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Manganese containing heterometallic clusters containing ligands derived from elements of Groups 15 and 16†

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The area of manganese-containing mixed-metal clusters is reviewed. Discussion is divided into two sections: that containing clusters bridged by ligands derived from elements of Group 15 and those containing ligands derived from the Group 16 elements of the Periodic Table. Emphasis is given to synthetic strategies and those reactivity features which result in Mn-containing new cluster formations.

Keywords: **Manganese, mixed-metal, group 15, group 16.**

INTRODUCTION

The subject of mixed-metal clusters continues to be of immense interest. A major challenge in this area of cluster chemistry has been to develop suitable methodologies for obtaining novel clusters of desired structural and reactivity features which may be modulated for particular applications. This review focuses on manganese-containing mixed-metal clusters, in particular, the synthetic methods used in which bridging and stabilizing ligands derived from elements of Groups 15 and 16 of the Periodic Table have been employed.

Clusters containing ligands derived from Group 15 elements:

Low temperature reaction of $[(MeC_5H_4)Mn(CO)_2(^tBu_2PH)]$ (**1**) with butyllithium and subsequent treatment with a THF solution of $[M(COD)Cl]_2$ (M = Rh, Ir) at -20ºC gives a phosphido bridged heterobimetallic compound $[(MeC_5H_4)(CO)MnM(COD)(\mu$-

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† **Dedicated to Professor Dr. Dieter Fenske on the occasion of his 65th birthday.**

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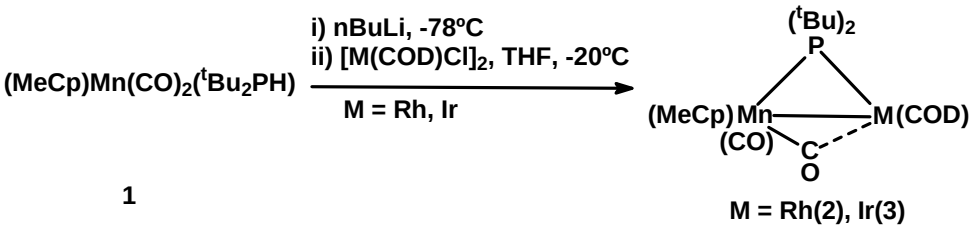
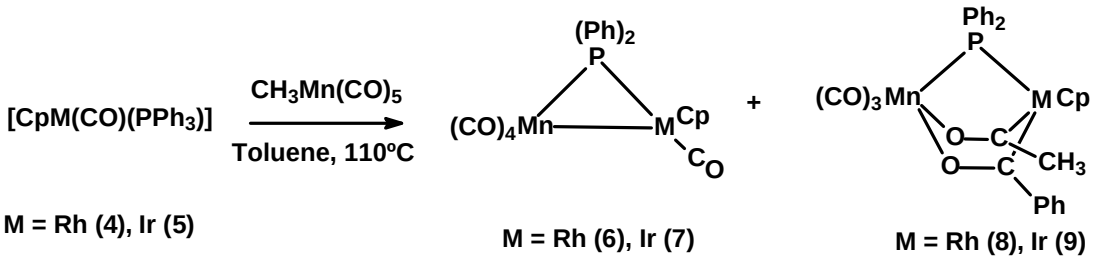
CO)(μ-P(^{t}Bu)$_2$] (M = Rh (**2**), Ir (**3**)) (Scheme 1) [1]. Compounds **2** and **3** are isostructural and consist of a doubly bridging ^{t}Bu$_2$P unit and a semi-doubly bridging carbonyl group between the Mn-M bond. Other ligands include a terminal carbonyl and a pentahapto MeC_5H_4 group bonded to manganese atom and a cyclooctadienyl group linked to Rh or Ir atom. Assuming that a donor - acceptor Mn→M bond (Mn-Rh = 2.708(2) Å, Mn-Ir = 2.627(4) Å) exists, the total electron count around manganese is 18 whereas rhodium or iridium have 16 electrons.



Scheme 1

Thermal reaction of a toluene solution of [CpM(CO)(PPh_3)] (M = Rh (**4**), Ir (**5**)) and [$CH_3Mn(CO)_5$] in reflux condition yields phosphido bridged mixed metal compounds [CpMMn(CO)$_4$(μ-PPh_2)] (M = Rh (**6**), Ir (**7**)) and [CpM{μ-C(Ph)O}{μ-C(CH_3)O}{μ-PPh_2}Mn(CO)$_3$] (M = Rh (**8**), Ir (**9**)) (Scheme 2) [2].



Scheme 2

A synthetic procedure involving dehalogenation reaction has been used to prepare several heterometallic phosphinidene type complexes. Complexes [($CH_3C_5H_4$)(CO)$_2$Mn(μ$_2$-PR^1R^2)Co(CO)$_3$] (**12** : R^1 = Ph, R^2 = H; **13**: R^1 = R^2 = Ph) (Figure 1) have been obtained by the reaction of [($CH_3C_5H_4$)(CO)$_2$MnPPhBr$_2$] (**10**) and [$NaCo(CO)_4$] or from the reaction between [($CH_3C_5H_4$)(CO)$_2$MnPPh_2Cl] (**11**) and [$NaCo(CO)_4$] [3]. X-ray structure has been solved for [($CH_3C_5H_4$)(CO)$_2$Mn(μ$_2$-

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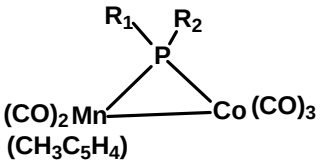
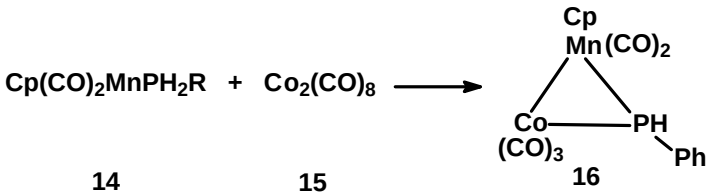
PPhH)Co(CO)$_3$] (**12**) and reveals the presence of a MnCoP triangular planar core in which the P(H)Ph group is doubly bridged to ($CH_3C_5H_4$)Mn(CO)$_2$ and Co(CO)$_3$ units.



