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## **Tetranuclear Group 7/8 Mixed-Metal and Open Trinuclear Group 7 Metal Carbonyl Clusters Bearing Bridging 2-mercapto-1-methylimidazole Ligands<sup>†</sup>**

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## Abstract

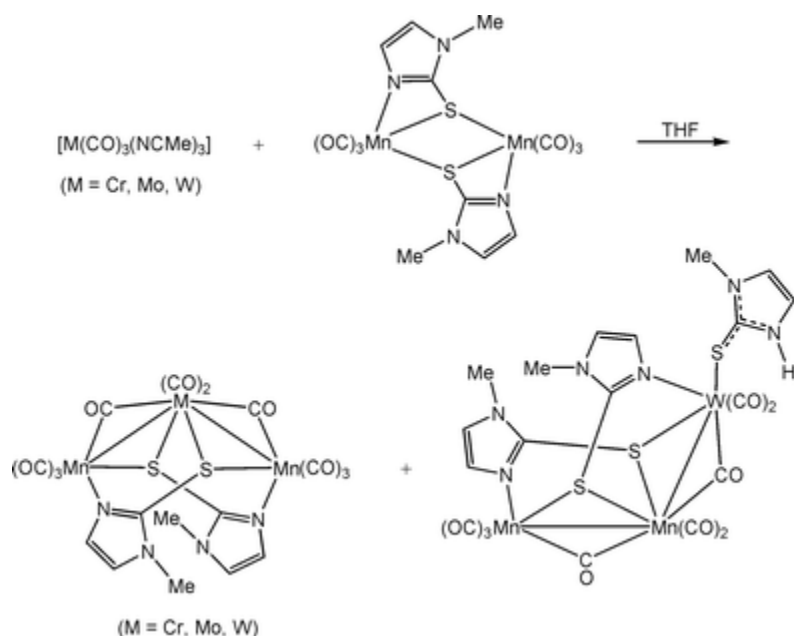
The reactivity of group 7 metal dinuclear [carbonyl](#) complexes  $[M_2(CO)_6(\mu-SN_2C_4H_5)_2]$  (**1**, M = Re; **2**, M = Mn) toward group 8 metal trinuclear [carbonyl](#) clusters were examined. Reactions of **1** and **2** with  $[Os_3(CO)_{10}(NCMe)_2]$  in refluxing [benzene](#) furnished the tetranuclear mixed-metal clusters  $[Os_3Re(CO)_{13}(\mu_3-SN_2C_4H_5)]$  (**3**) and  $[Os_3Mn(CO)_{13}(\mu_3-SN_2C_4H_5)]$  (**4**), respectively. Similar treatment of **1** and **2** with  $Ru_3(CO)_{12}$  yielded the ruthenium analogs  $[Ru_3Re(CO)_{13}(\mu_3-SN_2C_4H_5)]$  (**5**), and  $[Ru_3Mn(CO)_{13}(\mu_3-SN_2C_4H_5)]$  (**6**), but in the case of **2** a secondary product  $[Mn_3(CO)_{10}(\mu-Cl)(\mu_3-SN_2C_4H_5)_2]$  (**7**) was also formed. Compounds **3–6** have a butterfly core of four metal atoms with the M (Mn or Re) at a wingtip of the butterfly and containing a noncrystallographic mirror plane of symmetry. This result provides a potential method for the synthesis of a series of new group 7/8 mixed metal complexes containing a bifunctional heterocyclic [ligand](#). Compound **7** is a unique example of a 54-electron trimanganese complex having bridging 2-mercapto-1-methylimidazolate and chloride [ligands](#). Interestingly, the reaction of **1** with  $Fe_3(CO)_{12}$  at 70–75 °C furnished the tri- and dirhenium complexes  $[Re_3(CO)_{10}(\mu-H)(\mu_3-SN_2C_4H_5)_2]$  (**8**) and  $[Re_2(CO)_6(N_2C_4H_5)(\mu-SN_2C_4H_5)_2]$  (**9**), respectively instead of the expected formation of the mixed-metal clusters. The former is an interesting example of a 52-electron trirhenium-hydridic complex containing bridging 2-mercapto-1-methylimidazolate [ligand](#), while the latter can be viewed as a 1-methylimidazole adduct of **1**. No mixed Fe–Re complexes were produced in this reaction. The molecular structures of the new compounds **3–5** and **7–9** were established by [single-crystal X-ray diffraction](#) analyses and the DFT studies of compounds **5**, **7** and **8** are reported.

## Introduction

Over the last three decades, considerable attention has been focused on the chemistry of mixed-metal clusters of low-valent transition metals due to their unique structural properties and various potential applications resulting from having two metals with different chemical properties in close proximity.<sup>1–4</sup> The greatest stimulus for the development of this field of research is the cooperative reactivity of two or more coordination centers, which offer attractive perspective in stoichiometric and catalytic transformations.<sup>5–18</sup> In addition, heterobimetallic complexes may combine the catalytic features of each metal to provide new and unique reactivity that is inaccessible by the homobimetallic systems.<sup>19–21</sup>

Tetranuclear clusters with a butterfly structure have received much attention because of their intermediary position between tetrahedral and square-planar clusters.<sup>22,23</sup> They have been studied as intermediates in homogeneous catalytic processes,<sup>23–25</sup> and also considered as a model for chemisorption of small molecules.<sup>26</sup> Information about the structural properties of the butterfly framework as well as the chemistry of coordinated [ligands](#) can be easily obtained as both metal atoms and [ligands](#) can vary widely in butterfly-type clusters.<sup>23</sup>

Recently, we reported a series of group 6 and 7 mixed-metal complexes containing a 2-mercapto-1-methylimidazolate [ligand](#)<sup>27</sup> ([Scheme 1](#)). [2-Mercapto-1-methylimidazole](#) is a bifunctional [ligand](#) with great coordinative flexibility and versatility and introduces novel reactivities to the resultant complexes, many of which possess important biological and industrial applications.<sup>28–33</sup> A number of group 7 and 8 heterobimetallic complexes have been cited in literature. Deeming *et al.* reported a series of Re–Ru mixed-metal complexes from the reaction of  $[\text{Re}_2(\text{CO})_6(\mu\text{-pyS})_2]$  and  $\text{Ru}_3(\text{CO})_{12}$ .<sup>34,35</sup> Knight and Mays documented group 7 and 8 tri- and tetrameric mixed-metal clusters obtained from the reaction of the neutral [metal carbonyls](#)  $\text{M}_3(\text{CO})_{12}$  (M = Fe, Ru, Os) with the [metal carbonyl](#) anions  $[\text{M}'(\text{CO})_5]^-$  (M' = Mn, Re).<sup>36</sup> Atwood *et al.* also reported group 7 and 8 mixed-metal clusters from the electron transfer reaction between mononuclear [metal carbonyl](#) anions ( $[\text{M}(\text{CO})_5]^-$ , M = Mn, Re) and trinuclear clusters ( $\text{M}_3(\text{CO})_{12}$ ; M = Fe, Ru, Os).<sup>37</sup> The mixed-metal carbide cluster anions  $[\text{MnM}_3\text{C}(\text{CO})_{13}]^-$  (M = Ru, Os) and the butterfly clusters  $[\text{Fe}_3\text{M}(\text{CO})_{12}(\mu_4\text{-E})][\text{PPN}]$  (E = O, S; M = Mn, Re), were reported by Shriver and coworkers.<sup>38,39</sup> Struchkov *et al.* also documented the tetranuclear mixed Mn–Os cluster  $[\text{CpMnOs}_3(\text{CO})_{11}(\mu\text{-CO})(\mu\text{-H})(\mu\text{-CH=CHPh})]$  from the reaction of the vinylidene complex  $[\text{Cp}(\text{CO})_2\text{Mn}=\text{C}=\text{CHPh}]$  with  $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ .<sup>40</sup> The mixed Fe–Mn chalcogenide clusters  $[\text{Et}_4\text{N}][\text{MnFe}_2(\text{CO})_{10}(\mu_3\text{-Te})_2]$  and  $[\text{Et}_4\text{N}][\text{MnFe}_2(\text{CO})_9(\mu_3\text{-Se})_2]$  were reported by Shieh and coworkers<sup>41</sup> from the reaction between  $[\text{Fe}_3(\text{CO})_9(\mu\text{-E})_2]$  (E = Se, Te) and  $[\text{Mn}(\text{CO})_5]^-$ , while Shaposhnikova *et al.*<sup>42</sup> reported the mixed Fe–Re cluster  $[\text{Re}_2\text{Fe}(\text{CO})_9(\mu_3\text{-CH=CHC}_6\text{H}_4)]$  from the reaction of  $[\text{Re}_2(\text{CO})_8(\mu\text{-H})(\mu\text{-C}\equiv\text{CPh})]$  with  $\text{Fe}_3(\text{CO})_{12}$ . Herrmann *et al.* also reported the mixed Fe–Mn chalcogenide cluster  $[\text{Cp}'\text{MnFe}_2(\text{CO})_6(\mu\text{-CO})_2(\mu_3\text{-Te})]$  obtained from the reaction between the tellurium complex  $[(\mu\text{-Te})(\text{Cp}'\text{Mn}(\text{CO})_2)_2]$  and  $\text{Fe}_2(\text{CO})_9$ .<sup>43</sup> A major challenge in the synthesis of group 7 and 8 mixed-metal clusters of desired structural and reactivity features is the lack of suitable methods. As part of our ongoing research into the versatility of [2-mercapto-1-methylimidazole](#) containing metal compounds in the synthesis of mixed-metal complexes, we have explored the possibility of synthesising mixed-metal clusters consisting of group 7 and 8 metal atoms bearing this heterocyclic [ligand](#) and the results are reported herein.



