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

Md. Tuhinur Rahman Joy, Jagodish Chandra Sarker¹ and Shariff Enamul Kabir¹,*

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

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ABSTRACT

This article provides an overview of the rich chemistry of rhenium and manganese decacarbonyls, M₂(CO)₁₀ (M = Re, Mn) and their acetonitrile derivatives [M₂(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).

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

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),...
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 (Muettterties et al., 1977; 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 [M₂(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 hexahacarbonyl compound [Re₂(µ-pyS)₂(CO)₆] (1) in almost quantitative yield (Deeming et al., 1988b) from the reaction of [Re₂(CO)₁₀] with pyridine-2-thiol (pySH) in refluxing xylene. The corresponding 6-methylpyridine-2-thiolate analog [Re₂(µ-MepyS)₂(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 [Re₂(CO)₆(µ-pyS)₂] with the 6-methylsubstituted analog [Re₂(CO)₆(µ-MepyS)₂], for which the X-ray structure is reported (Fig. 1), at ambient temperature giving an equilibrium involving [Re₂(CO)₆(µ-pyS)(µ-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 [Mn₂(µ-pyS)₂(CO)₆] (4) and [Mn₂(µ-MepyS)₂(CO)₆] (5) from the Mn₃NO initiated reactions of Mn₂(CO)₁₀ with pyridine-2-thiol and 6-methylpyridine-2-thiol, respectively (Kabir et al., 1996).
Chart 3. Complexes derived from \([\text{Re}_2(\text{CO})_{10}]\) reactions with pyS/MepyS.

Fig. 1. The solid-state structure of \([\text{Re}(\mu-\text{MepyS})_2(\text{CO})_6]\) (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 \([\text{Re}_2(\mu-\text{MepyS})_2(\text{CO})_6]\) (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).

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 \([\text{M}_4(\text{CO})_{12}(\mu-\text{pymS})_4]\) (6, \(M = \text{Re}\); 7, \(M = \text{Mn}\)) from trimethylamine-N-oxide initiated reactions of \(\text{M}_2(\text{CO})_{10}\) (\(M = \text{Re}, \text{Mn}\)) 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 \(\text{fac-M(CO)}_3\) units are held together by tridentate pyrimidine-2-thiolate ligands.

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

Chart 4. Complexes derived from the reaction of \([\text{Mn}_2(\text{CO})_{10}]\) and pyS/MepyS.

Fig. 3. X-ray structures of 1 and 6.
Two of the pyrimidine-2-thiolate ligands lie above and two below the M₄ plane. The coordination geometry of each metal atom is a distorted octahedron with a *cis*-arrangement of the [M₂(CO)₆(µ-pyS)₂] (1, M = Re; 4, M = Mn) can form mixed-metal clusters when reacted with (Ph₃P)₂Ni(CO)₂, the reactions of 1 and 4 with the latter have been investigated. Treatment 4 with pyrimidine-2-thiolate ligands. Each metal atom achieves an 18-electron configuration without any appreciable metal-metal interaction considering that each pyrimidine-2-thiol 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.

**Reactivity of [M₂(CO)₆(µ-pyS)₂] (1, M = Re; 4, M = Mn) towards mono- and bidentate ligands.**

To explore whether the dinuclear complexes latter have been investigated. Treatment 4 with (Ph₃P)₂Ni(CO)₂ at room temperature furnished the dinuclear complex [Mn₂(CO)₅(PPh₃)(µ-pyS)] (9) and the mononuclear *fac-*[Mn(CO)₃(PPh₃)(κ²-pyS)] (10), the former being the first example of a carbonyl-substituted product of 4 (Rahman et al., 2012). In contrast, 1 reacts with (Ph₃P)₂Ni(CO)₂ at ambient temperature to give mononuclear complex *fac-*[Re(CO)₅(PPh₃)(κ²-pyS)] (8). Both 8 and 10 produce [M(CO)₂(PPh₃)₂(κ²-pyS)] (11, M = Re; 12, M = Mn) by CO substitution reaction when they are reacted further with (Ph₃P)₂Ni(CO)₂ at
room temperature. Additionally, complex 9 reacts further with (Ph₃P)₂Ni(CO)₂ to produce 10 and 12.