12: R^1 = Ph, R^2 = H
13: R^1 = R^2 = Ph

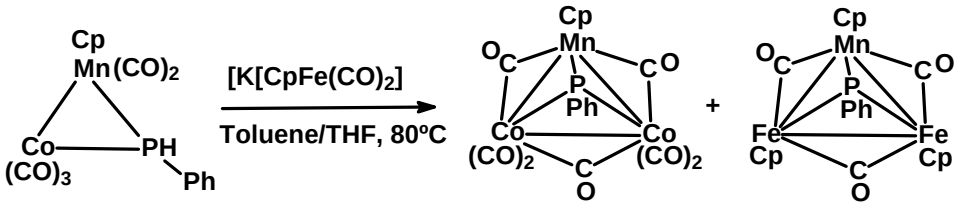
Figure 1

A metallacyclic phosphane type compound [CpMnCo(CO)$_5$(μ-P(H)Ph)] (**16**) has been obtained by the reaction of [Cp(CO)$_2$MnPH$_2$Ph] (**14**) with [Co$_2$(CO)$_8$] (**15**). It further reacts with [K{CpFe(CO)$_2$}] under thermolytic condition to give [CpMnCo$_2$(CO)$_4$(μ-CO)$_3$(μ$_3$-PPh)] (**17**) and a diiron-manganese cluster [Cp$_3$MnFe$_2$(μ-CO)$_3$(μ$_3$-PPh)] (**18**) (Scheme 3, 4) [4,5]. Both compounds (**17**, **18**) contain a tetrahedral MnM$_2$P core (M = Co, Fe), with each metal – metal bond bridged by a carbonyl ligand.



14 **15** **16**

Scheme 3



16 **17** **18**

Scheme 4

Thermolytic reaction of a toluene solution of [Cp$_2$(CO)$_4$Mo$_2$(μ-PH$_2$)(μ-H)] (**19**) with [Mn$_2$(CO)$_{10}$] results in the formation of a phosphorus bridged molybdenum-manganese heterometallic cluster, [Cp$_2$(CO)$_4$Mo$_2$Mn(CO)$_4$(μ$_3$-P)] (**20**) (Scheme 5) [6].

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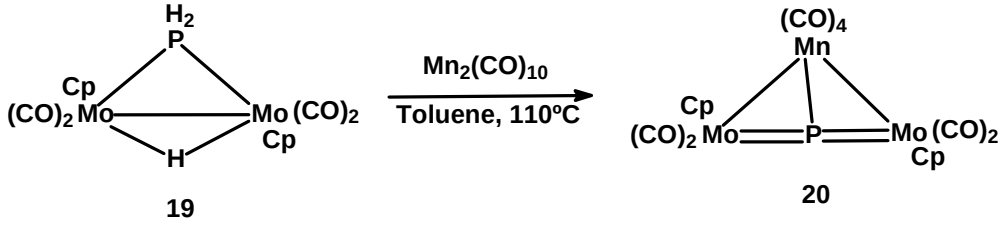
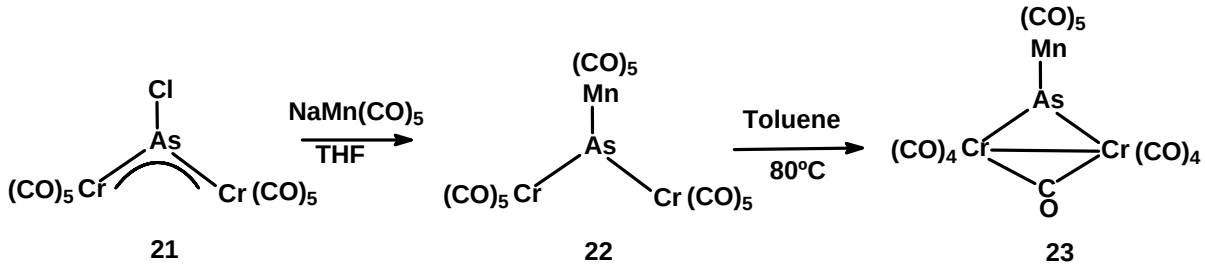
Its structural analysis reveals a planar Mo_2PMn core with two terminally bonded carbonyl ligands and one Cp ligand on each of the two molybdenum atoms and four terminal carbonyls attached to the manganese center. The average Mo-P bond length of 2.2619 Å is comparable to the Mo=P double bond distance (2.297(8) Å) in $[Cp_2(CO)_4Mo_2(\mu\text{-PMes})]$ [7]. Transformation of **19** (Mo-P-Mo bond angle of 86.19(5)º) to **20** causes an increase of the Mo-P-Mo bond angle to 170.06(4)º.



19 **20**

Scheme 5

Treatment of $[\{Cr(CO)_5\}_2\{\mu_2\text{-AsCl}\}]$ (**21**) with $[NaMn(CO)_5]$ in THF, results in formation of $[Mn(CO)_5\{Cr(CO)_5\}_2\{\mu_3\text{-As}\}]$ (**22**). Thermolysis of **22** results in the formation of a Cr_2Mn cluster, $[Mn(CO)_5\{Cr_2(CO)_9\}\{\mu_3\text{-As}\}]$ (**23**) (Scheme 6) [8] in which a μ_3 – As ligand bridges a $Cr_2(CO)_9$ unit (Cr-Cr = 3.001(6) Å) and a $Mn(CO)_5$ group.



21 **22** **23**

Scheme 6

Room temperature reaction of a THF solution of $[\{L'Mn(CO)_2\}\{ML\}\{\mu_2\text{-AsCl}\}]$ (L' = Cp, ML = $Cr(CO)_5$ (**24a**); L' = Cp', ML = $Mn(CO)_2Cp'$ (**24b**)) with $[CpMo(CO)_3Na]$ gives arsenic bridged heterometallic clusters $[\{L'Mn(CO)_2\}\{CpMo(CO)_2ML\}\{\mu_3\text{-As}\}]$ (L' = Cp, ML = $Cr(CO)_5$ (**25**); L' = Cp', ML = $Mn(CO)_2Cp'$ (**26**)) in which an arsenic atom triply bridges three metal atoms (Scheme 7) [8, 9].