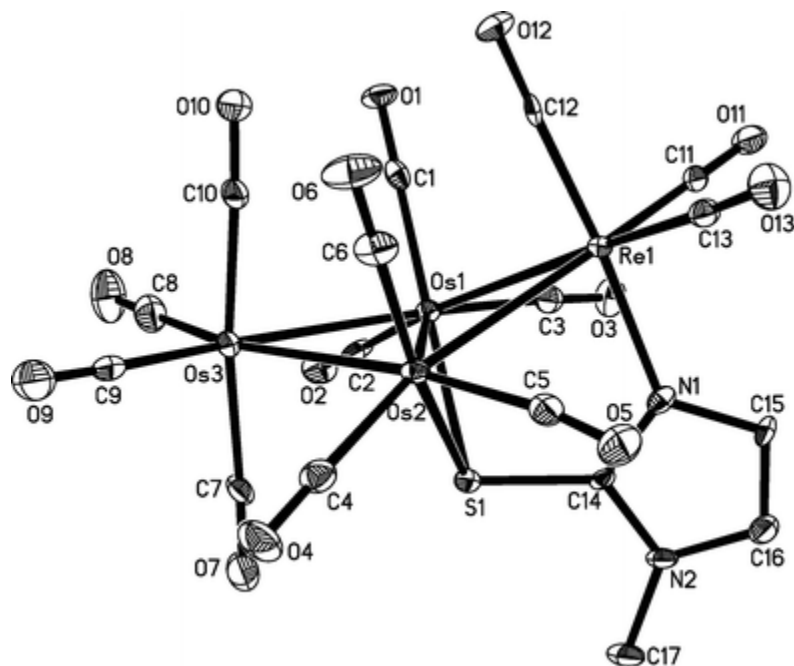
**Scheme 1**

## Results and discussion

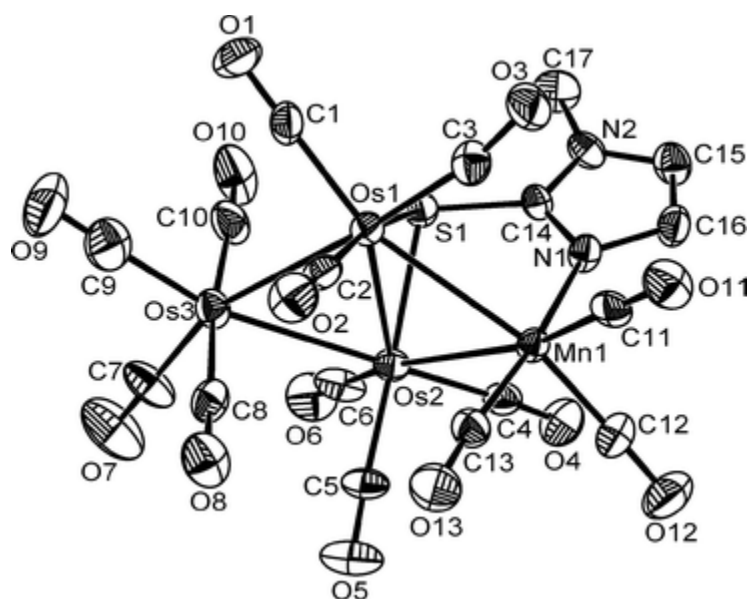
### (a) Tetranuclear mixed-metal butterfly clusters

Reactions of  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  with  $[\text{Re}_2(\text{CO})_6(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$  (**1**) and  $[\text{Mn}_2(\text{CO})_6(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$  (**2**) in refluxing [benzene](#) furnish the mixed-metal clusters  $[\text{Os}_3\text{Re}(\text{CO})_{13}(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)]$  (**3**) and  $[\text{Os}_3\text{Mn}(\text{CO})_{13}(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)]$  (**4**) in 60% and 88% yields, respectively. The analogous ReRu<sub>3</sub> compound  $[\text{Ru}_3\text{Re}(\text{CO})_{13}(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)]$  (**5**) was obtained in 24% yield *via* the reaction of **1** with  $\text{Ru}_3(\text{CO})_{12}$  ([Scheme 2](#)). All these compounds have been characterized by [elemental analysis](#), [IR](#) and [<sup>1</sup>H NMR](#) spectroscopic and mass spectroscopic data together with [single crystal X-ray diffraction](#) studies. The elemental analyses and mass spectrometric data of these clusters suggested a tetranuclear structure for them. Each of the FAB mass spectra exhibits the respective parent molecular ion peak as well as peaks corresponding to the sequential loss of thirteen [carbonyl ligands](#). The [infrared spectra](#) of **3**, **4**, and **5** indicate the presence of only terminal [carbonyl ligands](#). The [<sup>1</sup>H NMR spectra](#) of **3–5** contain resonances for the heterocyclic ring [protons](#) and the [methyl protons](#) with appropriate integrations and are similar to those reported for **1** and **2**. However, the precise attachment of the [ligand](#) to these clusters and the exact geometry of the metal core could only be determined by [X-ray diffraction](#) methods. ORTEP diagrams of the molecular structures of **3**, **4**, and **5** are shown in [Fig. 1–3](#), respectively, and selected bond distances and angles are listed in the caption. The clusters **3**, **4**, and **5** have the same overall structure. All contain four metal atoms: one manganese or rhenium and three of osmium or ruthenium. The four metal atoms form a butterfly skeleton where the group 7 metal (Mn or Re) occupies a wingtip position; whereas, in the known mixed-metal carbide cluster anion  $[\text{MnOs}_3\text{C}(\text{CO})_{13}]^-$  derived from the ketylenidene clusters  $[\text{Os}_3(\text{CO})_9\text{CCO}]^{2-}$  and  $[\text{Mn}(\text{CO})_3(\text{NCMe})_3]^+$ , the manganese atom occupies a hinge position.<sup>38</sup> However, in other mixed-metal

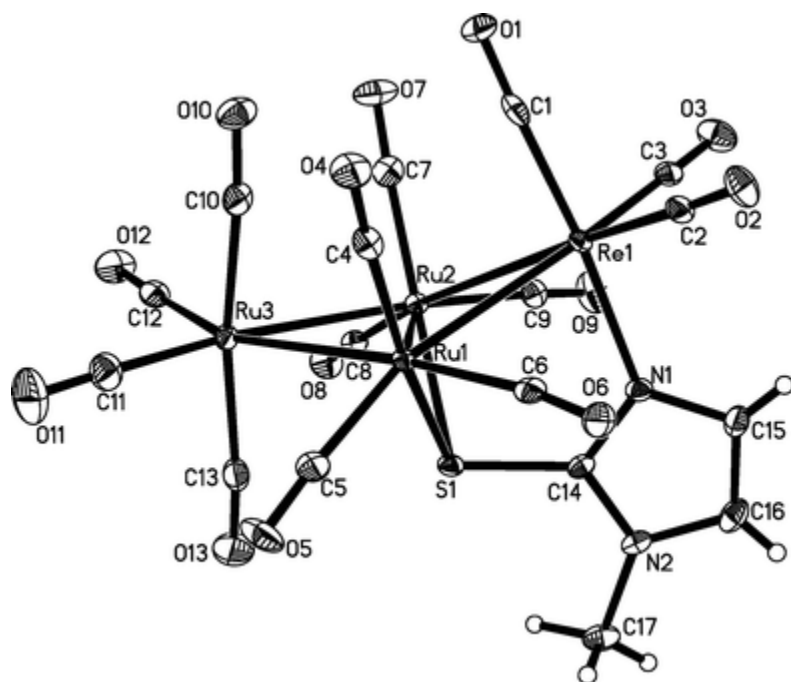
clusters with the butterfly core structure such as  $[\text{Fe}_3\text{Mn}(\text{CO})_{12}(\mu_4\text{-E})][\text{PPN}]$  ( $\text{E} = \text{O}, \text{S}$ ),<sup>39</sup>  $[\text{Ru}_3\text{Co}(\text{CO})_{11}(\text{PhCCPh})]^{-44}$  and  $[\text{CpCo}_3\text{Fe}(\text{CO})_7(\mu\text{-CO})_2(\mu_4\text{-C}=\text{CH}_2)]$ ,<sup>45</sup> the single metal atom Mn, Co, or Fe occupies a wingtip position as found in **3**, **4**, and **5**. The interplanar angle of the butterfly is  $152.7(1)^\circ$  in **3**,  $153.93(4)^\circ$  in **4**, and  $153.5(1)^\circ$  in **5** and on their convex side, facially located, lies the  $\mu_3\text{-SN}_2\text{C}_4\text{H}_5$  moiety such that it is bonded to three metal atoms through the sulfur and [nitrogen atom](#). In all structures the  $\mu_3\text{-SN}_2\text{C}_4\text{H}_5$  ligand bridges the hinge metal atoms through the sulfur, but coordinates to the wingtip group 7 metal (Mn or Re) through a [nitrogen atom](#) and all contain a noncrystallographic mirror plane of symmetry passing through the plane of the heterocyclic ring and also containing the wingtip metals of the butterfly.



