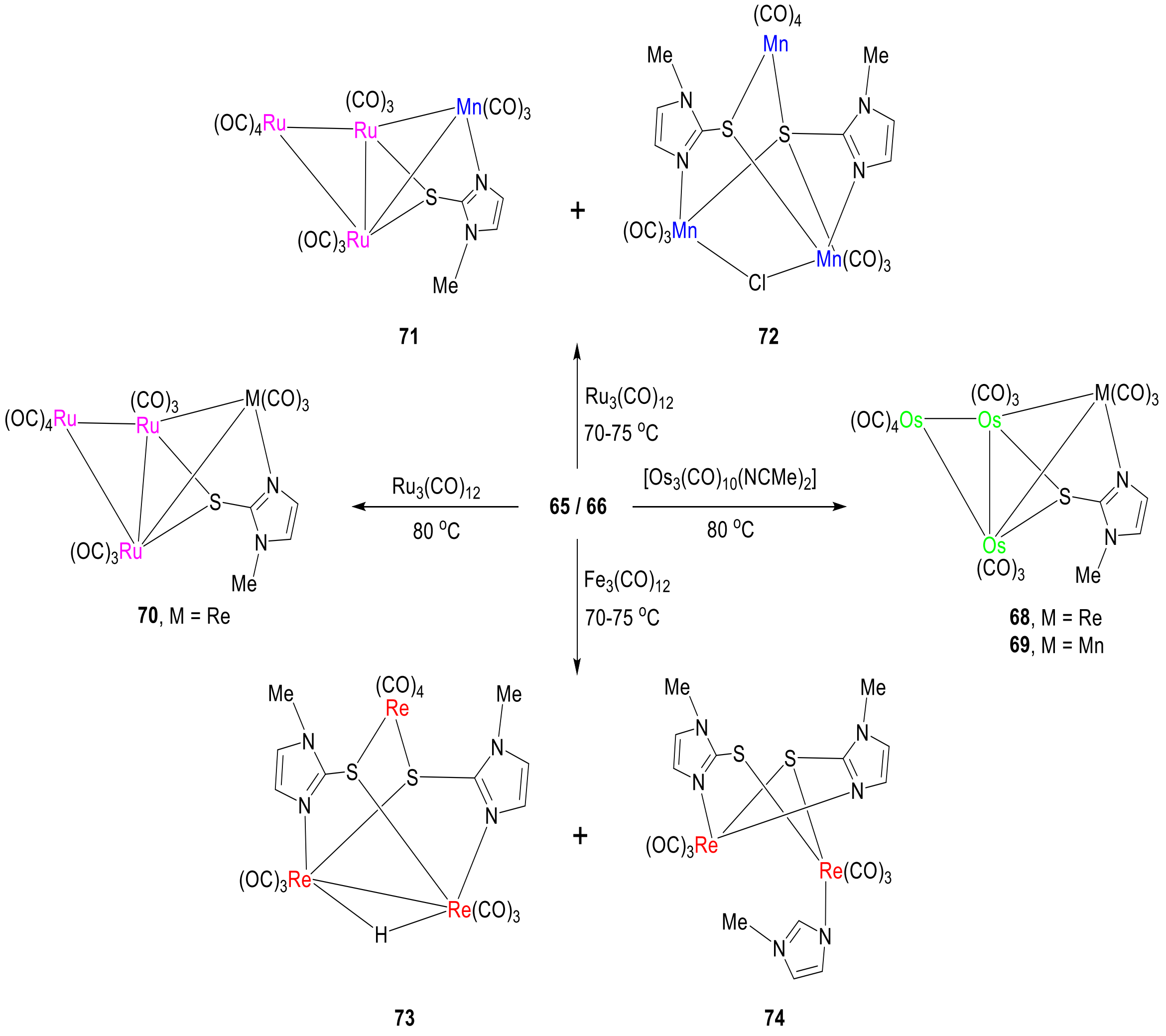
The tetranuclear **64** is isostructural with **6**, and the dinuclear **65** is a structural analog of **2**. Compound **63** provides a unique example of a bent open trirhenium cluster bearing two triply bridging 2-mercapto-1-methylimidazolate ligands, a semi-bridging CO, and a bridging hydride ligand.

In sharp contrast, two new dimeric products $[Mn_2(CO)_6(\mu\text{-}SN_2C_4H_5)_2]$ (**66**) and $[Mn_2(CO)_7(\mu\text{-}SN_2C_4H_5)_2]$ (**67**) have been obtained from the reaction of $[Mn_2(CO)_{10}]$ with 2-mercapto-1-methylimidazole in the presence of Me_3NO at 25 °C (Ghosh et al., 2009b). Both compounds are structurally characterized. Compound **66** consists of two $\mu\text{-}SN_2C_4H_5$ ligands, each of which is linked to two Mn atoms via the sulfur atom and one Mn atom via the nitrogen atom, producing a four-membered chelate ring. A comparable bonding mode to compound **66** exists in compound **67**. Still, one of the $\mu\text{-}SN_2C_4H_5$ ligands coordinates through one sulfur atom to an Mn atom and a nitrogen atom to another Mn atom. Complex **66** has also been synthesized as the sole product from the reaction of the bis-acetonitrile compound $[Mn_2(CO)_8(NCMe)_2]$ with 2-mercapto-1-methylimidazole at 80 °C.

Reactivity of $[M_2(CO)_6(\mu\text{-}SN_2C_4H_5)_2]$ (M = Re, Mn) towards $[M_3(CO)_{10}(L)_2]$ (M = Fe, Os, Ru; L = CO, NCMe)