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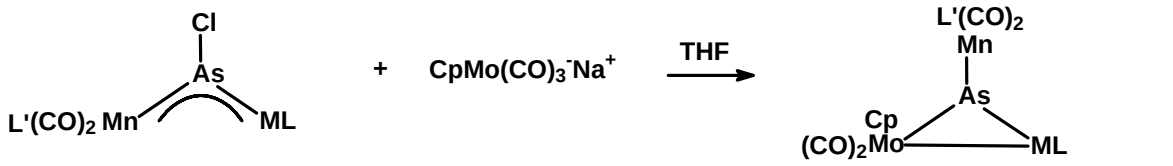
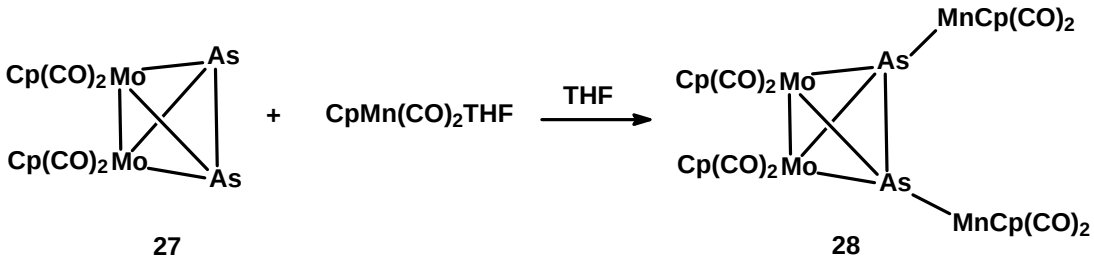


24a: ML = $Cr(CO)_5$, L' = Cp
24b: ML = $Mn(CO)_2Cp'$, L' = Cp'

25: ML = $Cr(CO)_5$, L' = Cp
26: ML = $Mn(CO)_2Cp'$, L' = Cp'

Scheme 7

A diarsenic Mo/Mn cluster $[Cp_2Mo_2(CO)_4(\mu_3\text{-}As_2)\{CpMn(CO)_2\}_2]$ (**28**) has been obtained by a reaction of $[Cp_2Mo_2(CO)_4(\mu\text{-}As_2)]$ (**27**) with $[CpMn(CO)_2THF]$. The structure of **28** shows a Mo_2As_2 framework with each arsenic atom bonded to a $CpMn(CO)_2$ unit (Scheme 8) [10].



27 **28**

Scheme 8

Iron-manganese heterometallic clusters (**29**-**32**, Scheme 9) containing bridging phosphorus atoms have been obtained from the reaction of $[LMn(CO)_2PCl_3]$ (L = Cp, $CH_3C_5H_4$) with $[Fe_2(CO)_9]$ in toluene at 50ºC (Scheme 9) [11]. Structural characterization of compounds **29**-**32** reveals a trigonal bipyramidal $[Fe_3(\mu_3\text{-}P)_2]$ framework in which the axial positions are occupied by the phosphorus atoms. One carbonyl group on each of the three iron atoms in **29** can be substituted by a phosphite ligand to give the trisubstituted derivative, **33** (Scheme 10).

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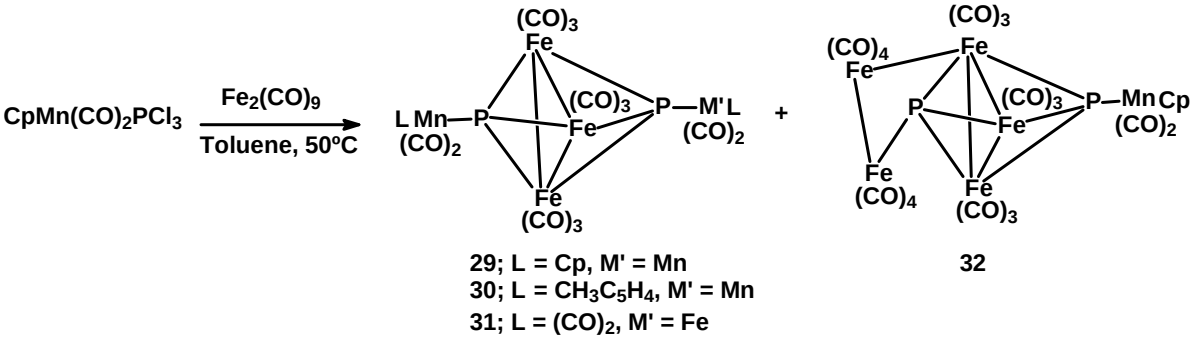
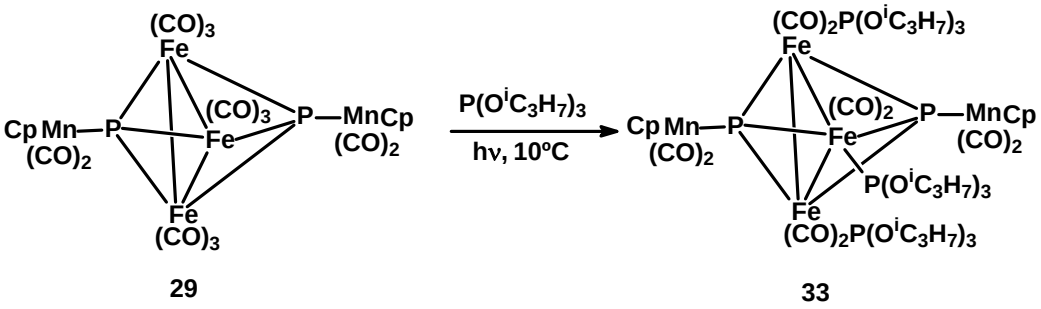
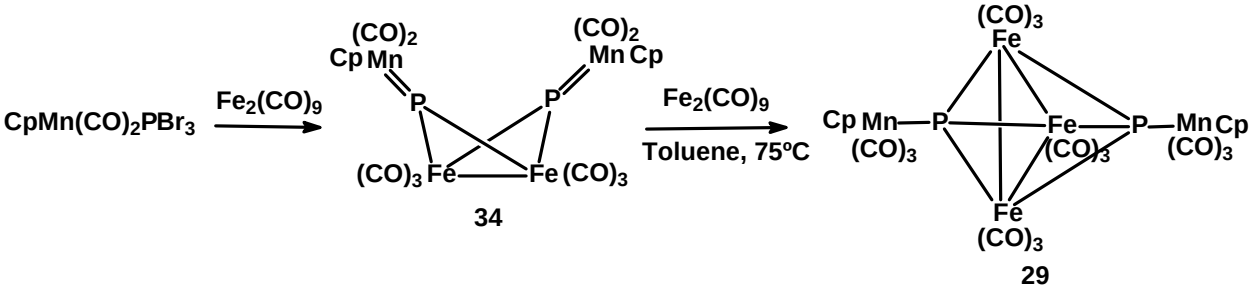