**Fig. 1** ORTEP diagram of the molecular structure of  $[\text{Os}_3\text{Re}(\text{CO})_{13}(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)]$  (**3**), showing 50% probability thermal ellipsoids. Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{Os}(1)\text{-Os}(2)$  2.7928(4),  $\text{Os}(1)\text{-Os}(3)$  2.8638(4),  $\text{Os}(2)\text{-Os}(3)$  2.8603(4),  $\text{Os}(1)\text{-Re}(1)$  2.9466(4),  $\text{Os}(2)\text{-Re}(1)$  2.9171(4),  $\text{Os}(1)\text{-S}(1)$  2.424(2),  $\text{Os}(2)\text{-S}(1)$  2.425(2),  $\text{Re}(1)\text{-N}(1)$  2.159(6),  $\text{C}(14)\text{-S}(1)$  1.748(7),  $\text{Os}(2)\text{-Os}(1)\text{-Os}(3)$  60.73(1),  $\text{Os}(2)\text{-Os}(1)\text{-Re}(1)$  61.03(1),  $\text{Os}(3)\text{-Os}(1)\text{-Re}(1)$  116.18(1),  $\text{Os}(1)\text{-Os}(2)\text{-Re}(1)$  62.09(1),  $\text{Os}(1)\text{-Os}(2)\text{-Os}(3)$  60.86(1),  $\text{Os}(3)\text{-Os}(2)\text{-Re}(1)$  117.25(1),  $\text{Os}(2)\text{-Re}(1)\text{-Os}(1)$  56.88(9),  $\text{Os}(2)\text{-Os}(3)\text{-Os}(1)$  58.40(1),  $\text{Os}(1)\text{-S}(1)\text{-Os}(2)$  70.33(5).



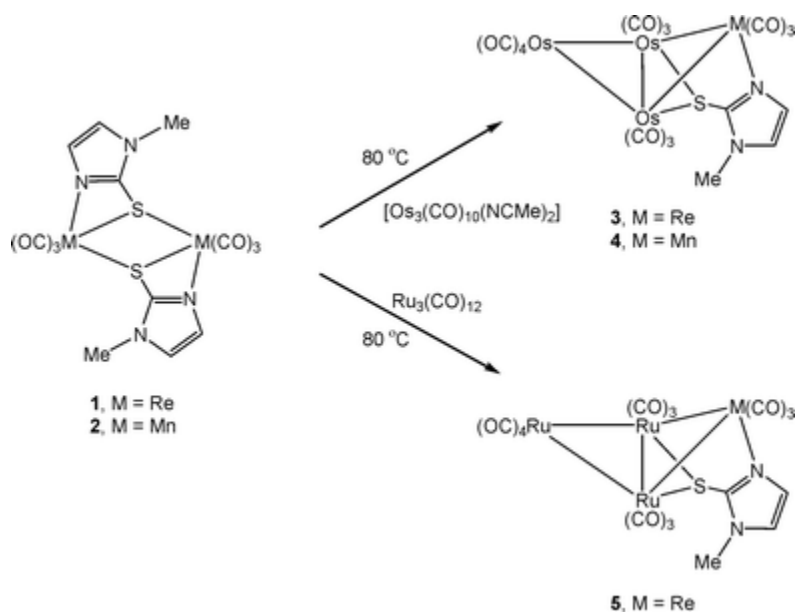
**Fig. 2** ORTEP diagram of the molecular structure of  $[\text{Os}_3\text{Mn}(\text{CO})_{13}(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)]$  (**4**), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Os(1)–Os(2) 2.7978(6), Os(1)–Os(3) 2.8635(7), Os(2)–Os(3) 2.8635(6), Os(1)–Mn(1) 2.867(2), Os(2)–Mn(1) 2.893(2), Os(1)–S(1) 2.419(3), Os(2)–S(1) 2.425(3), Mn(1)–N(1) 2.026(9), C(14)–S(1) 1.76(1), Os(2)–Os(1)–Os(3) 60.76(2), Os(2)–Os(1)–Mn(1) 61.40(3), Os(3)–Os(1)–Mn(1) 117.03(3), Os(1)–Os(2)–Mn(1) 60.48(3), Os(1)–Os(2)–Os(3) 60.76(2), Os(3)–Os(2)–Mn(1) 116.19(4), Os(2)–Mn(1)–Os(1) 58.13(3), Os(2)–Os(3)–Os(1) 58.49(2), Os(1)–S(1)–Os(2) 70.55(8).



**Fig. 3** ORTEP diagram of the molecular structure of  $[\text{Ru}_3\text{Re}(\text{CO})_{13}(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)]$  (**5**), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Ru(1)–Ru(2) 2.7853(4), Ru(1)–Ru(3) 2.8318(4), Ru(2)–Ru(3) 2.8327(4), Ru(1)–Re(1) 2.9069(3), Ru(2)–Re(1) 2.9342(3), Ru(1)–S(1) 2.3926(9), Ru(2)–S(1) 2.3987(9), Re(1)–N(1) 2.177(3), C(14)–S(1) 1.757(4), Ru(2)–Ru(1)–Ru(3) 60.56(1), Ru(2)–Ru(1)–Re(1)



62.015(9), Ru(3)–Ru(1)–Re(1) 117.24(1), Ru(1)–Ru(2)–Re(1) 61.029(8), Ru(1)–Ru(2)–Ru(3) 60.53(1), Ru(3)–Ru(2)–Re(1) 116.32(1), Ru(2)–Re(1)–Ru(1) 56.957(8), Ru(1)–Ru(3)–Ru(2) 58.906(9), Ru(1)–S(1)–Ru(2) 71.09(3).

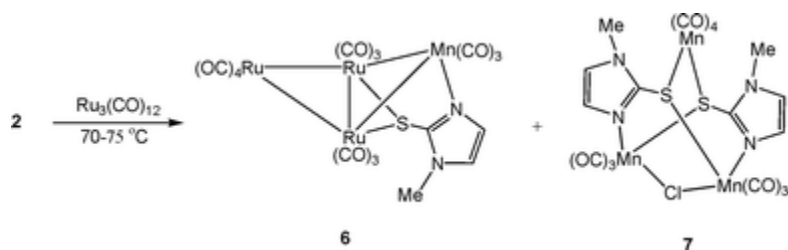


**Scheme 2**

All metal–metal distances in **3**, **4**, and **5** are different, but in the expected range for M–M' and M'–M' (M = Mn, Re; M' = Ru, Os) single bonds.<sup>34,35,38–41,43,46</sup> The hinge metal–metal distance is shorter than other metal–metal distances of the cluster, although the M(1)–S(1)–M(2) angle in all of them is acute (70.33(5)° in **3**; 70.55(8) in **4**; 71.09(3) in **5**), the strain can be alleviated by the lengthening of this edge. In the three clusters, the coordination of the thirteen [carbonyl ligands](#) is the same: three bonded with each of the hinge metal atoms (Ru or Os), three with the wingtip group 7 metal atom (Mn or Re) and four with the wingtip group 8 metal atom (Ru or Os). The  $\mu_3$ -SN<sub>2</sub>C<sub>4</sub>H<sub>5</sub> [ligand](#) symmetrically bridges the hinge metal–metal bonds and these Os–S and Ru–S bond lengths are within the range reported for related compounds.<sup>28a,47,48</sup> The Mn–N bond distance in **4** (2.026(9) Å) and the Re–N bond distances in **3** (2.159(6) Å) and **5** (2.177(3) Å) are quite similar to those observed in **2** (av. 2.054(9) Å) and [Re<sub>2</sub>(CO)<sub>6</sub>( $\mu$ -MepyS)<sub>2</sub>] (av. 2.187(6) Å).<sup>27,49</sup> All other features of these clusters are within the expected range and with an electron count of 62. Compounds **3**, **4**, and **5** are electronically saturated M<sub>4</sub> butterfly clusters. Density functional theory (DFT) calculations of **5** confirm geometric and electronic features of this butterfly cluster, giving an interplanar angle of 155.4°. Selected bond distances and frontier orbitals for **5** are reported in the ESI.<sup>†</sup>