Over the last three decades, considerable attention has been focused on the chemistry of bimetallic complexes because of their unique structural properties and various potential catalytic applications (Braunstein et al., 1995; Gade, 2000; Herberhold and Jin, 1994; Dennett et al., 2004). The group 7 metal dinuclear complexes $[M_2(CO)_6(\mu\text{-}SN_2C_4H_5)_2]$ (**65**, M = Re; **66**, M = Mn) show a moderate reactivity toward group 8 metal trinuclear carbonyl clusters (Ghosh et al., 2009c). Thus treatment of **65** and **66** with $[Os_3(CO)_{10}\text{-}(NCMe)_2]$ at 80 °C furnish the tetranuclear mixed-metal clusters $[Os_3Re(CO)_{13}(\mu_3\text{-}SN_2C_4H_5)]$ (**68**) and $[Os_3Mn(CO)_{13}(\mu_3\text{-}SN_2C_4H_5)]$ (**69**), respectively. Similar treatment of **65** and **66** with $Ru_3(CO)_{12}$ affords the ruthenium analogs $[Ru_3Re(CO)_{13}(\mu_3\text{-}SN_2C_4H_5)]$ (7**0**), and $[Ru_3Mn(CO)_{13}(\mu_3\text{-}SN_2C_4H_5)]$ (**71**), but in case of **66**, another product $[Mn_3(CO)_{10}(\mu\text{-}Cl)\text{-}(\mu_3\text{-}SN_2C_4H_5)_2]$ (**72**) has also been formed (Scheme 14). Compounds **68–71** possess a noncrystallographic mirror plane of symmetry and a butterfly-shaped core of four metal atoms, with the M (Mn or Re) located at the wingtip. This finding offers a viable strategy for synthesizing several novel group **7/8** mixed metal complexes with bifunctional heterocyclic ligands. A 54-electron trimanganese complex with bridging 2-mercapto-1-methylimidazolate and chloride ligands is only found in compound **72**, a rare instance of this type of complex. Surprisingly, treatment of 65 with $Fe_3(CO)_{12}$ at 70–75 °C afford the trirehenium and dirhenium complexes $[Re_3(CO)_{10}(\mu\text{-}H)(\mu_3\text{-}SN_2\text{-}C_4H_5)_2]$ (**73**) and $[Re_2(CO)_6(N_2C_4H_5)(\mu\text{-}SN_2C_4H_5)_2]$ (7**4**), respectively instead of the formation of the expected mixed-metal clusters. The former is an interesting example of a 52-electron trirhenium-hydride complex with a bridging 2-mercapto-1-methylimidazolate ligand, and the latter may be thought of as a 1-methylimidazole adduct of **65**. It is interesting to note that the reaction has not produced any Fe–Re mixed-metal complexes.

Reactions of **66** with group 6 metal carbonyls such as $[Cr(CO)_3(NCMe)_3]$ and $[Mo(CO)_3(NCMe)_3]$ in boiling THF produced the mixed-metal clusters $[CrMn_2(CO)_8(\mu\text{-}CO)_2(\mu_3\text{-}SN_2C_4H_5)_2]$ (**75**) and $[MoMn_2(CO)_8(\mu\text{-}CO)_2(\mu_3\text{-}SN_2C_4H_5)_2]$(76), respectively, in which two Mn–M (M = Mo, Cr) bonds were created (Ghosh et al., 2009b). In contrast, an analogous reaction of $[W(CO)_3(NCMe)_3]$ with **66** affords two W–Mn clusters $[Mn_2W(CO)_8(\mu\text{-}CO)_2(\mu_3\text{-}SN_2C_4H_5)_2]$ (**77**) and $[Mn_2W(CO)_7(\mu\text{-}CO)_2(SN_2\text{-}C_4H_5)(\mu_3\text{-}SN_2\text{-}C_4H_5)_2]$ (**78**). The reaction of **66** with $[Fe_3(CO)_{12}]$ at 70–75 °C yields the mixed-metal cluster $[FeMn_2(CO)_8(\mu\text{-}CO)(\mu_3\text{-}SN_2C_4H_5)_2]$ (**79**) and the by-product $[Fe_2(CO)_6(\mu\text{-}S_2N_2C_4H_5)_2]$ (**80**) (Scheme 15). All compounds, except **78** and **79**, have a noncrystallographic two-fold axis of symmetry. Compounds **75–79** have a bent open structure composed of three metal atoms connected by two



Scheme 14. Reactions of [$M_2(CO)_6(\mu\text{-}SN_2C_4H_5)_2$] (65, M = Re; 66, M = Mn) with group 8 trimetallic carbonyls.

metal-metal bonds. Structure-wise, compound 78 is identical to compound 77, except it has an Mn–Mn bond rather than an Mn–W bond and an $SN_2C_4H_6$ ligand mono coordinated through the exocyclic sulfur atom to the W atom.Two bridging $S_2N_2C_4H_5$ ligands, produced by combining 2-mercapto-1-methylimidazole with sulfur, make up compound 80. Compound 79 provides an unusual example of a Mn_2Fe trimetallic cluster with two Fe–Mn bonds.

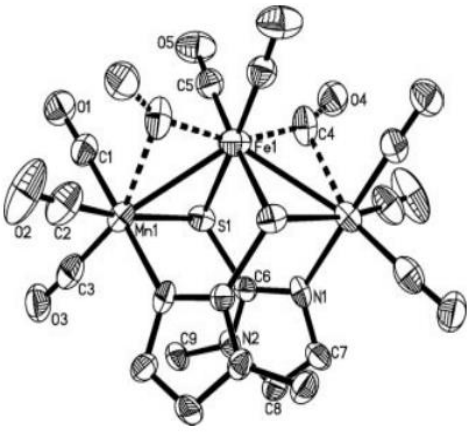
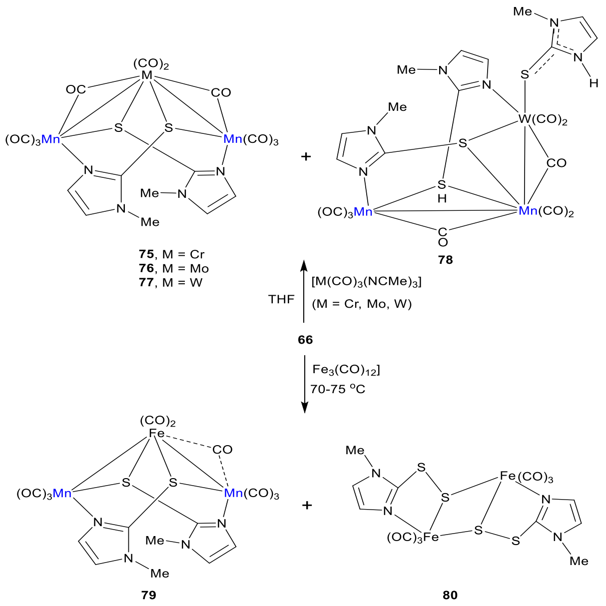


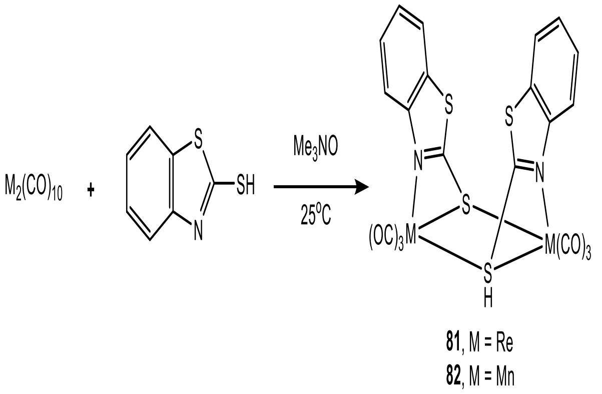
Fig. 4. The solid-state structure of [$FeMn_2(CO)_8(\mu\text{-}CO)(\mu_3\text{-}SN_2C_4H_5)_2$] (79).