Scheme 9



Scheme 10

Room temperature reaction between $[CpMn(CO)_2PBr_3]$ and $[Fe_2(CO)_9]$ gives the tetranuclear iron-manganese compound $[Fe_2(CO)_6\{PMnCp(CO)_2\}_2]$ (**34**), which on heating in toluene at 75ºC gives **29** (Scheme 11) [12]. Structure of compound **34** has been characterized by X-ray crystallography and contains a butterfly Fe_2P_2 framework with two triply bridging phosphorus atoms at the wing tip positions. Each phosphorus atom is further bonded to a $[CpMn(CO)_2]$ unit.



Scheme 11

The arsenic - bridged Fe_3Mn cluster, $[Fe_3(CO)_9\{\mu_3\text{-}AsMnCp(CO)_2\}_2]$ (**35**) has been obtained by first a low temperature reaction between $[CpMn(CO)_2THF]$ and $AsCl_3$

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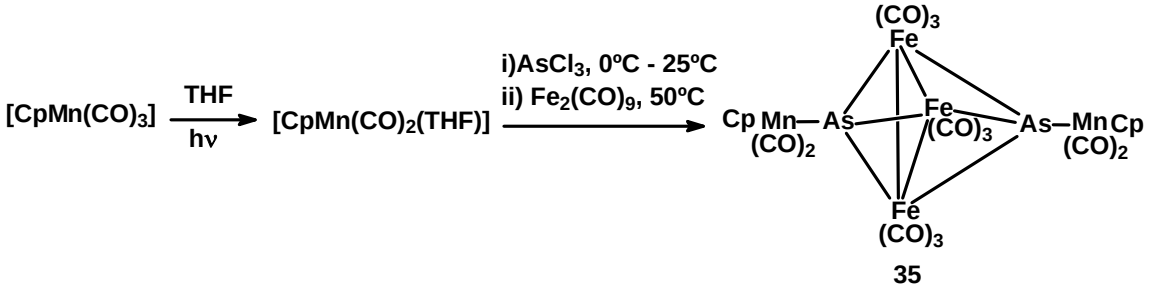
and then by addition of $[Fe_2(CO)_9]$ and mild thermolysis of the reaction mixture (Scheme 12). On the other hand, the antimony analogue $[Fe_3(CO)_9\{\mu_3\text{-}SbMnCp(CO)_2\}_2]$ (**37**), is isolated by a room temperature reaction of $[ClSb\{CpMn(CO)_2\}_2]$ (**36**) with $[Na_2Fe_2(CO)_8]$ (Scheme 13).



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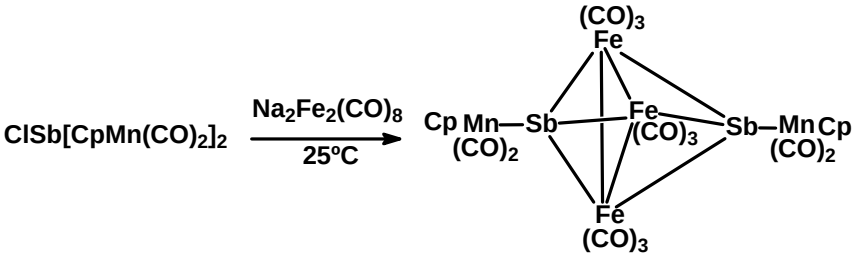
Scheme 12



36 **37**

Scheme 13

Manganese phosphine complexes, $[Cp(CO)_2MnPRCl_2]$ (R = C_6H_5 (**38**), $CH_2C_6H_5$ (**39**)), undergo dehalogenation reactions to form a variety of mixed metal clusters containing triply bridging phosphido ligand. Thus, $[Cp(CO)_2MnPRCl_2]$ (R = C_6H_5 (**38**), $CH_2C_6H_5$ (**39**)) reacts with $[Fe_2(CO)_9]$ at 40ºC in toluene to give three Fe-Mn heterometallic clusters (**40**-**42**) (Scheme 14) [13,14,15]. Compound **40** undergoes two reversible decarbonylations to form **41** and **42**. When a toluene solution of $[Cp(CO)_2MnPRCl_2]$ (R = C_6H_5 (**38**), $CH_2C_6H_5$ (**39**)) and $[CpCo(CO)_2]$ are heated at 115ºC, a trimetallic cluster $[Cp_2Co_2(CO)_2\{\mu\text{-}P(R)(CpMn(CO)_2)\}]$ (R = C_6H_5 (**43a);** $CH_2C_6H_5$ **(43b)**) are formed (Scheme 14) [16]. Structure analysis of **43b** reveals a $Cp_2Co_2(CO)_2$ unit in which the Co-Co bond (Co-Co = 2.549(2) Å) is bridged by a $[P(CH_2C_6H_5)(CpMn(CO)_2)]$ group forming a triangular Co_2P plane. The Cp ligands on