A similar reaction of **2** with Ru<sub>3</sub>(CO)<sub>12</sub> affords [Ru<sub>3</sub>Mn(CO)<sub>13</sub>( $\mu_3$ -SN<sub>2</sub>C<sub>4</sub>H<sub>5</sub>)] (**6**) and the trimanganese complex [Mn<sub>3</sub>(CO)<sub>10</sub>( $\mu$ -Cl)( $\mu_3$ -SN<sub>2</sub>C<sub>4</sub>H<sub>5</sub>)<sub>2</sub>] (**7**) in 18 and 15% yields, respectively ([Scheme 3](#)). As we could not obtain single crystals of **6** suitable for [X-ray diffraction analysis](#), its molecular structure was determined from spectroscopic data and [elemental analysis](#). The spectroscopic data of **6** indicate that it is a direct analog

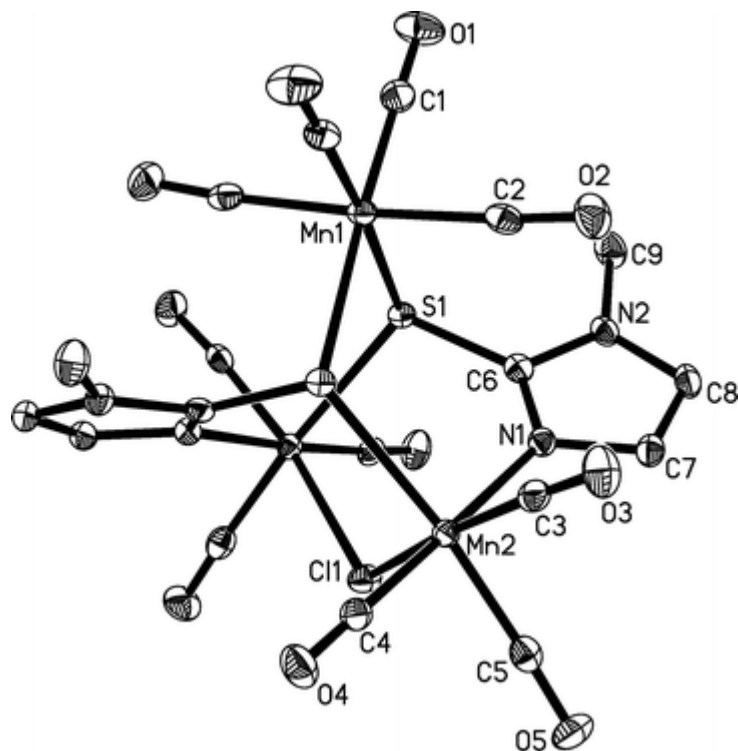
of **3**, **4**, and **5**. The [infrared spectrum](#) in the [carbonyl](#) stretching region is very similar to that of **5** indicating structural similarity whereas the FAB mass spectrum shows the parent molecular ion at  $m/z$  837 together with ions due to the sequential loss of thirteen carbonyl groups. Like **3–5**, the  $^1\text{H}$  NMR spectrum consists of three resonances at  $\delta$  7.11, 6.80, and 3.60 with a relative intensity of 1:1:3 corresponding to the ring [protons](#) and the [methyl protons](#) of the heterocyclic [ligand](#). To our knowledge complexes **3–6** are the first examples of butterfly mixed-metal organometallic clusters of group 7/8 metals with a  $\mu_3$ -heterocyclic [ligand](#).



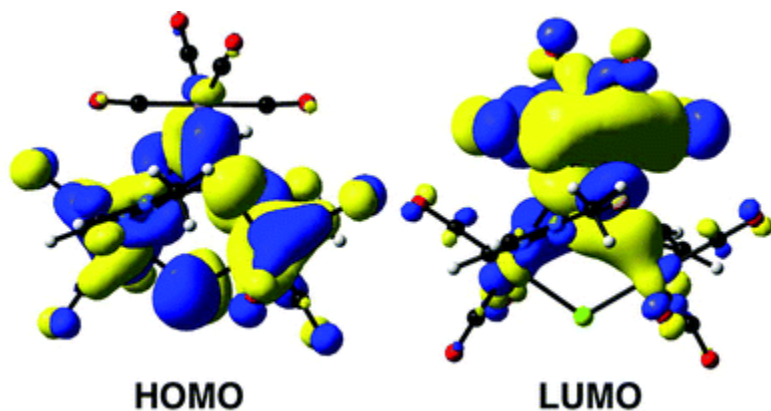
**Scheme 3**

An ORTEP diagram of the molecular structure of **7** is depicted in [Fig. 4](#), and selected bond lengths and angles are listed in the caption. The molecule consists of a trinuclear framework of three manganese atoms with ten terminal carbonyl groups, two triply bridging 2-mercapto-1-methylimidazolate [ligands](#) and a bridging chloride [ligand](#). One manganese atom (Mn(1)) is bonded to four carbonyl groups while the other two manganese atoms bond with three carbonyl groups. Each  $\mu_3$ -SN<sub>2</sub>C<sub>4</sub>H<sub>5</sub> ligand bridges two manganese atoms through the sulfur atom while coordinating with the third manganese atom through a [nitrogen atom](#). The  $\mu_3$ -SN<sub>2</sub>C<sub>4</sub>H<sub>5</sub> [ligands](#) are spatially oriented on opposite sides relative to the Mn<sub>3</sub> plane and bridge the manganese atoms through the sulfur atom (Mn(1) and Mn(2) or Mn(1) and Mn(2)#1) quite asymmetrically (Mn(1)–S(1) 2.3942(6), Mn(2)#1–S(1) 2.4435(6), Mn(1)–S(1)#1 2.3941(6), Mn(2)–S(1)#1 2.4435(6) Å). The Mn–N and the Mn–S bond distances in **7** are close to those observed in **1**.<sup>27</sup> The source of the chloride [ligand](#) was not identified in this study. We can only speculate that it probably came from chlorinated [solvent](#) during chromatographic separation or [recrystallization](#). The chloride [ligand](#) symmetrically bridges (Mn(2)#1–Cl(1) 2.3631(5) Å) the Mn(2) and Mn(2)#1 atoms and the Mn–Cl distance in **7** is somewhat shorter than those observed in [Mn( $\mu$ -Cl){C(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>NMe<sub>2</sub>)}]<sub>2</sub> (av. 2.4275(9) Å) and [Mn(THF)( $\mu$ -Cl){C(SiMe<sub>3</sub>)<sub>2</sub>(SiMe<sub>2</sub>OME<sub>2</sub>)}]<sub>2</sub> (av. 2.488(9) Å).<sup>50</sup> The three Mn···Mn distances in **7** are very long (Mn(1)···Mn(2) 4.169(1) Å, and Mn(2)···Mn(2)#1 3.997 Å) which clearly ruled out the presence of any Mn–Mn bond. Assuming the 2-mercapto-1-methylimidazolate [ligand](#) serves as a 5-electron donor each manganese atom achieves an 18-electron configuration without any metal–metal bond. The [infrared spectrum](#) of **7** indicates the presence of only terminal carbonyl groups while the  $^1\text{H}$  NMR spectrum shows three singlets at  $\delta$  3.99, 6.99, and 7.34 due to the [methyl](#) and ring [protons](#) of the heterocyclic [ligand](#) in a 3:1:1 ratio which is consistent with the solid state structure. To our knowledge there are no known examples of 54-electron trimanganese compounds, which are direct analogs of **7**. Geometry

optimization of **7** by DFT gave a highly symmetric structure, which is in good agreement with X-ray data. The computed Mn(2)–Mn(2)#1 distance is 4.156 Å, and both canonical and NBO<sup>51</sup> population analyses confirm that no interaction is occurring between the two metal atoms. HOMO and LUMO orbitals for **7** are reported in Fig. 5.



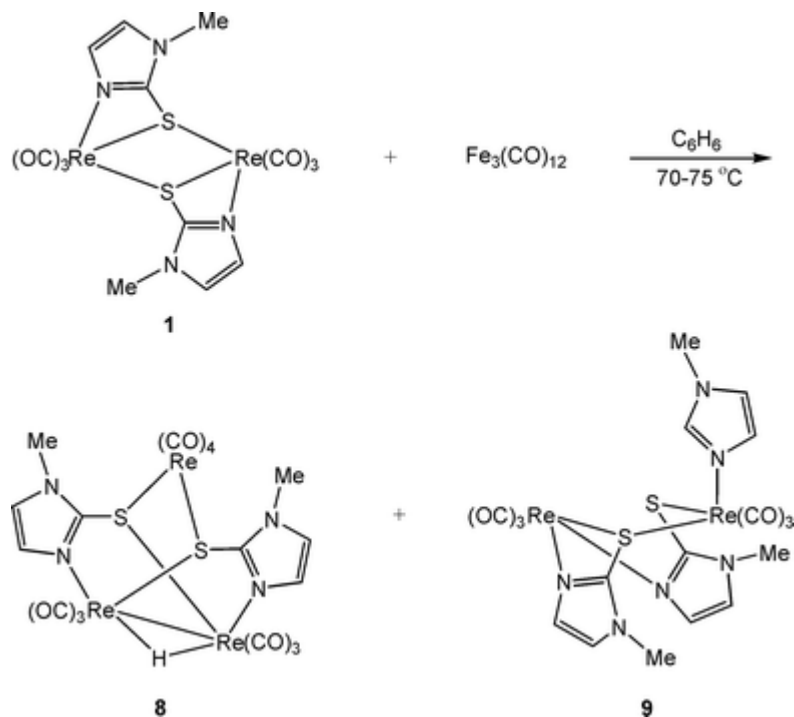
**Fig. 4** ORTEP diagram of the molecular structure of  $[\text{Mn}_3(\text{CO})_{10}(\mu\text{-Cl})(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)_2]$  (**7**), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Mn(1)–S(1) 2.3942(6), Mn(1)–S(1)#1 2.3941(6), Mn(2)–S(1)#1 2.4435(6), Mn(2)#1–S(1) 2.4435(6), Mn(2)–N(1) 2.058(2), Mn(2)#1–Cl(1) 2.3631(5), C(6)–S(1) 1.753(2), S(1)#1–Mn(1)–S(1) 85.27(3), N(1)–Mn(2)–S(1)#1 93.98(5), Cl(1)–Mn(2)–S(1)#1 95.21(2), Mn(2)#1–Cl(1)–Mn(2) 115.52(3).