Scheme 2. Reactivity of [M₂(CO)₆(µ-pyS)₂] (1, M = Re; 4, M = Mn) towards monodentate ligands.

Compound 5 reacts with PPh₃ and dpmm [dpmm = Ph₂PCH₂PPh₂ = bis(diphenylphosphino)methane] in refluxing cyclohexane to give [Mn(MepyS)(PPh₃)(CO)₃] (13) and [Mn(MepyS)(η²-dpmm)(CO)₂] (14), respectively (Kabir et al., 1996), the latter containing a dangling dpmm ligand. The NMR spectrum identified the η¹ mode of coordination of dpmm in compound 14. The two ³JPH₁ values (8 and 1.5 Hz) designate that the two phosphorus atoms in dpmm are not equivalent; one is bonded to metal while the other is free from coordination.

Scheme 3. Reactivity of [Mn₂(µ-MepyS)₂(CO)₆] (5) towards mono- and bidentate ligands.

Formation of mixed-metal clusters: Reactivity of complexes 1 and 4 towards [M₃(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 Ru₃(CO)₁₂ has received some attention (Cockerton et al., 1991). Heating 1 with Ru₃(CO)₁₂ in toluene at 138 °C affords a series of Re–Ru mixed-metal clusters with varying nuclearity like ReRu₃, Re₂Ru, and Re₂Ru₂ 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 [M₃(CO)₁₀(µ-pyS)₂] (1, M = Re; 4, M = Mn) with [Os₃(CO)₁₀(NCMe)₂] in refluxing benzene at 80 °C furnish the mixed-metal clusters [MOs₃(CO)₁₅(µ₃-pyS)] (15, M = Re; 16, M = Mn) (Ghosh et al., 2010a). Similar reaction between 1 and Ru₃(CO)₁₂ at 80 °C produces [ReRu₃(CO)₁₅(µ₃-pyS)] (17), whereas at 110 °C the tetraruthenium cluster [Ru₄(CO)₁₂(µ-pyS)₂(µ₄-S)] (18) has been obtained as the only product (Scheme 4). Thus, the products obtained from reaction 1 with Ru₃(CO)₁₂ are temperature dependent. Compound 18 comprises two Ru₂(CO)₁₆(µ-py)₂ 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 [Mn₂(CO)₆(µ-pyS)₂] (4) reacts with Ru₃(CO)₁₂ to afford [MnRu₃(CO)₁₃(µ₃-pyS)] (19) as the sole product. Introduction of PPh₃ to 15 in the presence of Me₃NO yields both the mono- and bis(phosphine) substituted products [ReO₃(CO)₁₂(PPH₃)(µ₃-pyS)] (20) and [ReO₃(CO)₁₁(PPH₃)₂(µ₃-pyS)] (21), respectively (Scheme 4).

They then examined the reactions of 1 and 4 with Fe₂(CO)₁₂ at 110 °C, from which two completely different products have been isolated; the Fe₂Ru mixed-metal sulfido cluster [Fe₂Ru₂(CO)₁₅(µ-pyS)(µ₄-S)] (22) and the tetraruthenium cluster [Fe₄(CO)₁₂(µ-pyS)₂(µ₄-S)] (23) (Scheme 5), respectively. All the mixed-metal clusters have been structurally characterized.

To see whether the manganese dimer [Mn₂(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 [Mn₂(CO)₆(pyS)₂] (4) with [CpMo(CO)₆]₂. Thus boiling a toluene solution of the dimer 4 at 110 °C yields the Mo–Mn mixed metal complex [CpMoMn(CO)₆(µ-CO)(µ-η²-pyS)(µ-η¹-pyS)], the
Scheme 4. Formation of mixed-metal clusters from the reactions of \([\text{M}_2(\text{CO})_6(\mu-\text{pyS})_2]\) (M = Re, Mn) with \([\text{M}_3(\text{CO})_{10}(\text{L})_2]\) (M = Os, Ru; L = CO, NCMe).