Scheme 15. Reactions of $[Mn_2(CO)_6(\mu\text{-}SN_2C_4H_5)_2]$ (66) with $Fe_3(CO)_{12}$ and $[M_3(CO)_3(NCMe)]$ (M = Cr, Mo, W).

Reactions of $[M_2(CO)_{10}]$ (M = Re, Mn) with 2-mercaptobenzothazole-2-thiol (MBTH) and 2-mercaptobenzooxazol.

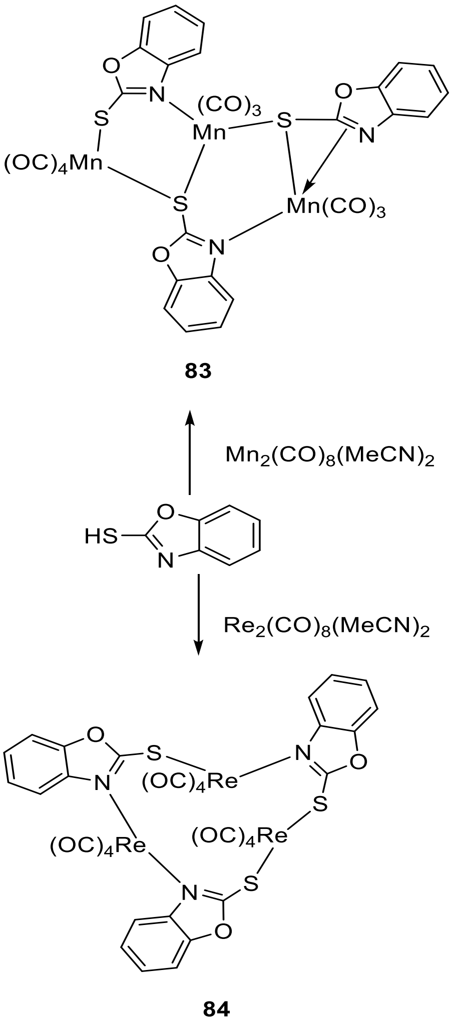
Following a method analogous to that reported by Kabir and co-workers for the synthesis of $[Mn_2(CO)_6(\mu\text{-}pyS)_2]$ (Kabir et al., 1996), compound $[Re_2(CO)_6(\mu\text{-}MBT)_2]$ (**81**) has been synthesized from the Me_3NO-mediated reaction of $Re_2(CO)_{10}$ with 2-mercaptobenzothiazole at room temperature (Ghosh et al., 2010b). The complex has a chiral structure with C_2 symmetry being similar to that of previously reported for compound $[Re_2(CO)_6(\mu\text{-}pyS)_2]$ (Deeming et al., 1988b). Each 2-mercaptobenzothiazolate ligand forms a four-membered chelate ring by coordinating with one metal atom, while the sulfur serves as a bridge between the ligand and the dirhenium core. On the other hand, a reaction between $Mn_2(CO)_{10}$ and 2-mercaptobenzothiazole in the presence of Me_3NO at 25 °C gives the dimanganese complex $[Mn_2(CO)_6(\mu\text{-}MBT)_2]$ (**82**) (Scheme 16) (Ghosh et al., 2012). In **82**, two manganese atoms are arranged in a dinuclear framework that is held together by two MBT ligands, six carbonyls, and two other atoms. Three carbonyls that are organized in a face pattern are linked to each manganese atom. Both MBT ligands bind with a single manganese atom through the nitrogen atom and create a bridge between the manganese atoms, forming four-membered chelate rings.



Scheme 16. Reactivity of $[M_2(CO)_{10}]$ (M = Re, Mn) towards MBTH.

Hoque and co-workers carried out analogous reactions of 2-mercaptobenzoxazol with $[Mn(CO)_8(NCMe)_2]$ and observed the unexpected formation of trimanganese cluster $[Mn_3(CO)_{10}(\mu\text{-}SCNOC_6H_4)_3]$ (**83**), which has been structurally characterized. The most striking feature of 83 is three different binding modes (A–C) of 2-mercaptobenzoxazolate (Chart 6) in one molecule. Bonding modes A–B has been found in other complexes (Brodie et al., 1983; Brodie et al., 1986; Wang et al., 2012), while C is found in **83**. Ligand A formally acts as a 3-electron donor, while B and C are 5-electron donors. Thus cluster 83 has a VEC of 54 electrons, consistent with the absence of any direct metal-metal interaction.

A similar reaction of 2-mercaptobenzoxazol with $Re_2(CO)_8(NCMe)_2$ also resulted in the isolation of a trinuclear product, namely $[Re_3(CO)_{12}(\mu\text{-}SCNOC_6H_4)_3]$ (**84**). The solid-state structure determination **84** confirms that each 2-mercaptobenzoxazolate ligand is of type A (Chart 7), spanning $Re(CO)_4$ centers through nitrogen and sulfur atoms. Since each 2-mercaptobenzoxazolate ligand is a 3-electron donor, cluster **84** also has a VEC of 54 electrons.



Scheme 17. Reactivity of [$M_2(CO)_8(NCMe)_2$] (M = Re, Mn) towards 2-mercaptobenzooxazol.

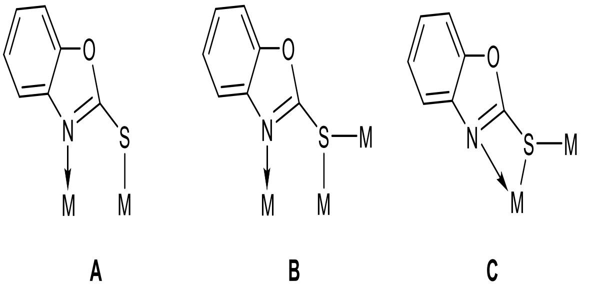
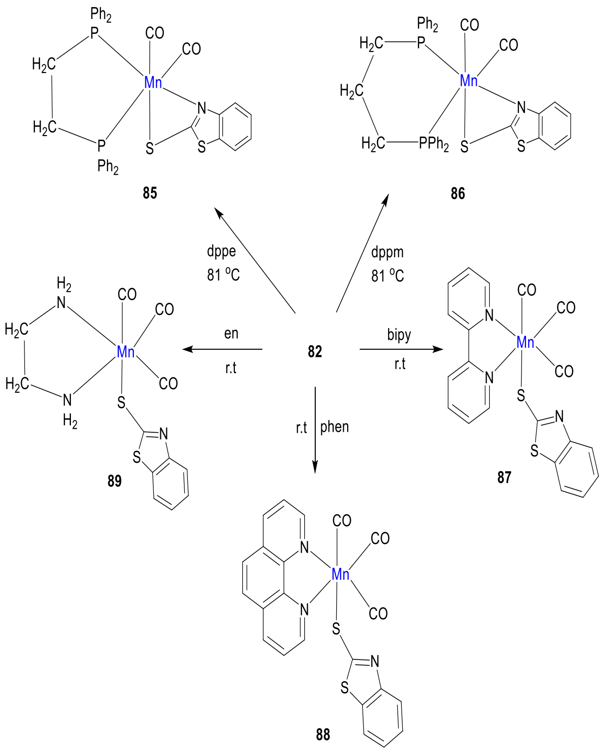


Chart 7. Three different coordination modes of 2-mercaptobenzoxazol.