**Fig. 5** HOMO and LUMO orbitals for **7**.

## (b) Formation of di- and trinuclear rhenium complexes

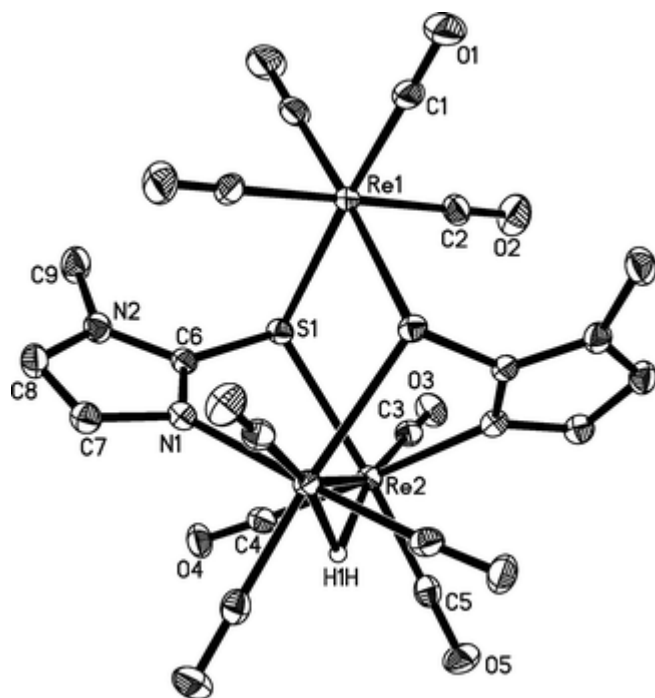
An unprecedented reaction took place when **1** is treated with  $\text{Fe}_3(\text{CO})_{12}$ . Recently, we reported that the reaction of **2** with  $\text{Fe}_3(\text{CO})_{12}$  at 70–75 °C afforded the mixed Fe–Mn complex  $[\text{FeMn}_2(\text{CO})_8(\mu\text{-CO})(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)_2]$ ;<sup>27</sup> whereas, **1** under the same conditions reacts with  $\text{Fe}_3(\text{CO})_{12}$  to give the tri- and dirhenium complexes  $[\text{Re}_3(\text{CO})_{10}(\mu\text{-H})(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)_2]$  (**8**) and  $[\text{Re}_2(\text{CO})_6(\text{N}_2\text{C}_4\text{H}_5)(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$  (**9**) in 11 and 27% yields, respectively (Scheme 4). No other bands were observed in TLC-plates. Heating **2** under the same conditions in the absence of  $\text{Fe}_3(\text{CO})_{12}$  did not make any change. These rhenium complexes have been characterized by elemental analysis, IR and <sup>1</sup>H NMR spectroscopic and mass spectroscopic data and single crystal X-ray diffraction analysis.



Scheme 4

An ORTEP drawing of the molecular structure of **8** is shown in Fig. 6, and selected bond distances and angles are listed in the caption. The molecule contains a trimetallic core of three rhenium atoms with ten terminal carbonyl groups, two 2-mercapto-1-methylimidazole ligands and a bridging hydride complete the coordination sphere of the complex. According to electron counting procedures, the complex should contain a Re–Re bond for each metal atom to achieve the 18-electron configuration. The structure is similar to that of **7** except that a bridging hydride and a metal–metal bond replace the bridging chloride ligand in **7**. The hydride is located in structural analysis and is found to span across the bonding metal–metal edge (Re(2)–Re(2)#1). The Re–Re bond distance in **8** (3.3486(3) Å) is considerably longer than those observed in  $[\text{Re}_3(\text{CO})_8(\mu\text{-CO})(\mu\text{-H})(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)_2]$  (av. 2.9964(13) Å),<sup>27</sup>  $[\text{Re}_2(\text{CO})_7(\text{MeCN})(\mu\text{-C}\equiv\text{CPh})(\mu\text{-H})]$ <sup>52</sup> (3.0788(4) Å)

and the nonhydride bridging vector in  $[\text{Re}_2(\text{CO})_8(\mu\text{-SnPh}_2)]$  (3.1902(4) Å)<sup>53</sup> while the average Re–N and Re–S bond distances in **8** (2.180(13) Å and 2.475(1) Å) are within the range reported for related complexes.<sup>27,49</sup>



**Fig. 6** ORTEP diagram of the molecular structure of  $[\text{Re}_3(\text{CO})_{10}(\mu\text{-H})(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)_2]$  (**8**), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (°): Re(2)–Re(2)#1 3.3486(3), Re(1)–S(1)#1 2.511(1), Re(1)–S(1) 2.511(1), Re(2)–N(1)#1 2.179(4), Re(2)–S(1) 2.550(1), Re(2)–H(1H) 1.97(5), C(6)–S(1) 1.751(4), Re(2)#1–N(1) 2.179(4), S(1)#1–Re(1)–S(1) 84.45(5), C(5)–Re(2)–Re(2)#1 104.4(1), C(4)–Re(2)–Re(2)#1 100.6(1), C(3)–Re(2)–Re(2)#1 159.8(1), N(1)–Re(2)–Re(2)#1 78.7(1), S(1)–Re(2)–Re(2)#1 77.11(2), Re(2)#1–Re(2)–H(1H) 32(2), Re(1)–S(1)–Re(2) 117.62(4).

DFT calculation provides a good description of the geometry and electronic structure of **8**, confirming the presence of a metal–metal bond between Re(2) and Re(2)#1 (see Fig. 6). The computed Re(2)–Re(2)#1 bond distance is 3.477 Å. As shown in Fig. 7, HOMO-3, HOMO-4 and HOMO-5 can account for such an interaction. HOMO and LUMO orbitals in **8** are similar to the frontier orbitals of **7** (Fig. 5 and 7). In both clusters the HOMO is delocalized over the three metal centers, while the LUMO is localized on the Re(1) center. In **7**, however, the HOMO has anti-phase character between Mn(2) and Cl(1) and between Mn(2)#1 and Cl(1), which can account for the long Mn(2)–Mn(2)#1 bond distance (4.156 Å). Calculated Mn(2)–Mn(1) and Mn(2)#1–Mn(1) bond distances are both 4.316 Å, ~0.21 Å shorter than the Re(2)–Re(1) and Re(2)#1–Re(1) ones in **8**. Compound **8** represents a rare example of a 52-electron trirhenium cluster containing a bridging [hydride](#) and two triply bridging heterocyclic [ligands](#). The spectroscopic data of complex **8** are consistent with the solid-state structure being maintained in solution. In addition to the resonances for the [protons](#) of the heterocyclic [ligands](#), the <sup>1</sup>H NMR spectrum shows a singlet at δ–9.41 due to the bridging [hydride ligand](#). The [FAB mass spectrum](#) exhibits the molecular ion at *m/z* 1066 and other ions due to the sequential loss of ten carbonyl groups.