Scheme 5. Reactivity of \([\text{M}_2(\text{CO})_6(\mu-\text{pyS})_2]\) (M = Re, Mn) towards \(\text{Fe}_3(\text{CO})_{12}\).

unsaturated trimolybdenum cluster \([\text{Cp}_3\text{Mo}(\mu-\text{CO})_2(\mu-S)(\mu_3-S)(\mu-\eta^1-\text{NCMe}_3\text{H}_4)]\) (26) and the mononuclear molybdenum complex \([\text{CpMo}(\mu-\text{CO})_2(\eta^3-\text{pyS})]\) (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 \(\mu-\eta^2\)-pyridine-2-thiolato, a \(\mu-\eta^1\)-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 \([\text{M}_4(\text{CO})_{12}(\mu-\text{pymS})_4]\) (6, M = Re; 7, M = Mn) towards mono– and bidentate ligands

Kabir and co-workers reported that the reactions of \([\text{M}_4(\text{CO})_{12}(\mu-\text{pymS})_4]\) (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.
In those articles, they showed that a 2-electron donor ligand, PPh$_3$ reacts with 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 pyrimidined-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 dpdm and dppe, 6 affords [Re(CO)$_2$(κ$^1$-pymS)(κ$^2$-dppe)] (32) and [Re(CO)$_2$(κ$^3$-pymS)(κ$^1$-dppe)$_2$] (33), respectively, whereas 7 gives [Mn(CO)$_2$(κ$^2$-pymS)(κ$^1$-dppe)$_2$] (34) and [Mn(CO)$_2$(κ$^2$-pymS)(κ$^2$-dppe)] (35) under similar experimental conditions (Chart 5).

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 \([M_4(CO)_{12}(\mu-pymS)_4]\) (6, \(M = \text{Re}\); 7, \(M = \text{Mn}\)) towards \((\text{PPh}_3)_2\text{Ni(CO)}_2\).

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

Kabir and co-workers have detailed the reactivity 6 and 7 towards \([M_3(CO)_{10}(\text{L})_2]\) (M = Fe, Os, Ru; \(\text{L} = \text{CO, NCMe}\)). Heating the tetrameric complexes 6 and 7 with \([\text{Os}_3(CO)_{10}(\text{NCMe})_2]\) furnish butterfly mixed-metal clusters \([\text{MOs}_3(CO)_{13}(\mu_3-\kappa^2-\text{pymS})]\) (40, \(M = \text{Re}\); 41, \(M = \text{Mn}\)) 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 \([\text{MRu}_3(CO)_{14}(\mu_2-\text{S})(\mu-\kappa^1-\eta^1-\text{pym})]\) (42, \(M = \text{Re}\); 43, \(M = \text{Mn}\)) (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 \([M_4(CO)_{12}(\mu-pymS)_4]\) (6, \(M = \text{Re}\); 7, \(M = \text{Mn}\)) with \([\text{Os}_3(CO)_{10}(\text{NCMe})_2]\).

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

The reactivity of \([\text{Re}_2(CO)_{10}]\) towards tetrahydropyrimidine-2-thiol (thpymSH) follows a different and unique path. Two dirhenium complexes \([\text{Re}_2(CO)_{6}(\mu-\text{thpymS})_2]\) (44) and eq-\(\text{Re}_2(CO)_8[\kappa^1-(S)-\text{SN}_2\text{C}_3\text{H}_8]\) (45) (Scheme 8) have been obtained from the reactions of thpymSH with \([\text{Re}_2(CO)_{6}(\text{NCMe})_2]\) or \([\text{Re}_2(CO)_{10}]\) (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 \([\text{Mn}_2(CO)_{9}(\text{NCMe})]\) with thpymSH at 25 °C affords the mono- and dinuclear complexes \([\text{Mn}_2(CO)_{9}(\kappa^1:\eta^1-\text{SCNH-C}_3\text{H}_6\text{NCO})]\) (46) and \([\text{Mn}_2(CO)_{10}(\mu-\text{thpymS})_2]\) (47), respectively (Ghosh et al., 2011). Carbon–nitrogen coupling is observed in compound 46, resulting in the formation of \(\kappa^1:\eta^1-\text{SCNH}=\text{C}_3\text{H}_6\text{NCO}\) ligand, while compound 47 adopts a centrosymmetric structure (Scheme 8).
Reactivity of $[\text{Re}_2(\text{CO})_6(\mu-\text{thpymS})_2]$ towards mono– and bidentate ligands.