Reactivity of [$Mn_2(CO)_6(\mu\text{-MBT})_2$] (82) towards mono– and bidentate ligands

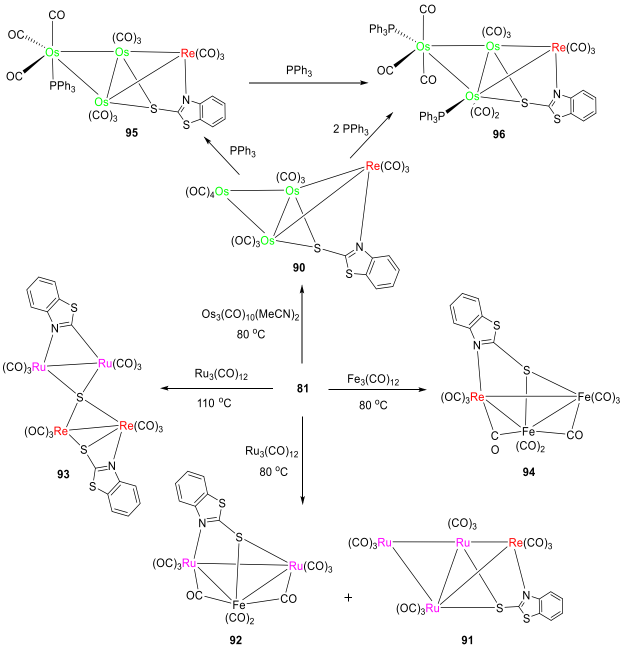
Compound **82**, in turn, acts as a useful precursor to mononuclear complexes upon the addition of diphosphines and diamines. Thus reactions of **82** with 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) in cyclohexane at boiling temperature furnish cis-[$Mn(CO)_2(\kappa^2\text{-MBT})(\kappa^2\text{-dppe})$] (**85**) and cis-[$Mn(CO)_2(\kappa^2\text{-MBT})(\kappa^2\text{-dppp})$] (**86**), respectively which have been crystallographically characterized (Ghosh et al., 2012). As predicted for an octahedral compound with two carbonyl ligands in the cis orientation, 85 and 86 show two absorption bands in the carbonyl stretching region in the infrared spectra. Molecule 85 comprises a single manganese atom coordinated by two terminal carbonyls, a dppe, and MBT ligands. The carbonyls are in the cis position in relation to one another, and the MBT and diphosphine form chelates with manganese. Under the assumption that the MBT ligand acts as a 3-electron donor, complexes 85 and 86 are 18-electron species. Again, the reactions of 82 with diamines, e.g., 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and ethylenediamine (en) at room temperature afford fac-[$Mn(CO)_3(\kappa^1\text{-MBT})(\kappa^2\text{-bipy})$] (**87**), fac-[$Mn(CO)_3(\kappa^1\text{-MBT})(\kappa^2\text{-phen})$] (**88**) and fac-[$Mn(CO)_3(\kappa^1\text{-MBT})(\kappa^2\text{-en})$] (**89**), respectively (Scheme 18) (Ghosh et al., 2012).



Scheme 18. Reactivity of [$Mn_2(CO)_6(\mu\text{-MBT})_2$] (82) towards bidentate ligands.

Reactivity of $[M_2(CO)_6(\mu\text{-MBT})_2]$ (81, M = Re; 82, M = Mn)) towards the trinuclear clusters $[M_3(CO)_{10}(L)_2]$ (M = Fe, Os, Ru; L = CO, NCMe)

The group 8 trimetallic carbonyl clusters show reactivity towards dirhenium compound $[Re_2(CO)_6(\mu\text{-}S_2NC_7H_4)_2]$ (**81**) to afford new tri- and tetranuclear mixed-metal clusters (Ghosh et al., 2010b). $[Os_3(CO)_{10}(NCMe)_2]$ reacts with 81 in refluxing benzene to yield the tetranuclear mixed-metal cluster $[Os_3Re(CO)_{13}(\mu_3\text{-}C_7H_4NS_2)]$ (**90**) (Scheme 18) as the sole product. Interestingly, for $Ru_3(CO)_{12,}$ the reaction products are temperature dependent. At 80 °C, $[Ru_3Re(CO)_{13}(\mu_3\text{-MBT})]$ (**91**) and $Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-MBT})]$ (**92**) are formed, while at 110 °C a completely different tetranuclear mixed-metal cluster (93), is formed resulting from C-S bond cleavage. On the other hand, the reaction of **81** with $Fe_3(CO_{12}$ at 80 °C affords 94. The reactivity of **94** (Scheme 19) with PPh_3 in the presence of Me_3NO at 25 °C results in ligand substitution to furnish mono- and disubstituted derivatives $[Os_3Re(CO)_{12}(PPh_3)(\mu_3\text{-MBT})]$ (**95**) and $[Os_3Re(CO)_{11}(PPh_3)_2(\mu_3\text{-MBT})]$ (**96**). In **95**, the PPh_3 ligand is located at an axial position on the wingtip osmium. In contrast, in **91**, one PPh_3 ligand is equatorially coordinated to the wingtip osmium, and the other is bound to the hinge osmium.



Scheme 19. Reactions of $[Re_2(CO)_6(\mu\text{-}S_2NC_7H_4)_2]$ (81) with M3(CO)12 different metal carbonyls.