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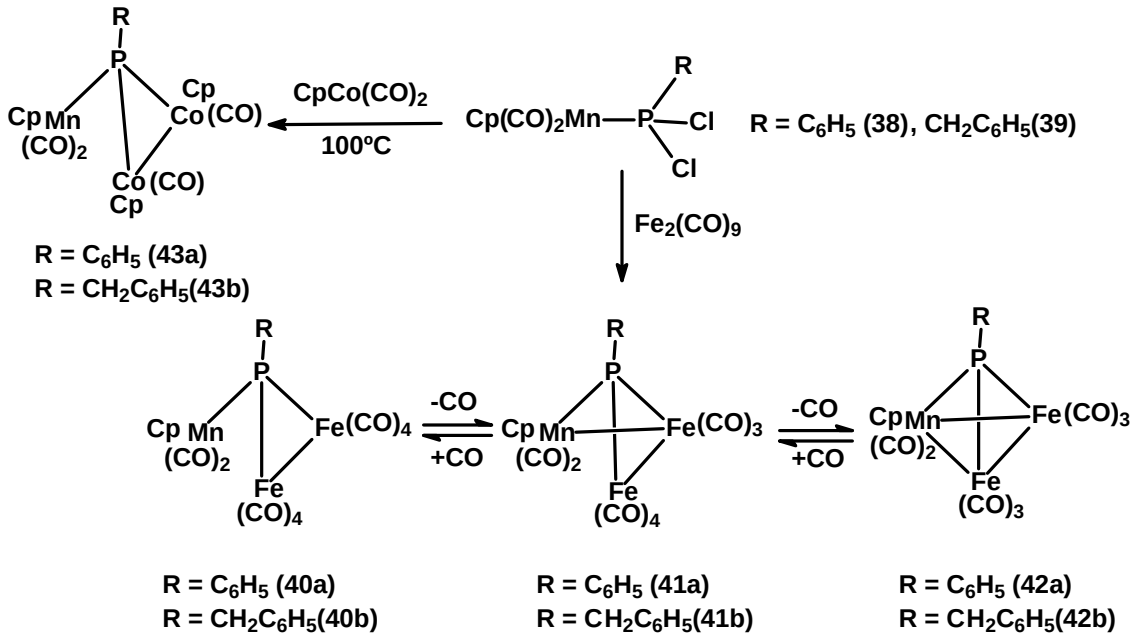
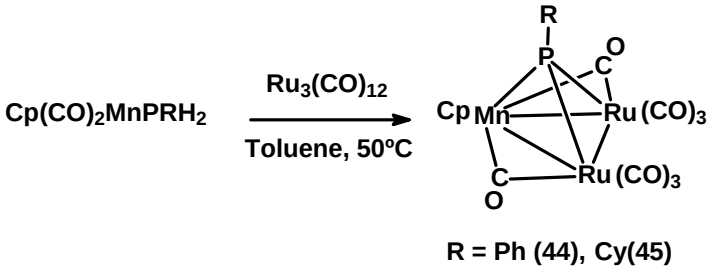
the cobalt atoms are on the opposite side of the triangular plane mutually *trans* to each other, and a $CpMn(CO)_2$ unit is attached to the phosphorus atom.



Scheme 14

Reaction of complexes $[Cp(CO)_2MnPRH_2]$ (R = Ph, Cy) with $[Ru_3(CO)_{12}]$ in toluene at 50ºC yields the Ru_2Mn clusters, $[CpMnRu_2(CO)_8(\mu_3\text{-}PR)]$ (R = Ph (**44**), Cy (**45**)) (Scheme 15) [17]. The structure reveals a $MnRu_2$ triangle with a μ_3-PR ligand bridging the three metal atoms. In addition to three terminal carbonyls on each ruthenium atom, a bridging CO spans across each Mn-Ru bond.



Scheme 15

Stepwise synthesis of a chiral heterometallic cluster $[(R)P(Cp^*)Fe_2Mn(CO)_8(\mu_2\text{-}CO)]$ (**50**) has been achieved by the reaction of $[(R)(Cp^*)P{=}Mn(CO)_4]$ (**46**) (R = 2,4,6-$Bu^t{}_3C_6H_2O$) with $[Fe_2(CO)_9]$. Room temperature stirring of the two reactants initially

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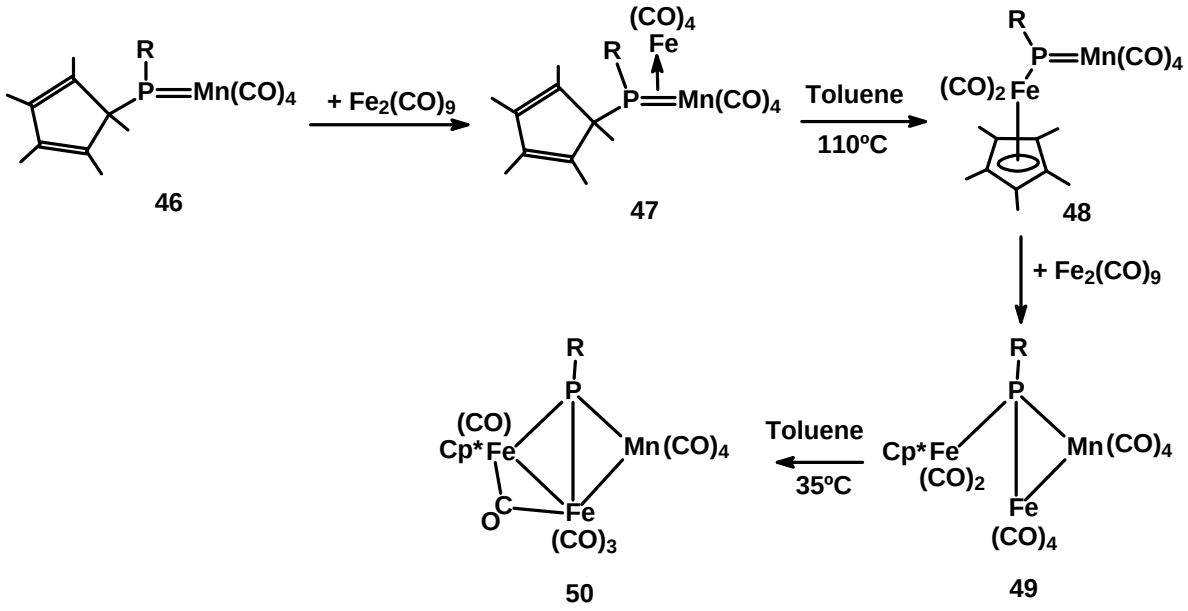
yields [η^2-{(R)(η^1-Cp*)P=Mn(CO)$_4$}Fe(CO)$_4$] (**47**), which on reflux in toluene undergoes a formal insertion of a Fe(CO)$_2$ unit into the P-C bond to form [(R)(η^5-Cp*)Fe(CO)$_2$}P=Mn(CO)$_4$] (**48**). Complex **48** reacts further with [Fe$_2$(CO)$_9$] at room temperature to afford **49** which, on thermolysis converts to [(R)P(Cp*)Fe$_2$Mn(CO)$_8$(μ_2-CO)] (**50**) (Scheme 16) [18].