The dimer $[\text{Re}_2(\text{CO})_6(\mu-\text{thpymS})_2]$ (44) shows moderate reactivity towards mono– and diphosphines. The reactions of 44 with PPh$_3$ and dppe yield the mononuclear complexes fac-Re(\text{CO})$_3$(PPh$_3$)(κ$^2$-thpymS) (48) and fac-Re(\text{CO})$_3$. (κ$^1$-dppe)(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 dppe reacts with 44 to give [Re(\text{CO})$_3$(κ$^1$-dppe)(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 $[\text{Re}_2(\text{CO})_4(\mu-\text{dppe})(\mu,\kappa^2$-thpymS)$_2]$ (51) is formed (Scheme 9), which has two thiolates and one dppe ligand bridging Re–Re bond. On the other hand, the reaction of 44 with more flexible dppe at room temperature affords $[\text{Re}(\text{CO})_3(\kappa^2$-thpymS)$_2(\mu,\kappa^1,\kappa^1$-dppe)] (52) where each phosphine center is...
bonded to a d⁶-ML₅ 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(κ²-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(κ¹-dppe)(κ²-thpymS)] (53) containing two dangling dppe ligands (Scheme 10).

Reactivity of [M₂(CO)₆(µ-2-thpymS)]₂ (M = Re, Mn) towards [M₃(CO)₁₀(L)₂] (M = Fe, Os, Ru; L = CO, NCMe)

The reaction of 44 with Ru₃(CO)₁₂ in refluxing THF results tetranuclear butterfly complexes ReRu₂(CO)₁₃(µ₃-thpymS) (54, 55) where the capping pyrimidine-2-thiolate ligand is positioned differently on the cluster surface (Ahmad et al., 2013) (Scheme 11). The Ru₃ face is covered by the tetrahydro pyrimidine-2-thiolate in the thermodynamic isomer 55, whereas the ReRu₂ face is covered in the kinetic isomer 54. In refluxing benzene, a similar reaction with [Os₃(CO)₁₀(NCMe)₂] yields mostly the ReOs₃ cluster [ReOs₃(CO)₁₃(µ₃-thpymS)] (56), together with trace quantities of [(µ-H)Os₃(CO)₆(µ₃-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 [Os₃(CO)₁₀(NCMe)₂] in refluxing benzene furnishes the MnOs mixed-metal cluster [MnOs₃(CO)₁₃(µ₃-thpymS)] (59) which has a butterfly-shaped skeleton made up of four metal atoms whereas Ru₃(CO)₁₂ at 110 °C produces the mixed Mn–Ru cluster [MnRu₃(CO)₁₄(µ₂-S)(κ¹:η¹-C₄H₈N₂)] (60) (Ghosh et al., 2011). In contrast, reaction of 47 with Fe₃(CO)₁₂ at 80 °C affords two triiron clusters [Fe₃(CO)₉(µ₃-S)(µ₃-k¹:η¹-C₄H₈N₂)] (61) and [Fe₃(CO)₆(µ₃-S)₂(η¹-C₄H₈N₂)] (62). The former is also formed from the direct reaction of thpymSH with Fe₃(CO)₁₂, and it reacts with H₂S to produce 62 (Scheme 12).
Reactivity of [M₂(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 [Re₂(CO)₈(NCMe)₂] was reacted with 2-mercapto-1-methylimidazole at 80 °C affording a mixture of di-, tri-, and tetrarhenium complexes [Re₃(CO)₁₂(μ-CO)(μ₃-SN₂C₄H₅)(μ-H)] (63), [Re₄(CO)₁₆(μ-SN₂C₄H₅)₄] (64), and [Re₂(CO)₆(μ-SN₂C₄H₅)₂] (65) (Ghosh et al., 2009b) (Scheme 13).
In sharp contrast, two new dimeric products \([\text{Mn}_2(\text{CO})_6(\mu-\text{SN}_2\text{C}_3\text{H}_5)_2]\) (66) and \([\text{Mn}_2(\text{CO})_3(\mu-\text{SN}_2\text{C}_3\text{H}_5)_2]\) (67) have been obtained from the reaction of \([\text{Mn}_2(\text{CO})_{10}]\) with 2-mercapto-1-methylimidazole in the presence of \(\text{Me}_3\text{NO}\) at 25 °C (Ghosh et al., 2009b). Both compounds are structurally characterized. Compound 66 consists of two \(\mu\text{-SN}_2\text{C}_3\text{H}_5\) 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 \(\mu\text{-SN}_2\text{C}_3\text{H}_5\) 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 \([\text{Mn}_2(\text{CO})_8(\text{NCMe})_2]\) with 2-mercapto-1-methyl-imidazole at 80 °C.