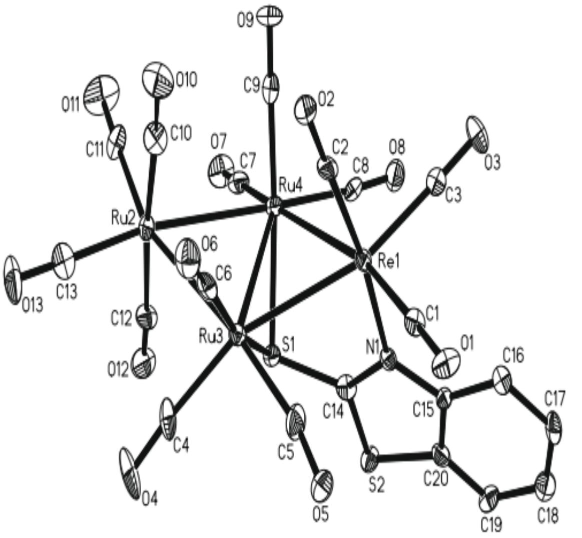


Fig. 5. The ORTEP structure of $[Ru_3Re(CO)_{13}(\mu_3\text{-MBT})]$ (91).

Concluding remarks

It is clear from this review that many rhenium and manganese carbonyl complexes bearing heterocyclic thiolate ligands are reported. These compounds range from mononuclear to tetranuclear. Moderate to high yielding synthetic routes to binuclear $[M_2(CO)_6(\mu\text{-}L)_2]$ and the tetranuclear square-type complexes $[M_4(CO)_{12}(\mu\text{-}L)_4]$ (L = pyridine-2-thiolato, pyrimidine-2-thiolato, tetrahydropyrimidine-2-thiolato, 2-mercapto-1-methyl- imidazolato, 2-mercapto-benzothiolate, etc. as appropriate) are described. These compounds contain labile M-S bonds which make them excellent sources of the 16-electron mononuclear species $[M(CO)_3(\kappa^2\text{-}L)]$ in solution. The further reactivity of the resultant $[M(CO)_3(\kappa^2\text{-}L)]$ species with various mono and bidentate ligands reveals that they are versatile precursors for mononuclear products of differing coordination of the $M(CO)_3(L)$ fragments. The lability of the M-S bonds makes these di and tetranuclear complexes excellent precursors for the synthesis of two isostructural series of mixed-metal cluster complexes, namely $[MM'_3(CO)_{13}(\mu_3\text{-}L)]$ (M = Re, Mn; M′ = Ru, Os) and $[MM''_2(CO)_{10}(\mu_3\text{-}L)]$ (M = Re, Mn; M′′= Mo, Cr, W). The trinuclear mixed-metal clusters consist of an open structure of two rhenium or manganese atoms and a third metal atom, M (M = W, Mo, Cr), connected by two M−Re/Mn bonds, two triply bonded thiolato ligands, and two asymmetrically bound μ-CO ligands.

In contrast, the tetranuclear mixed-metal clusters consist of a butterfly skeleton of four metal atoms, with the unique metal atom occupying wingtip positions. A notable feature is that the reactivity Fe3(CO)12 reactivitytowards the synthesis of mixed-metal clusters is quite different from those of its heavier congeners. In the case of their group 7 metal carbonyl chemistry, although most of the heterocyclic thiols share a common reactivity trait, in some cases, their outcome is completely different.

Acknowledgments

One of us (SEK) gratefully acknowledges the University Grants Commission Bangladesh for the award of a UGC Professorship and Jagannath University for support.

Conflicts of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this review.

References

Adams RD and Barnard TS. Does a metal to metal “ligand” effect influence the catalytic activity of bimetallic cluster complexes? Synthesis and catalytic activity of $\mathrm{Pt_3Ru_6(CO)_{19}(SMe_2)(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)}$. *Organometallics* 1998b; 17: 2885-2890.

Adams RD and Cotton FA (eds.). *Catalysis by Di– and Polynuclear Metal Cluster Complexes* Wiley-VCH, Newyork 1998a.

Ahmad MF, Sarker JC, Azam KA, Kabir SE, Ghosh S, Hogarth G, Siddiquee TA, and Richmond MG. $\mathrm{Re_2(CO)_6(\mu\text{-}thpymS)_2}$ (thpymSH = tetrahydropyrimidine-2-thiol) as a versatile precursor to mono– and polynuclear complexes: X-Ray crystal structures of *fac*-$\mathrm{Re(CO)_3(PPh_3)(\kappa^2\text{-}thpymS)}$ and two isomers of $\mathrm{ReRu_3(CO)_{13}(\mu_3\text{-}thpymS)}$. *J. Organomet. Chem.* 2013; 728: 30-37.

Azam K, Hursthouse M, Hussain S, Kabir S, Malik K, Rahman M, and Rosenberg E. Triosmium clusters containing thiazolide ligand: Crystal structures of $\mathrm{[(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}3,4\text{-}\eta^2\text{-}HC{=}NC{=}CHS)]}$ and $\mathrm{[(\mu\text{-}H)Os_3(CO)_9(\mu\text{-}3,4\text{-}\eta^2\text{-}HC{=}NC{=}CHS)(PPh_3)]}$. *J. Organomet. Chem.* 1998a; 559: 81-89.

Azam KA, Dilshad R, Kabir SE, Khatoon K, Nessa L, Rahman MM, Rosenberg E, Hursthouse MB, Malik KMA, and Deeming AJ. Triosmium and triruthenium clusters containing the 4-methylthiazolide ligand: Crystal structures of $\mathrm{[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}2,3\text{-}\eta^2\text{-}CNC\text{-}MeCHS)]}$, $\mathrm{[Os_3\text{-}(\mu\text{-}H)(CO)_9(\mu\text{-}2,3\text{-}\eta^2\text{-}CNCMeCHS)(PPh_3)]}$ and $\mathrm{[Os_3(\mu\text{-}H)(CO)_8(\mu\text{-}2,3\text{-}\eta^2\text{-}CNCMe\text{-}HS)(PPh_3)_2]}$. *J. Chem. Soc., Dalton Trans.*1996: 1731-1739.

Azam KA, Hursthouse MB, Kabir SE, Malik KA, Tesmer M, and Vahrenkamp H. A novel pentaruthenium cluster containing three thiazole derived ligands; X-xay structure of $\mathrm{[Ru_3(CO)_9(\mu\text{-}H)(\mu_5\text{-}\eta^5\text{-}HC\text{-}NC\text{-}CHS)Ru_2(CO)_4\text{-}(\mu\text{-}H)(\eta^1\text{-}HC{=}NCH{=}CHS)(\mu\text{-}2,3\text{-}\eta^3\text{-}C{=}\ NCH{=}\ CHS)]}$. *Inorg. Chem. Commun.* 1998b; **1**: 402-404.