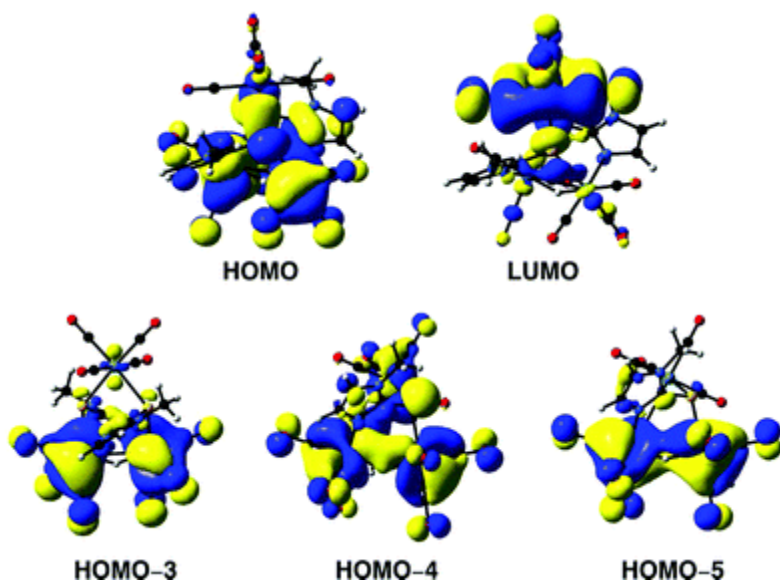
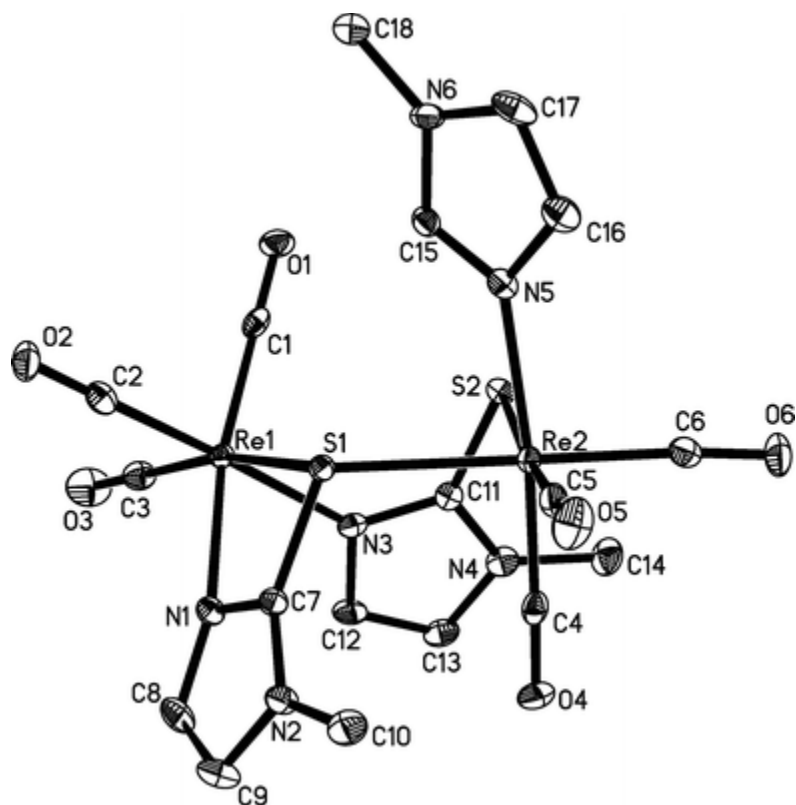


Fig. 7 Selected molecular orbitals of **8**.

An ORTEP diagram of the molecular structure of **9** is depicted in Fig. 8, and selected bond distances and angles are listed in the caption. The molecule consists of a dinuclear framework of two rhenium atoms ligated by six terminal carbonyl groups, three of which are bonded to each of the two rhenium atoms, two bridging 2-mercapto-1-methylimidazolate ligands and a monocoordinated 1-methylimidazole ligand. The coordination modes of the bridging ligands are different: one bridges the rhenium atoms through the sulfur and a nitrogen atom whereas the other bridges the rhenium atoms through the sulfur atom while forming a four-membered chelate ring by coordinating through a nitrogen atom. The 1-methylimidazole is axially coordinated to Re(2). The salient feature of **9** reveals that one of the heterocyclic ligands has undergone C–S bond cleavage upon coordinating to the metal framework, while the other two remain intact within the complex. The average Re–N and Re–S bond distances in **9** (2.186(3) Å and 2.545(1) Å) are comparable to those of **8** and are also in the range found in the literature.<sup>27,49</sup> The Re···Re distance is very long (4.420(1) Å) and clearly a nonbonding distance. The spectroscopic data of compound **9** are fully consistent with the solid-state structure. The <sup>1</sup>H NMR spectrum displays seven resonances at δ 3.65, 3.77, 6.59, 6.82, 6.89, 7.29 and 7.98 in 6:3:2:2:1:1:1 ratio. The resonances at δ 3.65, 6.59 and 6.82 are due to the protons of the bridging 2-mercapto-1-methylimidazolate ligands and the rest of the resonances are due to the protons of the 1-methylimidazole ligand. The FAB mass spectrum shows the parent molecular ion at *m/z* 848 together with fragmentation ions due to the successive loss of six carbonyl groups.





**Fig. 8** ORTEP diagram of the molecular structure of  $[\text{Re}_2(\text{CO})_6(\text{N}_2\text{C}_4\text{H}_5)(\mu\text{-SN}_2\text{C}_4\text{H}_5)]$  (**9**), showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles ( $^\circ$ ): Re(1)–N(1) 2.183(3), Re(1)–N(3) 2.173(3), Re(2)–N(5) 2.203(3), Re(1)–S(1) 2.5873(9), Re(2)–S(1) 2.5245(9), Re(2)–S(2) 2.5222(9), C(7)–S(1) 1.752(4), C(11)–S(2) 1.726(4), N(3)–Re(1)–N(1) 81.6(1), N(3)–Re(1)–S(1) 88.25(8), N(1)–Re(1)–S(1) 65.68(8), N(5)–Re(2)–S(2) 82.33(8), N(5)–Re(2)–S(1) 82.85(8), S(2)–Re(2)–S(1) 86.78(3), Re(2)–S(1)–Re(1) 119.70(3), C(4)–Re(2)–N(5) 173.6(1), C(6)–Re(2)–S(1) 178.4(1), C(5)–Re(2)–S(2) 173.1(1).

## Conclusions

This report demonstrates that the dinuclear complexes **1** and **2** are versatile synthons for the synthesis of group 7/8 tetranuclear mixed-metal clusters **3–6** containing 2-mercapto-1-methylimidazole [ligand](#), all of which possess 62-electron butterfly skeletal arrangement with the group 7 metal (Mn or Re) in a wingtip position. In these reactions, the usefulness of **1** and **2** to open up a novel synthetic strategy to furnish a new butterfly cluster is remarkable. Most probably, the facile M–S bond cleavage in **1** and **2** generates the  $[\text{M}(\text{CO})_3(\text{SN}_2\text{C}_4\text{H}_5)]$  (M = Mn, Re) species in the reaction mixture which reacts with  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  and  $\text{Ru}_3(\text{CO})_{12}$  to form these butterfly clusters. The highly symmetric structure of **7** is consistent with DFT calculations. The mechanism of formation of **7** remains obscure, as attempts to obtain **7** by the reaction of **2** with  $\text{Mn}_2(\text{CO})_{10}$  or  $[\text{Mn}_2(\text{CO})_8(\text{NCMe})_2]$  in refluxing  $\text{CH}_2\text{Cl}_2$  or in [benzene](#) at 70–75  $^\circ\text{C}$ , by heating **7** in [benzene](#) at 70–75  $^\circ\text{C}$  without  $\text{Ru}_3(\text{CO})_{12}$  are, however, unsuccessful. In contrast to the reaction of **2** with  $\text{Fe}_3(\text{CO})_{12}$  which afforded the mixed Mn–Fe complex  $[\text{FeMn}_2(\text{CO})_8(\mu\text{-CO})(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)_2]$ ,<sup>27</sup> the reaction of **1** with  $\text{Fe}_3(\text{CO})_{12}$  did not provide mixed Re–Fe complexes, but led to the formation of the trirhenium complex **8** and the dirhenium complex **9** which can not be obtained from the direct reaction

between  $[\text{Re}_2(\text{CO})_8(\text{NCMe})_2]$  and [2-mercapto-1-methylimidazole](#).<sup>27</sup> Like **7**, compound **8** also has a highly symmetric structure and to our knowledge **8** possesses the longest Re–Re bond (3.3486(3) Å) which is in good agreement with DFT calculations.

## Experimental

All reactions were performed under a [nitrogen](#) atmosphere using standard Schlenk techniques unless otherwise stated. Reagent-grade [solvents](#) were dried by standard procedures and were distilled from appropriate drying agents prior to use. [Infrared spectra](#) were recorded on a Shimadzu FTIR 8101 [spectrophotometer](#). [NMR spectra](#) were recorded on a Bruker DPX 400 instrument. [Mass spectra](#) were recorded on a Varian Mat 312 [mass spectrometer](#). The [metal carbonyl](#) compounds  $(\text{Os}_3(\text{CO})_{12})$ ,  $(\text{Ru}_3(\text{CO})_{12})$ ,  $(\text{Fe}_3(\text{CO})_{12})$ ,  $(\text{Re}_2(\text{CO})_{10})$ , and  $(\text{Mn}_2(\text{CO})_{10})$  were purchased from Strem Chemical Inc. and used without further [purification](#). [2-Mercapto-1-methylimidazole](#) was purchased from Aldrich and used as received. The compounds  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ ,<sup>54</sup>  $[\text{Re}_2(\text{CO})_8(\text{NCMe})_2]$ ,<sup>55</sup>  $[\text{Re}_2(\text{CO})_6(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$ <sup>27</sup> (**1**), and  $[\text{Mn}_2(\text{CO})_6(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$ <sup>27</sup> (**2**) were prepared according to the published procedures.