**Reactivity of \([\text{M}_2(\text{CO})_6(\mu-\text{SN}_2\text{C}_3\text{H}_5)_2]\) (\(\text{M} = \text{Re}, \text{Mn}\)) towards \([\text{M}_3(\text{CO})_{10}(\text{L})_2]\) (\(\text{M} = \text{Fe}, \text{Os, Ru}; \text{L} = \text{CO, NCMe}\))**

Over the last three decades, considerable attention has been focused on the chemistry of bimetallic metal clusters. The former is an electron trirhenium and chloride ligands is only found in compound 72, a rare instance of this type of complex. Surprisingly, treatment of 65 with \(\text{Fe}_2(\text{CO})_{12}\) at 70–75 °C afford the triethyniun and dirhenium complexes \([\text{Re}_2(\text{CO})_{10}(\mu-H)(\mu_3\text{-SN}_2\text{C}_3\text{H}_5)_2]\) (73) and \([\text{Re}_2(\text{CO})_6(\text{NCMe})_2(\mu_3\text{-SN}_2\text{C}_3\text{H}_5)_2]\) (74), 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-methylimidazolyl ligand, and the latter may be thought of as a 1-methylimidazolyl 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 \([\text{Cr}(\text{CO})_3(\text{NCMe})_3]\) and \([\text{Mo}(\text{CO})_3(\text{NCMe})_3]\) in boiling THF produced the mixed-metal clusters \([\text{CrMn}_2(\text{CO})_8(\mu_3\text{-SN}_2\text{C}_3\text{H}_5)_2]\) (75) and \([\text{MoMn}_2(\text{CO})_6(\mu_3\text{-SN}_2\text{C}_3\text{H}_5)_2]\) (76), respectively, in which two Mn–M (M = Mo, Cr) bonds were created (Ghosh et al., 2009b). In contrast, an analogous reaction of \([\text{W}(\text{CO})_{13}(\text{NCMe})_3]\) with 66 affords two W–Mn clusters \([\text{Mn}_2\text{W}(\text{CO})_8(\mu_3\text{-SN}_2\text{C}_3\text{H}_5)_2]\) (77) and \([\text{Mn}_2\text{W}(\text{CO})_7(\mu_3\text{-CO})_2(\text{SN}_2\text{C}_3\text{H}_5)_2(\mu_3\text{-SN}_2\text{C}_3\text{H}_5)_2]\) (78). The reaction of 66 with \(\text{Fe}_2(\text{CO})_{12}\) at 70–75 °C yields the mixed-metal cluster \([\text{FeMn}_2(\text{CO})_6(\mu_3\text{-CO})_2(\mu_3\text{-SN}_2\text{C}_3\text{H}_5)_2]\) (79) and the by-product \([\text{Fe}_2(\text{CO})_6(\mu_3\text{-SN}_2\text{C}_3\text{H}_5)_2]\) (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.
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$_2$C$_4$H$_6$ ligand mono coordinated through the exocyclic sulfur atom to the W atom. Two bridging S$_2$N$_2$C$_4$H$_5$ ligands, produced by combining 2-mercapto-1-methylimidazole with sulfur, make up compound 80. Compound 79 provides an unusual example of a Mn$_2$Fe trimetallic cluster with two Fe–Mn bonds.