Scheme 16

A diphosphorus heterometallic cluster, [Co$_2$(CO)$_6$P$_2${Cp(CO)$_2$Mn}$_2$] (**53**), has been prepared by the reaction of trihalophosphane complexes, [Cp(CO)$_2$MnPX$_3$] (X = Cl (**51**), Br (**52**)) with [NaCo(CO)$_4$], whereas the reaction of [Cp(CO)$_2$MnPX$_3$] (X = Cl, Br) with [Co$_2$(CO)$_8$] leads to the formation of a P – bridged Co$_3$Mn cluster, [Co$_3$(CO)$_9$(μ_4-P)MnCp(CO)$_2$] (**54**) (Scheme 17) [3]. Structure of **53** consists of a Co$_2$P$_2$ tetrahedron core with a CpMn(CO)$_2$ moiety bonded to each of the μ_4-phosphorus atoms. Compound **54** has a Co$_3$P tetrahedral core and a CpMn(CO)$_2$ unit bonded to the phosphorus atom of the Co$_3$P core.

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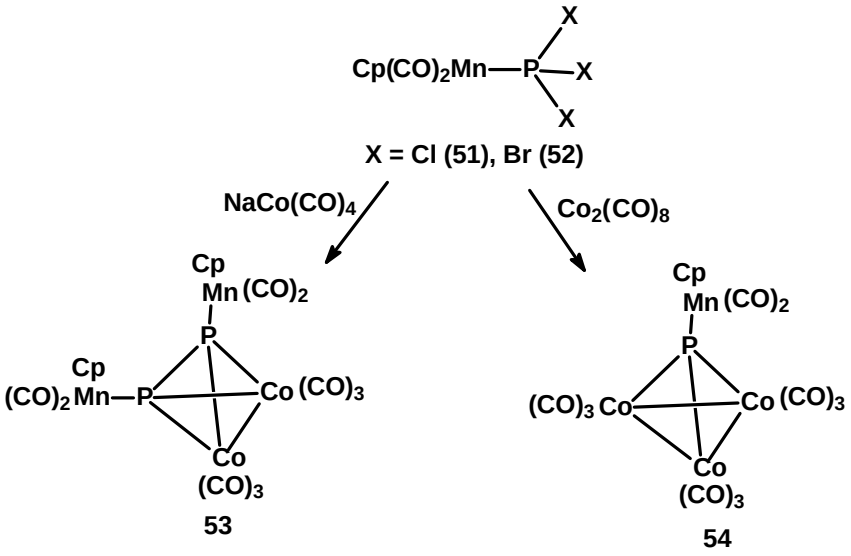

Scheme 17

Carbonyl substitution reaction of **54** with PR_2R' or $P(OR'')_3$ leads to mono, di or trisubstituted derivatives (**55**-**58**) as shown in Figure 2 [3].

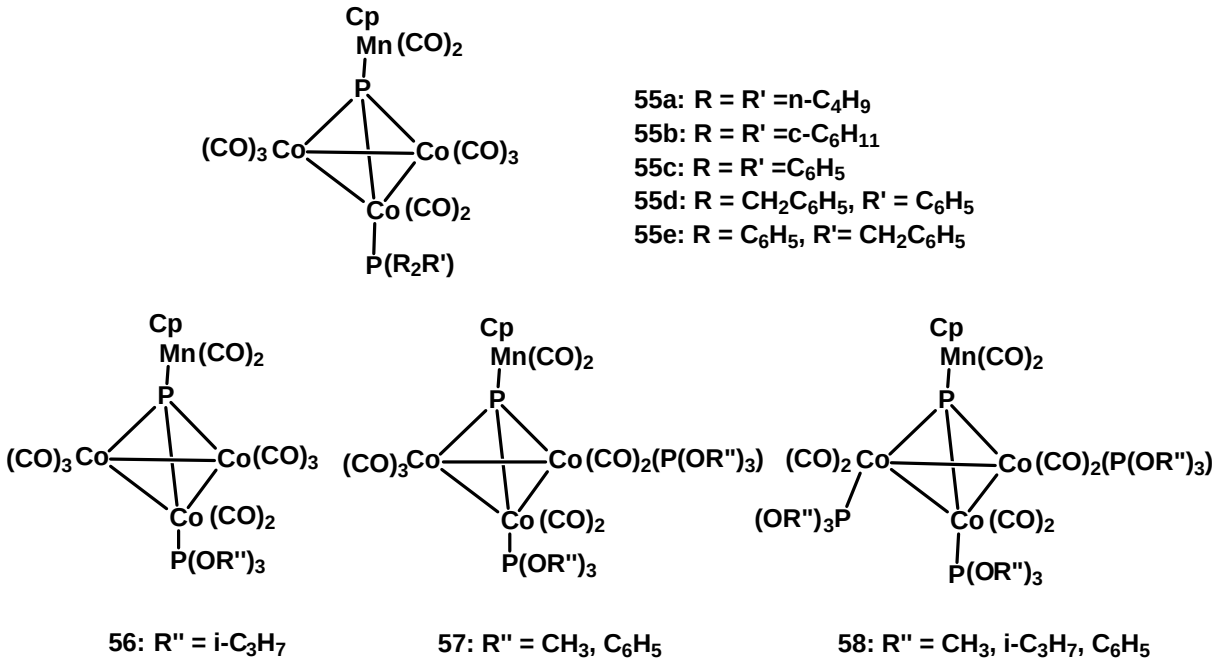

Figure 2

Equimolar amounts of $PPh_4[MM'(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_8]$ (M = M' = Mn (**59a**), M = Mn, M' = Re (**59b**)) and [{Rh(COD)}{ClO_4}] (**60**) react in presence of carbonmonoxide to give mixed metal clusters $[MM'Rh(\mu\text{-}PCy_2)(\mu\text{-}CO)_2(CO)_8]$ (M = M'