### Reaction of $[\text{Re}_2(\text{CO})_6(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$ (**1**) with $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$

A solution of  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  (125 mg, 0.134 mmol) and  $[\text{Re}_2(\text{CO})_6(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$  (**1**) (80 mg, 0.104 mmol) in [benzene](#) (100 mL) was heated to reflux for 1 h during which time the color changed from yellow to red. The [solvent](#) was removed under reduced pressure, and the residue chromatographed by [TLC](#) on [silica](#) gel. [Elution](#) with [hexane/acetone](#) (4:1, v/v) developed two bands. The second band afforded  $[\text{Os}_3\text{Re}(\text{CO})_{13}(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)]$  (**3**) (100 mg, 60%) as red crystals from  $\text{CH}_2\text{Cl}_2$ /[hexane](#) at 4 °C. The first band gave too little product for complete characterization. Spectral data for **3**: Anal. Calcd for  $\text{C}_{17}\text{H}_5\text{N}_2\text{O}_{13}\text{Os}_3\text{ReS}$ : C, 16.54; H, 0.41; N, 2.27. Found: C, 16.69; H, 0.43; N, 2.35%. [IR](#) ( $\nu_{\text{CO}}$ ,  $\text{CH}_2\text{Cl}_2$ ): 2108 (m), 2062 (w), 2043 (vs), 2023 (m), 2011 (m), 1983 (w), 1963 (w), 1909 (vw)  $\text{cm}^{-1}$ . [<sup>1</sup>H NMR](#) ( $\text{CDCl}_3$ ):  $\delta$  3.98 (s, 3H), 6.89 (d,  $J = 1.3$  Hz, 1H), 7.57 (d,  $J = 1.3$  Hz, 1H).

### Reaction of $[\text{Mn}_2(\text{CO})_6(\mu\text{-SN}_2\text{C}_4\text{H}_5)_2]$ (**2**) with $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$

A similar reaction to that above of  $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$  (225 mg, 0.241 mmol) and **2** (60 mg, 0.119 mmol) followed by similar chromatographic separation afforded  $[\text{Os}_3\text{Mn}(\text{CO})_{13}(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)]$  (**4**) as red crystals (236 mg, 88%) after [recrystallization](#) from [hexane](#)/ $\text{CH}_2\text{Cl}_2$  at 4 °C. Spectral data for **4**: Anal. Calcd for  $\text{C}_{17}\text{H}_5\text{MnN}_2\text{O}_{13}\text{Os}_3\text{S}$ : C, 18.51; H, 0.46; N, 2.54. Found: C, 18.62; H, 0.42; N, 2.51%. [IR](#) ( $\nu_{\text{CO}}$ ,  $\text{CH}_2\text{Cl}_2$ ): 2106 (m), 2069 (vw), 2040 (vs), 2021 (vw), 2002 (s), 1961 (w), 1917 (w) 1869 (vw)  $\text{cm}^{-1}$ . [<sup>1</sup>H NMR](#) ( $\text{CDCl}_3$ ):  $\delta$  3.97 (s, 3H), 7.06 (s, 1H), 8.04 (s, 1H). [MS](#):  $m/z$  1102 ( $\text{M}^+$ ).

### Reaction of **1** with $(\text{Ru}_3(\text{CO})_{12})$

To a [benzene](#) solution (50 mL) of  $(\text{Ru}_3(\text{CO})_{12})$  (86 mg, 0.134 mmol) was added **1** (100 mg, 0.130 mmol) and the mixture was heated to reflux for 45 min. The [solvent](#) was removed under vacuum, and the residue was taken up in  $\text{CH}_2\text{Cl}_2$  and applied to [silica](#) gel TLC plates. [Elution](#) with [hexane/acetone](#) (7:3, v/v) gave one major and several minor bands. The major band afforded  $[\text{ReRu}_3(\text{CO})_{13}(\mu_3\text{-SN}_2\text{C}_4\text{H}_5)]$  (**5**) as deep red crystals (31 mg, 24%) from [hexane](#)/ $\text{CH}_2\text{Cl}_2$  at 4 °C while the content of the minor bands was too small for complete



characterization. Spectral data for **5**: Anal. Calcd for  $C_{17}H_5N_2O_{13}ReRu_3S$ : C, 21.12; H, 0.52; N, 2.90. Found: C, 21.68; H, 0.49; N, 2.93%. [IR](#) ( $\nu_{CO}$ ,  $CH_2Cl_2$ ): 2100 (m), 2035 (s), 2002 (s), 1952 (m), 1911 (m), 1894 (m),  $cm^{-1}$ .  [\$^1H\$  NMR](#) ( $CDCl_3$ ):  $\delta$  4.07 (s, 3H), 6.97 (d,  $J = 1.3$  Hz, 1H), 7.46 (d,  $J = 1.3$  Hz, 1H).

### Reaction of **2** with $Ru_3(CO)_{12}$

A mixture of  $Ru_3(CO)_{12}$  (126 mg, 0.197 mmol) and **2** (100 mg, 0.198 mmol) in [benzene](#) was heated at 70–75 °C for 1 h. After removal of the [solvent](#) under reduced pressure, the residue was chromatographed by [TLC](#) on [silica](#) gel. [Elution](#) with [hexane](#)/ $CH_2Cl_2$  (7:3 v/v) developed three bands. The faster moving band gave unreacted  $Ru_3(CO)_{12}$  (trace), while the second and third bands afforded  $[Mn_3(CO)_{10}(\mu-Cl)(\mu_3-SN_2C_4H_5)_2]$  (**7**) as orange crystals (18 mg, 15%) and  $[Ru_3Mn(CO)_{13}(\mu_3-SN_2C_4H_5)]$  (**6**) as red crystals (30 mg, 18%), respectively, from  $CH_2Cl_2$ /[hexane](#) at 4 °C. Spectral data for **6**: Anal. Calcd for  $C_{17}H_5MnN_2O_{13}Ru_3S$ : C, 24.40; H, 0.60; N, 3.35. Found: C, 24.51; H, 0.64; N, 3.39%. [IR](#) ( $\nu_{CO}$ ,  $CH_2Cl_2$ ): 2099 (m), 2075 (w), 2044 (m), 2034 (s), 2004 (s), 1954 (m), 1925 (m)  $cm^{-1}$ .  [\$^1H\$  NMR](#) ( $CDCl_3$ ):  $\delta$  3.60 (s, 3H), 6.80 (s, 1H), 7.11 (s, 1H). [MS](#):  $m/z$  837 ( $M^+$ ). Spectral data for **7**: Anal. Calcd for  $C_{18}H_{10}ClMnN_3N_4O_{10}S_2$ : C, 34.78; H, 1.61; N, 9.02. Found: C, 34.92; H, 1.70; N, 9.38%. [IR](#) ( $\nu_{CO}$ ,  $CH_2Cl_2$ ): 2088 (m), 2035 (m), 2025 (vs), 2007 (s), 1967 (m), 1943 (s), 1928 (s)  $cm^{-1}$ .  [\$^1H\$  NMR](#) ( $CDCl_3$ ):  $\delta$  3.99 (s, 3H), 6.99 (s, 1H), 7.34 (s, 1H).

### Reaction of **1** with $Fe_3(CO)_{12}$

A mixture of  $Fe_3(CO)_{12}$  (200 mg, 0.396 mmol) and **1** (152 mg, 0.198 mmol) was heated at 70–75 °C for 2 h. The [solvent](#) was removed under vacuum, and the residue was chromatographed by [TLC](#) on [silica](#) gel. [Elution](#) with [hexane](#)/[acetone](#) (7:3, v/v) gave three bands. The first band was unreacted  $Fe_3(CO)_{12}$ . The second and third bands gave  $[Re_3(CO)_{10}(\mu-H)(\mu_3-SN_2C_4H_5)_2]$  (**8**) as white crystals (15 mg, 11%) and  $[Re_2(CO)_6(N_2C_4H_5)(\mu-SN_2C_4H_5)_2]$  (**9**) as colorless crystals (45 mg, 27%) after [recrystallization](#) from [hexane](#)/ $CH_2Cl_2$  at 4 °C. Spectral data for **8**: Anal. Calcd for  $C_{18}H_{11}N_4O_{10}Re_3S_2$ : C, 20.28; H, 1.04; N, 5.26. Found: C, 20.55; H, 1.09; N, 5.31%. [IR](#) ( $\nu_{CO}$ ,  $CH_2Cl_2$ ): 2104 (w), 2034 (m), 2020 (s), 2010 (m), 1999 (m), 1956 (m), 1922 (s)  $cm^{-1}$ .  [\$^1H\$  NMR](#) ( $CDCl_3$ ):  $\delta$  3.93 (s, 3H), 6.71 (d,  $J = 1.3$  Hz, 1H), 7.15 (d,  $J = 1.3$  Hz, 1H), -9.41 (s, 1H). [MS](#):  $m/z$  1066 ( $M^+$ ). Spectral data for **9**: Anal. Calcd for  $C_{18}H_{16}N_6O_6Re_2S_2$ : C, 25.47; H, 1.90; N, 9.90. Found: C, 25.63; H, 1.96; N, 9.94%. [IR](#) ( $\nu_{CO}$ ,  $CH_2Cl_2$ ): 2011 (vs), 1908 (vs, br)  $cm^{-1}$ .  [\$^1H\$  NMR](#) ( $CDCl_3$ ):  $\delta$  3.65 (s, 6H), 3.77 (s, 3H), 6.59 (s, 2H), 6.82 (s, 2H), 6.89 (s, 1H), 7.29 (s, 1H), 7.98 (s, 1H). [MS](#):  $m/z$  848 ( $M^+$ ).