Begum N, Kabir SE, Hossain GMG, Rahman AM, and Rosenberg E. Investigations of pyridine-2-thiol as a ligand: Synthesis and X-ray structures of the mixed Mo–Mn dinuclear complex $\mathrm{CpMoMn(CO)_3(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}pyS)(\mu\text{-}\eta^1\text{-}pyS)}$, the electron-deficient trimolybdenum cluster $\mathrm{Cp_3Mo_3(\mu\text{-}CO)_2(\mu\text{-}S)(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}NC_5H_4)}$, and the mononuclear $\mathrm{CpMo(CO)_2(\mu\text{-}\eta^2\text{-}pyS)}$. *Organometallics* 2005; 24: 266-271.

Berardini M and Brennan J. Europium pyridinethiolates: Synthesis, structure, and thermolysis. *Inorg. Chem.* 1995; 34: 6179-6185.

Beuken van den EK, Feringa BI. Bimetallic catalysis by late transition metal complexes. Tetrahedron 1998; 54: 12985.

Braunstein P and Rosé J. 7– Catalysis and related reactions with compounds containing heteronuclear metal–metal bonds. *Comprehensive Organometallic Chemistry* (1995) pp. 351-385.

Braunstein P and Rosé J., in Metal Clusters in Catalysis, ed. P. Braunstein, L. A. Oro and P. R. Raithby, Wiley-VCH, Weinheim, Germany, 1999, vol. 2, pp. 616.

Brodie AM, Holden HD, Lewis J and Taylor MJ. The interaction of heterocyclic thioamides with triosmium clusters: the X-ray crystal structure of $\mathrm{(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}SC{=}NCH_2CH_2S)}$. *J. Organomet. Chem.* 1983; 253**:** C1-C4.

Brodie AM, Holden HD, Lewis J and Taylor MJ. The reaction of $\mathrm{[Os_3(CO)_{10}(MeCN)_2]}$ with heterocyclic thioamides. The crystal and molecular structure of $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}SC{=}NCH_2CH_2S)$. *J. Chem. Soc., Dalton Trans.* 1986; 633-639.

Broussard ME, Juma B, Train SG, Peng W-J, Laneman SA, and Stanley GG. A bimetallic hydroformylation catalyst: High regioselectivity and reactivity through homobimetallic cooperativity. *Science* 1993; 260: 1784-1788.

Castro R, Durán ML, García-Vázquez JA, Romero J, Sousa A, Castiñeiras A, Hiller W, and Strähle J. Direct electrochemical synthesis of pyridine-2-thionato complexes of nickel (II): The crystal structure of (2,2′-bipyridine)bis(pyridine-2-thionato)nickel(II)-2,2′-bipyridine. *J. Chem. Soc. Dalton Trans.*1990: 531–534.

Cheng Y, Emge T, and Brennan J. Pyridineselenolate complexes of tin and lead: $Sn(2\text{-}SeNC_5H_4)_2$, $Sn(2\text{-}SeNC_5H_4)_4$, $Pb(2\text{-}SeNC_5H_4)_2$, and $Pb(3\text{-}Me_3Si\text{-}2\text{-}SeNC_5H_3)_2$. Volatile CVD precursors to group IV−group VI semiconductors. *Inorg. Chem*. 1996; 35: 342-346.

Cockerton B, Deeming AJ, Karim M, and Hardcastle KI. Mixed tetranuclear rhenium–ruthenium compounds formed by carbon–sulphur bond cleavage in reactions of $[Re_2(pyS)_2(CO)_6]$ (pyS = pyridine-2-thionate) with $[Ru_3(CO)_{12}]$. Crystal structures of $[ReRu_3(\mu_4\text{-}S)(\mu\text{-}C_5\text{-}H_4N)(CO)_{14}]$ and $[Re_2Ru_2(\mu\text{-}S)(\mu\text{-}C_5H_4N)(\mu\text{-}pyS)(CO)_{13}]$. *J. Chem. Soc., Dalton Trans.* 1991; 431-437.

Deeming AJ, Karim M, Bates PA, and Hursthouse MB. A new type of pyridine-2-thionato bridge: X-ray crystal structure of the complex $[Re_2(Mepys)_2(CO)_6]$ where MepyS is the 6-methylpyridine-2-thionato ligand. *Polyhedron* 1988b; 7: 1401-1403.

Deeming AJ, Karim M, Bates PA, and Hursthouse MB.Di- and tri-nuclear complexes of palladium(II) containing doubly- and triply-bridging pyridine-2-thionato (pyS) ligands: Crystal structure of $[Pd_3(C_6H_4CH_2NMe_2)_3(pyS)_2][BF_4]$. *J. Chem. Soc., Dalton Trans* 1988a; 2193-2199.

Deeming AJ, Hardcastle KI and Karim M. Suppression of cluster unsaturation by formation of extensive but long-range metal-metal bonding: crystal structures of $[Ru_3H\text{-}(pyS)(CO)_9]$ and $[\{Ru_3H(pyS)\ (CO)_7\}_3]$, where pyS Is the pyridine-2-thiolato ligand. *Inorg. Chem*. 1992; 31: 4792-4796.

Dennett JN, Jacke J, Nilsson G, Rosborough A, Ferguson MJ, Wang M, McDonald R, and Takats J. Alkene carbon−hydrogen bond activation at a heterobimetallic center: $[RuCo(CO)_3(\mu\text{-}CO)(\eta\text{-}C_5Me_5)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C(CF_3)\text{-}C(CF_3)\}]$. *Organometallics* 2004; 23: 4478-4485.

Dilshad R, Hanif KM, Hursthouse MB, Kabir SE, Malik KA, and Rosenberg E. Triruthenium clusters derived from the reactions of $[Ru_3(CO)_{12}]$ with benzothiazole, pyrimidine-2-thione and benzimidazole-2-thione; X-Ray structures of $[Ru_3(\mu\text{-}H)(\mu\text{-}2,3\text{-}\eta^2\text{-}NSC_7H_4)(CO)_{10}]$ and $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}SN_2C_4H_3)(CO)_9]$. *J. Organomet. Chem.*1999; 585: 100-105.

Fujita M, Ibukuro F, Seki H, Kamo O, Imanari M, and Ogura K. Catenane formation from two molecular rings through very rapid slippage. A möbius strip mechanism. *J. Am. Chem. Soc.* 1996; 118: 899-900.

Fujita M, Yazaki J, and Ogura K. Preparation of a macrocyclic polynuclear complex, $[(en)Pd(4,\ 4'\text{-}bpy)]_4(NO_3)_8$ (en = ethylenediamine, bpy = bipyridine), which recognizes an organic molecule in aqueous media. *J. Am. Chem. Soc.* 1990; 112: 5645-5647.