**Scheme 14.** Reactions of [M$_2$(CO)$_6$(μ-SN$_2$C$_4$H$_5$)$_2$] ($65, M = Re; 66, M = Mn$) with group 8 trimetallic carbonyls.

**Fig. 4.** The solid-state structure of [FeMn$_2$(CO)$_6$(μ-CO)($μ_3$-SN$_2$C$_4$H$_5$)$_2$] (79).
Reactions of \([\text{Mn}_2(\text{CO})_6(\mu-\text{SN}_2\text{C}_6\text{H}_5)_2]\) (66) with \(\text{Fe}_3(\text{CO})_{12}\) and \([\text{M}_3(\text{CO})_3(\text{NCMe})]\) (\(\text{M} = \text{Cr}, \text{Mo}, \text{W}\)).

Reactions of \([\text{M}_2(\text{CO})_{10}\] (\(\text{M} = \text{Re}, \text{Mn}\)) with 2-mercaptobenzothiazole-2-thiol (MBTH) and 2-mercaptobenzoxazol.

Following a method analogous to that reported by Kabir and co-workers for the synthesis of \([\text{Mn}_2(\text{CO})_6(\mu-\text{pyS})_2]\) (Kabir et al., 1996), compound \([\text{Re}_2(\text{CO})_6(\mu-\text{MBT})_2]\) (81) has been synthesized from the \(\text{Me}_3\text{NO}\)-mediated reaction of \(\text{Re}_2(\text{CO})_{10}\) with 2-mercaptobenzothiazole at room temperature (Ghosh et al., 2010b). The complex has a chiral structure with \(\text{C}_2\) symmetry being similar to that of previously reported for compound \([\text{Re}_2(\text{CO})_6(\mu-\text{pyS})_2]\) (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 \(\text{Mn}_2(\text{CO})_{10}\) and 2-mercaptobenzothiazole in the presence of \(\text{Me}_3\text{NO}\) at 25 °C gives the dimanganese complex \([\text{Mn}_2(\text{CO})_6(\mu-\text{MBT})_2]\) (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 \([\text{M}_2(\text{CO})_{10}\] (\(\text{M} = \text{Re}, \text{Mn}\)) towards MBTH.

Hoque and co-workers carried out analogous reactions of 2-mercaptobenzoxazol with \([\text{Mn}(\text{CO})_6(\text{NCMe})_2]\) and observed the unexpected formation of trimanganese cluster \([\text{Mn}_3(\text{CO})_{10}(\mu-\text{SCNOC}_6\text{H}_4)_3]\) (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 \(\text{Re}_2(\text{CO})_6(\text{NCMe})_2\) also resulted in the isolation of a trinuclear product, namely \([\text{Re}_3(\text{CO})_{12}(\mu-\text{SCNOC}_6\text{H}_4)_3]\) (84). The solid-state structure determination 84 confirms that each 2-mercaptobenzoxazolate ligand is of type A (Chart 7), spanning Re(\text{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.
with 1,2-bis(diphenylphosphino)ethane (dppe) and 1,3-bis(diphenylphosphino)propane (dppp) in cyclohexane at boiling temperature furnish cis-
[Mn(CO)$_3$(κ$^2$-MBT)(κ$^2$-dppe)] (85) and cis-
[Mn(CO)$_3$(κ$^2$-MBT)(κ$^2$-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)$_3$(κ$^1$-MBT)(κ$^2$-bipy)] (87), fac-[Mn(CO)$_3$(κ$^1$-MBT)(κ$^2$-phen)] (88) and fac-[Mn(CO)$_3$(κ$^1$-MBT)(κ$^2$-en)] (89), respectively (Scheme 18) (Ghosh et al., 2012).