### X-Ray structure determinations

Single crystals were mounted on fibres and [diffraction data](#) collected at low temperature (see [Table 1](#)) on Bruker [AXS](#) SMART APEX2 [CCD](#) (for compounds **3**, **5**, **7**, **8** and **9**) and Nonius KappaCCD (for compound **4**) diffractometers using Mo and Cu  $K\alpha$  radiation ( $\lambda = 0.71073, 1.54178$  Å). Data collection, indexing and initial cell refinements were all done using SMART<sup>56</sup> (for compounds **3**, **5**, **7**, **8** and **9**) and DENZO and COLLECT<sup>57</sup> (for compound **4**) softwares. Data [reduction](#) was accomplished with SAINT<sup>58</sup> and DENZO and COLLECT<sup>57</sup> (for compound **4**) softwares and the SADABS<sup>59</sup> and SORTAV<sup>60</sup> programs were used to apply empirical absorption corrections. The structures were solved by direct methods<sup>61</sup> and refined by full [matrix](#) least-squares.<sup>62</sup> All non-hydrogen atoms were refined anisotropically and hydrogen atoms were

included using a riding model. Scattering factors were taken from International Tables for [X-ray Crystallography](#).<sup>63</sup> Additional details of data collection and structure refinement are given in [Table 1](#).

**Table 1** [Crystallographic data](#) and structure refinement for **3–5** and **7–9**

Compound	3	4	5	7	8	9
Empirical formula	C <sub>17</sub> H <sub>5</sub> N <sub>2</sub> O <sub>13</sub> Os <sub>3</sub> ReS	C <sub>17</sub> H <sub>5</sub> MnN <sub>2</sub> O <sub>13</sub> Os <sub>3</sub> S	C <sub>17</sub> H <sub>5</sub> N <sub>2</sub> O <sub>13</sub> Re Ru <sub>3</sub> S	C <sub>18</sub> H <sub>10</sub> ClMn <sub>3</sub> N <sub>4</sub> O <sub>10</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>11</sub> N <sub>4</sub> O <sub>10</sub> R e <sub>3</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>16</sub> N <sub>6</sub> O <sub>6</sub> R e <sub>2</sub> S <sub>2</sub>
Formula weight	1234.09	1102.83	966.70	706.69	1066.03	848.89
Temp (K)	100(2)	150(2)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	1.54178	0.71073	1.54178	1.54178	1.54178	1.54178
Crystal system	triclinic	triclinic	monoclinic	trigonal	monoclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 32 2 1	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<i>a</i> /Å	8.5336(2)	8.6591(2)	8.7351(1)	9.4042(1)	15.3127(3)	9.1679(1)
<i>b</i> /Å	9.8660(2)	9.8458(1)	17.1338(3)	9.4042(1)	9.9180(2)	11.5587(2)
<i>c</i> /Å	15.0910(3)	15.1081(2)	16.4842(2)	24.1341(4)	18.0203(3)	12.2641(2)
$\alpha$ /°	107.084(1)	106.8599(8)	90	90	90	74.976(1)
$\beta$ /°	91.436(1)	91.7599(8)	91.253(1)	90	110.084(1)	87.691(1)
$\gamma$ /°	92.688(1)	93.1069(7)	90	120	90	76.220(1)
<i>V</i> /Å <sup>3</sup>	1212.15(4)	1229.42(4)	2466.53(6)	1848.44(4)	2570.34(8)	1218.74(3)
<i>Z</i>	2	2	4	3	4	2
<i>D</i> <sub>calc</sub> (Mg m <sup>-3</sup> )	3.381	2.979	2.603	1.905	2.755	2.313
$\mu$ (Mo <i>K</i> $\alpha$ ) (mm <sup>-1</sup> )	39.929	16.107	25.380	15.473	29.085	21.142
<i>F</i> (000)	1088	988	1792	1050	1936	792
Crystal size (mm)	0.22 × 0.15 × 0.15 × 0.12 × 0.12	0.15 × 0.12 × 0.12 × 0.12 × 0.12	0.35 × 0.24 × 0.20 × 0.20 × 0.20	0.55 × 0.22 × 0.21 × 0.21 × 0.21	0.41 × 0.18 × 0.13 × 0.13 × 0.13	0.44 × 0.18 × 0.10 × 0.10 × 0.10
$\vartheta$ range (°)	4.70–67.24	3.01–25.50	5.16–67.47	5.43–66.98	5.23–67.84	3.73–67.72
Index ranges	– 9 ≤ <i>h</i> ≤ 10, –11 ≤ <i>k</i> ≤ 10, ≤ <i>l</i> ≤ 17	–10 ≤ <i>h</i> ≤ 10, –11 ≤ <i>k</i> ≤ 18, –18 ≤ <i>l</i> ≤ 18	–10 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 19, 0 ≤ <i>l</i> ≤ 19	–11 ≤ <i>h</i> ≤ 5, 0 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 28	–18 ≤ <i>h</i> ≤ 17, 0 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 21	–10 ≤ <i>h</i> ≤ 10, –12 ≤ <i>k</i> ≤ 13, 0 ≤ <i>l</i> ≤ 14
Reflections collected	10170	24356	20686	15358	10588	10091
Independent reflections ( <i>R</i> <sub>int</sub> )	3988 (0.0253)	4553 (0.1376)	4288 (0.0314)	2167 (0.0307)	2284 (0.0229)	4142 (0.0197)
Max. and min. transmission	0.0866 and 0.0413	0.2481 and 0.1961	0.0806 and 0.0408	0.1395 and 0.0429	0.1161 and 0.0295	0.2263 and 0.0387
Data/restraints/parameters	3988/0/336	4553/0/336	4288/0/350	2167/0/193	2284/0/172	4142/0/311
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.070	1.039	1.064	1.074	1.034	1.053
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0256, <i>wR</i> <sub>2</sub> = 0.0647	<i>R</i> <sub>1</sub> = 0.0665, <i>wR</i> <sub>2</sub> = 0.1809	<i>R</i> <sub>1</sub> = 0.0201, <i>wR</i> <sub>2</sub> = 0.0502	<i>R</i> <sub>1</sub> = 0.0183, <i>wR</i> <sub>2</sub> = 0.0429	<i>R</i> <sub>1</sub> = 0.0190, <i>wR</i> <sub>2</sub> = 0.0505	<i>R</i> <sub>1</sub> = 0.0201, <i>wR</i> <sub>2</sub> = 0.0544

Compound	3	4	5	7	8	9
<i>R</i> indices (all data)	$R_1 =$ 0.0277, $wR_2 =$ 0.0659	$R_1 =$ 0.0679, $wR_2 =$ 0.1840	$R_1 =$ 0.0214, $wR_2 =$ 0.0509	$R_1 =$ 0.0187, $wR_2 =$ 0.0430	$R_1 =$ 0.0191, $wR_2 =$ = 0.0506	$R_1 =$ 0.0207, $wR_2 =$ = 0.0548
Largest difference in peak and hole ( $e \text{ \AA}^{-3}$ )	1.640 -0.837	and 3.290 -4.927	and 0.795 -0.487	and 0.283 -0.186	and 0.790 -0.991	and 1.009 -0.561

## Computational details

Calculations were performed with the Gaussian 03 (G03) program package<sup>64</sup> employing the DFT method with Becke three parameter hybrid functional<sup>65</sup> and Lee–Yang–Parr's gradient corrected correlation functional (B3LYP).<sup>66</sup> Geometry optimization of **5**, **7**, and **8** in the gas phase was performed employing the LanL2DZ basis set.<sup>67</sup> No symmetry constraints were adopted in the geometry optimization of all the compounds. The nature of all stationary points was confirmed by normal mode analysis. Selected geometry parameters for **5**, **7** and **8** are reported in the ESI.<sup>†</sup>

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## Footnote

† Electronic supplementary information (ESI) available: Selected geometry parameters for the DFT optimized structures and LUMO orbitals for **5**. CCDC reference numbers 665809 for **3**, 686167 for **4**, 665810 for **5**, 665806 for **7**, 693306 for **8**, and [crystallographic data](#) in CIF or other electronic format see DOI:[10.1039/b819226j](https://doi.org/10.1039/b819226j)