Fusi A, Ugo R, Psaro R, Braunstein P, and Dehand J. Homogeneous catalysis with transition metal complexes. Part VII: Heteronuclear platinum clusters as hydrogenation catalysts of carbon–carbon multiple bonds. *J. Mol. Catal.* 1982; 16: 217-230.

Gade LH. Highly polar metal–metal bonds in “early-late” heterodimetallic complexes. *Angew. Chem., Int. Ed. Engl.* 2000; 39: 2658-2678.

Gauther S, Scopelliti R, and Severin K. A Heterobimetallic Rhodium (I)- Ruthenium (II) Catalyst for the Oppenauer-Type Oxidation of Primary and Secondary Alcohols under Mild Conditions. *Organometallics* 2004; 23: 3769-3771.

Ghosh S, Ahmed F, Al-Mamun R, Haworth DT, Lindeman SV, Siddiquee TA, Bennett DW, and Kabir SE. Investigations of 2-thiazoline-2-thiol as a ligand: Synthesis and X-ray structures of $[Mn_2(CO)_7(\mu\text{-}NS_2C_3H_4)_2]$ and $[Mn(CO)_3(PPh_3)\text{-}$

$(\kappa^2\text{-}NS_2C_3H_4)]$. *J. Chem. Crystallogr.* 2009a; 39: 595-602.

Ghosh S, Camellia FK, Fatema K, Hossain MI, Al-Mamun MR, Hossain GMG, Hogarth G and Kabir SE. Centrosymmetric $[Mn_2(CO)_6(\mu\text{-thpymS})_2]$ (thpymS = tetrahydropyrimidine-2-thionato) as a synthon to mixed–metal clusters. *J. Organomet. Chem.* 2011; 696: 2935-2942.

Ghosh S, Kabir SE, Pervin S, Hossain GMG, Haworth DT, Lindeman SV, Siddiquee TA, Bennett DW, and Roesky HW. New mixed-metal carbonyl complexes containing bridging 2-mcapto-1-methylimidazole ligand. *Z. Anorg. Allg. Chem.* 2009b; 635: 76-87.

Ghosh S, Kabir SE, Pervin S, Raha AK, Hossain GMG, Haworth DT, Lindeman SV, Bennett DW, Siddiquee TA, and Salassa L. Tetranuclear group 7/8 mixed-metal and open trinuclear group 7 metal carbonyl clusters bearing bridging 2-mercapto-1-methylimidazole ligands. *Dalton Trans.*2009c: 3510-3518.

Ghosh S, Khanam KN, Hossain GMG, Haworth DT, Lindeman SV, Hogarth G and Kabir SE. The rational synthesis of tetranuclear heterometallic butterfly clusters: Reactions of $[M_2(CO)_6(\text{-pyS})_2]$ (M = Re, Mn) with Group VIII metal carbonyls. *New J. Chem*. 2010a; 34: 1875-1884.

Ghosh S, Khanam KN, Hossain MK, Hossain GMG, Haworth DT, Lindeman SV, Hogarth G, and Kabir SE. Mixed-metal cluster synthesis: $[Re(CO)_3(\mu\text{-}S_2NC_7H_4)]_2$ as a precursor for tri- and tetranuclear 2-mercaptobenzothiolato capped clusters. *J. Organomet. Chem.* 2010b; 695: 1146-1154.

Ghosh S, MA Mia, E Begum, GG Hossain, and SE Kabir. Synthesis, structure and reactivity of $[Mn_2(CO)_6(\mu\text{-MBT})_2]$ (MBT = 2-mercaptobenzothiazolato): A Versatile precursor for mono- and polynuclear compounds. *Inorg. Chim. Acta* 2012; 384: 76-82.

Hanif KM, Hursthouse MB, Kabir SE, and Malik KMA, Rosenberg E. Ring-opening reactions of thiomorpholine and thiazolidine by $[Ru_3(CO)_{12}]$: Crystal structures of $[Ru_3(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}SCH_2CH_2\text{-}NH_2)(CO)_9]$ and $[Ru_2(\mu\text{-}\eta^3\text{-}SCH_2CH_2NHCH_2)(CO)_6]$. *J. Organomet. Chem.* 1999; 580: 60-65.

Herberhold M and Jin GX. Heterodimetallic complexes with an unbridged, polar metal–metal bond. *Angew. Chem., Int. Ed. Engl.*1994; 33: 964-966.

Hoque A, Islam S, Karim M, Ghosh S and Hogarth G. Variations in binding modes of 2-mercaptobenzoxazolates in the novel cyclic trinuclear complexes $[Mn_3(CO)_{10}(\mu\text{-}SCNO\text{-}C_6H_4)_3]$ and $[Re_3(CO)_{12}(\mu\text{-}SCNOC_6H_4)_3$. *Inorg. Chem. commun.* 2015; 54: 69-72.

Kabir S, Alam J, Ghosh S, Kundu K, Hogarth G, Tocher DA, Hossain GMG, and Roesky HW. *Dalton Trans.* 2009; 4458-4467.

Kabir SE, Ahmed F, Das A, Hassan MR, Haworth DT, Lindeman SV, Hossain GMG, Siddiquee TA, and Bennett DW. Reactivity of $[Re_2(CO)_8(NCMe)_2]$ with thiazoles: Hydrido bridged dirhenium compounds bearing thiazoles in different coordination modes. *J. Organomet. Chem.* 2007; 692: 4337-4345.

Kabir SE, Karim MM, Kundu K, Ullah SB, and Hardcastle KI. Some pyridine-2-thiolato and 6-methylpyridine-2-thiolato complexes of manganese: Crystal structure of $[Mn_2(\mu\text{-pyS})_2(CO)_6]$ (pyS = pyridine-2-thiolato ligand). *J. Organomet. Chem.*1996; 517: 155-159.

Kabir SE, Malik KA, Molla E, and Mottalib MA. Reactivity of $[(\mu\text{-}H)Os_3(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ with organic heterothiols: X-ray structures of $[H((\mu\text{-}H)Os_3(CO)_8(\eta^2\text{-pyS})\{Ph_2P\text{-}CH_2P(Ph)C_6H_4\}]$ and $[Os_3(CO)_8(\mu\text{-}\eta^2\text{-pyS})\{Ph_2\text{-}PCH_2P(Ph)C_6H_4\}]$. *J. Organomet. Chem.* 2000; 616: 157-164.

Kalck P. Cooperative effect between two metal centres in hydroformylation: Routes towards heterobimetallic catalysis. *Polyhedron* 1988; 7: 2441-2450.