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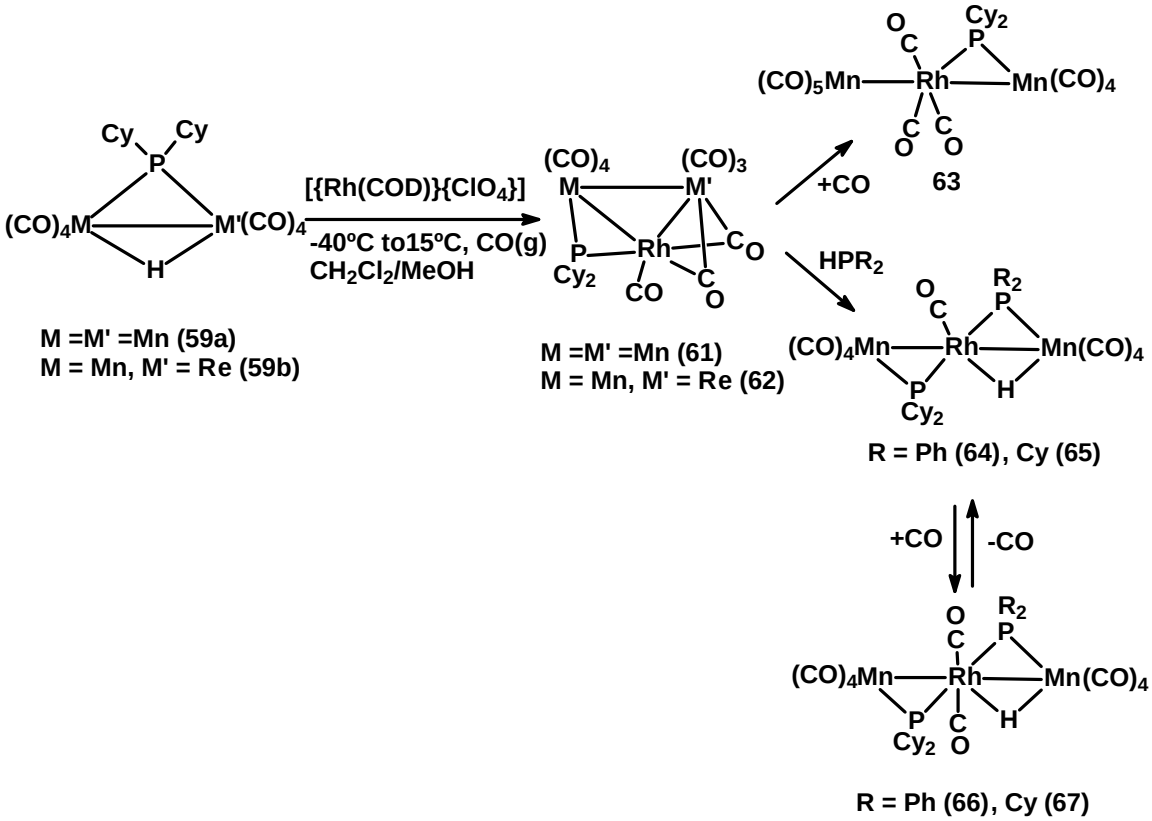
= Mn (**61**), M = Mn, M' = Re (**62**)) [19]. Cluster **61** reacts with CO or PHR_2 (R = Ph, Cy) to yield $[MnRh(\mu\text{-}PCy_2)(CO)_7Mn(CO)_5]$ (**63**) or $[MnRh(\mu\text{-}PCy_2)(\mu\text{-}H)(CO)_5Mn(\mu\text{-}PR_2)(CO)_4]$ (R = Ph (**64**), Cy (**65**)) respectively. On reaction with CO, compound $[MnRh(\mu\text{-}PCy_2)(\mu\text{-}H)(CO)_5Mn(\mu\text{-}PR_2)(CO)_4]$ (**64**/**65**) undergoes reversible conversion to $[MnRh(\mu\text{-}PCy_2)(\mu\text{-}H)(CO)_6Mn(\mu\text{-}PR_2)(CO)_4]$ (R = Ph (**66**), Cy (**67**)) (Scheme 18) [19]. The structures of compounds **61**, **63**, **65** and **66** have been determined by X-ray analysis. Compound **61** has Mn_2Rh core with a doubly bridging $P(Cy)_2$ ligand between manganese and rhodium atoms and contains two bridging carbonyls and eight terminal carbonyls bonded to the metals. Compound **63** and **65** have a Mn-Rh-Mn unit in which a PCy_2 group is bridging the rhodium-manganese bond in **63** whereas in **65** two bridging PCy_2 groups and a μ-H ligand are bonded to the metals.



Scheme 18

Reaction of a THF solution of *cis*-$[PtCl_2(PPh_2Cl)_2]$ (**68**) with $[Na\{Mn(CO)_5]$ from 0ºC to 25ºC gives phosphido - bridged platinum-manganese clusters

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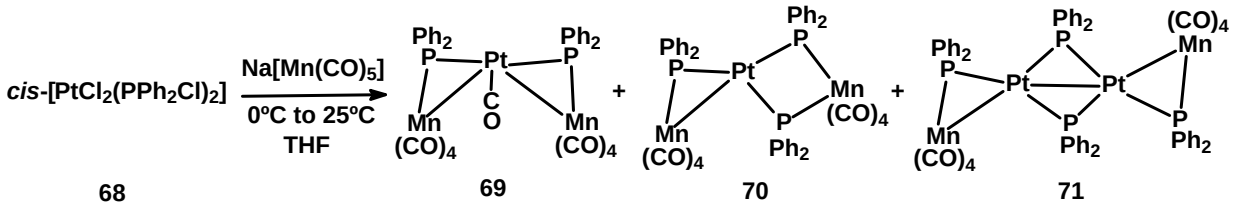
$[PtMn_2(CO)_9(\mu\text{-}PPh_2)_2]$ (**69**), $[PtMn(CO)_4(\mu\text{-}PPh_2)_3Mn(CO)_4]$ (**70**) and $[Pt_2Mn_2(CO)_8(\mu\text{-}PPh_2)_4]$ (**71**) (Scheme 19) [20]. Compound **69** consists of a bent MnPtMn chain with two μ – PPh_2 bridges stabilizing the two Mn-Pt bonds. Compound **70** can formally be considered to be derived from **69** by replacement of one Mn-Pt bond of **69** by a μ – PPh_2 bridge. Compound **71** consists of a MnPtPtMn chain in which the two Mn-Pt bonds are bridged by a single μ - PPh_2 group while the Pt-Pt bond is bridged by two μ - PPh_2 groups.