Scheme 18. Reactivity of [Mn$_2$(CO)$_6$(µ-MBT)$_2$] (82) towards bidentate ligands.
Reactivity of \([\text{M}_2(\text{CO})_6(\mu-\text{S}_2\text{NC}_3\text{H}_2)_2]\) (81, \(\text{M} = \text{Re}; 82, \text{M} = \text{Mn}\)) towards the trinuclear clusters \([\text{M}_3(\text{CO})_{10}(\text{L})_2]\) (\(\text{M} = \text{Fe}, \text{Os}, \text{Ru}; \text{L} = \text{CO}, \text{NCMe}\))

The group 8 trimetallic carbonyl clusters show reactivity towards dirhenium compound \([\text{Re}_2(\text{CO})_6(\mu-\text{S}_2\text{NC}_3\text{H}_2)_2]\) (81) to afford new tri- and tetranuclear mixed-metal clusters (Ghosh et al., 2010b). \([\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]\) reacts with 81 in refluxing benzene to yield the tetranuclear mixed-metal cluster \([\text{Os}_3\text{Re}(\text{CO})_{13}(\mu_3-\text{C}_3\text{H}_2\text{NS}_2)]\) (90) (Scheme 18) as the sole product. Interestingly, for \(\text{Ru}_3(\text{CO})_{12}\), the reaction products are temperature dependent. At 80 °C, \([\text{Ru}_3\text{Re}(\text{CO})_{13}(\mu_3-\text{MBT})]\) (91) and \(\text{Ru}_3(\text{CO})_{14}(\mu-H)(\mu_3-\text{MBT})\) (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 \(\text{Fe}_3(\text{CO})_{12}\) at 80 °C affords 94. The reactivity of 94 (Scheme 19) with \(\text{PPh}_3\) in the presence of \(\text{Me}_2\text{NO}\) at 25 °C results in ligand substitution to furnish mono- and disubstituted derivatives \([\text{Os}_3\text{Re}(\text{CO})_{12}(\text{PPh}_3)(\mu_3-\text{MBT})]\) (95) and \([\text{Os}_3\text{Re}(\text{CO})_{11}(\text{PPh}_3)_2(\mu_3-\text{MBT})]\) (96). In 95, the \(\text{PPh}_3\) ligand is located at an axial position on the wingtip osmium. In contrast, in 91, one \(\text{PPh}_3\) ligand is equatorially coordinated to the wingtip osmium, and the other is bound to the hinge osmium.

![Scheme 19. Reactions of \([\text{Re}_3(\text{CO})_6(\mu-\text{S}_2\text{NC}_3\text{H}_2)_2]\) (81) with \(\text{M}_3(\text{CO})_{12}\) different metal carbonyls.](image)

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 \([\text{M}_2(\text{CO})_6(\mu-\text{L})_2]\) and the tetranuclear square-type complexes \([\text{M}_4(\text{CO})_{12}(\mu-\text{L})_4]\) (\(\text{L} = \text{pyridine-2-thiolato, pyrimidine-2-thiolato, tetrahydroxypirimidine-2-thiolato, 2-mercaptop-1-methyl-imidazolato, 2-mercaptop-benzothiolate, etc. as appropriate}\)) are described. These compounds contain labile M-S bonds which make them excellent sources of the 16-electron mononuclear species \([\text{M}(\text{CO})_5(\kappa^2-\text{L})]\) in solution. The further reactivity of the resultant \([\text{M}(\text{CO})_5(\kappa^2-\text{L})]\) species with various mono and bidentate ligands reveals that they are versatile precursors for mononuclear products of differing coordination of the \(\text{M}(\text{CO})_5(\text{L})\) fragments. The lability of the M-S bonds makes these di and tetranuclear complexes excellent precursors for the synthesis of two isosstructural series of mixed-metal cluster complexes, namely \([\text{MM'}_2(\text{CO})_{13}(\mu_3-\text{L})]\) (\(\text{M} = \text{Re, Mn}; \text{M'} = \text{Ru, Os}\)) and \([\text{MM'}_2(\text{CO})_{10}(\mu_3-\text{L})]\) (\(\text{M} = \text{Re, Mn}; \text{M'} = \text{Mo, Cr, W}\)). The trimuclear mixed-metal clusters consist of an open structure of two rhenium or manganese atoms and a third metal atom, \(\text{M} (\text{M} = \text{W, Mo, Cr})\), connected by two \(\text{M-}\text{Re/Mn}...\)
bonds, two triply bonded thiolato ligands, and two asymmetrically bound $\mu$-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 $\text{Fe}_3(\text{CO})_{12}$ reactivity towards 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.

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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.

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