Katiyar D, Tiwari VK, Tripathi RP, Srivastava A, Chaturvedi V, R. Srivastava, Srivastava BS. Synthesis and antimycobacterial activity of 3,5-disubstituted thiadiazine thiones. *Bioorg. Med. Chem.* 2003; 11:4369-4375.

Kienitz CO, Thöne C, and Jones PG. Coordination chemistry of 2, 2 ‘-dipyridyl diselenide: X-ray crystal structures of pysesepy, $[Zn(pySe\text{-}Sepy)Cl_2]$,$[(pySeSepy)Hg(C_6F_5)_2]$, $[Mo(Sepy)_2(CO)_3]$, $[W(Sepy)_2(CO)_3]$, and $[Fe(Sepy)_2\text{-}(CO)_2]$(pySeSepy = $C_5H_4NSeSeC_5H_4N$; Sepy = $[C_5H_4N(2\text{-}Se)N,Se]$). *Inorg. Chem.* 1996; 35: 3990-3997.

Lee J, Emge T, and Brennan J. Heterometallic lanthanide-group 14 metal chalcogenolates. *Inorg. Chem.* 1997; 36: 5064-5068.

Liaw W-Fe, Chen C-H, Lee G-H, and Peng S-M. Iron pyridine-2-thiolate complexes: Interconversion of $[Fe^0(CO)_4(SC_5H_4N)]^-$, *cis*-$[Fe^{II}(CO)_2(SC_5H_4N)_2]$, and $[Fe^{II}$ $(SC_5H_4N)_2]$ $^-$ Organometallics, 1998; 17: 2370.

Moni MR, Ghosh S, Mobin SM, Tocher DA, Hogarth G, Richmond MG, and Kabir SE. Diphosphine-induced thiolate-bridge scission of $[Re(CO)_3(\mu\text{-}k^2\text{-}S,N\text{-}thpymS)]_2$ (thpymS = 1,4,5,6-tetrahydropyrimidine-2-thiolate): Structural and computational studies of configurational isomers of $[Re(CO)_3(k^2\text{-}S,N\text{-}thpymS)]_2(\mu\text{-}k^1, k^1\text{-}dppe)]$, *J. Organomet. Chem.* 2018; 871**:** 167-177.

Muetterties E, Rhodin T, Band E, Brucker C, and Pretzer W. Clusters and Surfaces. *Chem. Rev.*1979; 79**:** 91-137.

Muetterties E. Molecular metal clusters: Cluster chemistry may provide valuable Insights to Chemisorption and Catalysis on Surfaces. *Science* 1977; 196: 839-848.

Neumann HP and Ziegler ML. μ_3-Arsenic trimolybdenum clusters with oxygen and sulphur bridging the transition metals. *J. Chem. Soc., Chem. Commun*. 1988: 498-500.

Quebatte L, Scoppelliti R, and Severin K. Combinatorial catalysis with bimetallic complexes: robust and efficient catalysts for atom-transfer radical additions.*Angew. Chem., Int. Ed.* 2004; 43: 1520-1524.

Rahman MdS, Sarker JC, Ghosh S, and Kabir SE. The first carbonyl substituted derivative of $[Mn_2(CO)_6$ $(\mu\text{-}pyS)_2$ $(CO)_6]$. *Aust. J. Chem.* 2012; 65: 796-801.

Rose DJ, Chang Y-D, Chen Q, and Zubieta JReactions of uranyl thiolate complexes with molecular oxygen: Syntheses and crystal and molecular structures of the uranyl thiolate peroxo species $(HNEt_3)_2[(UO_2)_2(O_2)(SC_4N_2H_3)_4]$ and $(HNEt_3)[H(UO_2)_2(O_2)(SC_4N_2H_2Me)_4]\cdot Me_2CO\cdot 0.5Et_3N$ and of the uranyl thiolate oxo cluster $(HNEt_3)_2[(UO_2)_4(O)_2(SC_5NH_4)_6]\cdot Me_2CO$. *Inorg. Chem.* 1994; 33: 5167-5168.

Rose DJ, Chang YD, Chen Q, Kettler PB, and Zubieta J. Synthesis and characterization of Gallium and Indium thiolate Complexes. Crystal and Molecular Structures of $[M(SC_5H_4N)_3]$(M = Ga, In), $[In(SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$, and $[M_2(OC_2H_4)_2(SC_5H_4N)_4]$ (M = Ga, In). *Inorg. Chem.* 1995; 34: 3973-3979.

Rosenfield SG, Berends HP, Gelmini L, Stephan DW, and Mascharak PK. New octahedral thiolato complexes of divalent nickel: Syntheses, structures, and properties of $(Et_4N)[Ni(SC_5H_4N)_3]$ and $(Ph_4P)[Ni(SC_4H_3N_2)_3].CH_3CN$. *Inorg. Chem.* 1987; 26: 2792-2797.

Stang PJ and Cao DH. Transition metal based cationic molecular boxes. Self-assembly of macrocyclic platinum (II) and palladium (II) tetranuclear complexes. *J. Am. Chem. Soc.* 1994a; 116: 498-4982.

Stang PJ and Olenyuk B. Directed self-assembly of chiral, optically active macrocyclic tetranuclear molecular squares. *Angew. Chem., Int. Ed. Engl.* 1996a; 35: 732-736.

Stang PJ and Whiteford JA. Mixed, neutral-charged, platinum-platinum and platinum-palladium macrocyclic tetranuclear complexes. *Organometallics* 1994b; 13: 3776-3777.

Stang PJ, Cao DH, Saito S, and Arif AM. Self-assembly of cationic, tetranuclear, Pt (II) and Pd (II) macrocyclic squares. X-ray crystal structure of $[Pt^{2+}(dppp)(4,4'\text{-}bipyridyl)^{2-}OSO_2CF_3]_4$. *J. Am. Chem. Soc.* 1995; 117: 6273-6283.

Stang PJ, Olenyuk B, Fan J, and Arif AM. Combining ferrocenes and molecular squares: Self- assembly of heterobimetallic macrocyclic squares incorporating mixed transition metal systems and a main group element. Single-crystal X-ray structure of $[Pt(dppf)(H_2O)_2][OTf]_2$. *Organometallics* 1996b; 15: 904-908.

Umakoshi K, Ichimura A, Kinoshita I, and Ooi S. The dinuclear palladium(II) complex of pyridine-2-thiol: Synthesis, structure, and electrochemistry. *Inorg. Chem.* 1990; 29: 4005-4010.

Wang Z, Jiang L, Liu Z, Gan CRR, Liu Z,Zhang X, Zhao J and Hor TSA. Facile formation and redox of benzoxazole-2-thiolate-bridged dinuclear Pt(II/III) complexes. *Dalton Trans.* 2012; 12568-12576.