68 **69** **70** **71**

Scheme 19

Replacement of either the μ – H or the hydride of the bridging phosphido group in $[Mn_2(\mu\text{-}H)(\mu\text{-}PCyH)(CO)_8]$ (**72a**) occurs to form **73a** and **74a** respectively on reaction of **72a** with $[ClAuPPh_3]$ in presence of DBU (1,8-diazabicyclo[5,4,0]undec-7-en). Both types of hydride can also be replaced to form **75a**. Additionally a Mn_2Au_2 cluster, **76a** is also isolated from the reaction (Scheme 20) [21,22,23,24].

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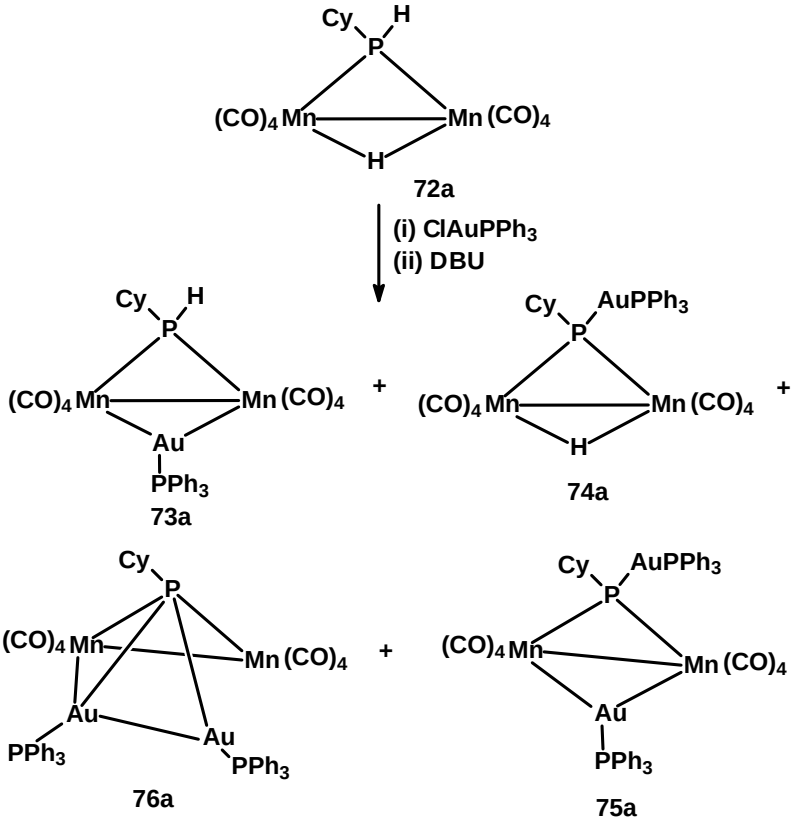

Scheme 20

In contrast, reaction of μ – PPh_2 or μ – PCy_2 bridged compounds [Mn_2(μ-H)(μ-PR_2)$(CO)_8$] (R = Ph (**72b**), Cy (**72c**)) with [PPh_3AuCl] in presence of LiPh forms [Mn_2(μ-PR_2)$(CO)_8$($AuPPh_3$)] (R = Ph (**77a**), Cy (**77b**), [Mn_2(μ-PR_2)(μ-C(R')O)$(CO)_6$($AuPPh_3$)$_2$] (**78a:** R = Ph, R' = Ph, **78b:** R = Cy, R' = Ph) and [Mn_2(μ-PR_2)$(CO)_6$($AuPPh_3$)$_3$] (R = Ph (**79a**), Cy (**79b**)) demonstrating the addition of a single, two and three Au(PPh_3) groups to the phosphido bridged dimanganese compound (Scheme 21) [25]. Structurally, **77a** is similar to **73a**. Compounds **78a,b** contain Mn_2Au_2 tetrahedral frameworks with a PR_2 and a C(Ph)O-group bridging the dimanganese edge. Compounds **79a,b** consist of trigonal bipyramid Mn_2Au_3 metal cores with the two manganese atoms occupying equatorial positions. A PR_2 ligand is doubly bridges the two manganese atoms and each Au contains a PPh_3 ligand.

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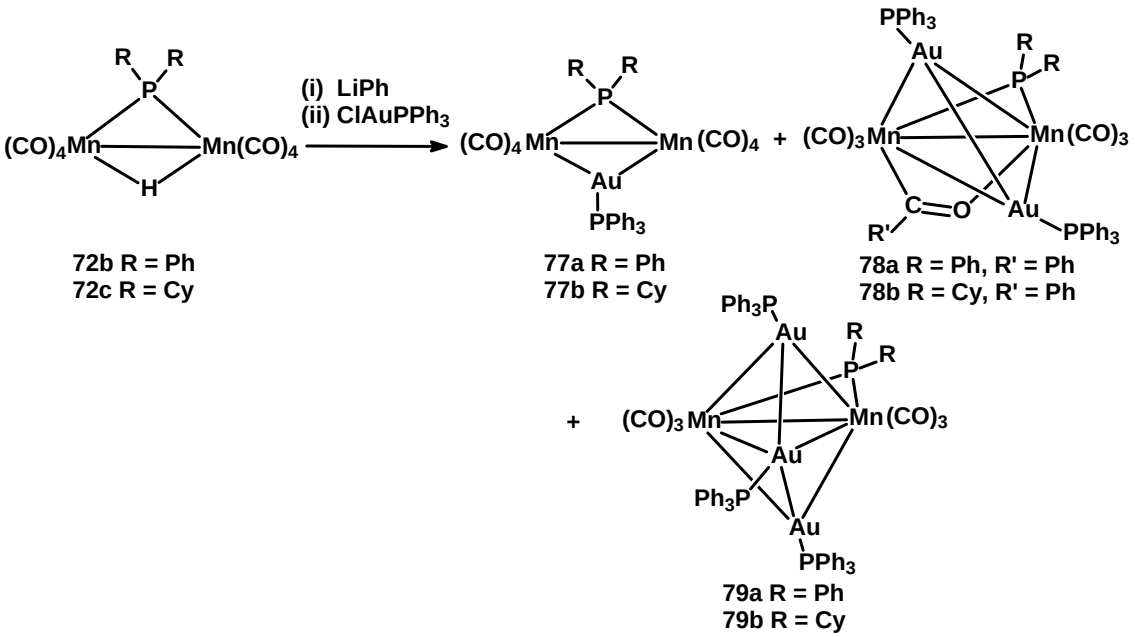
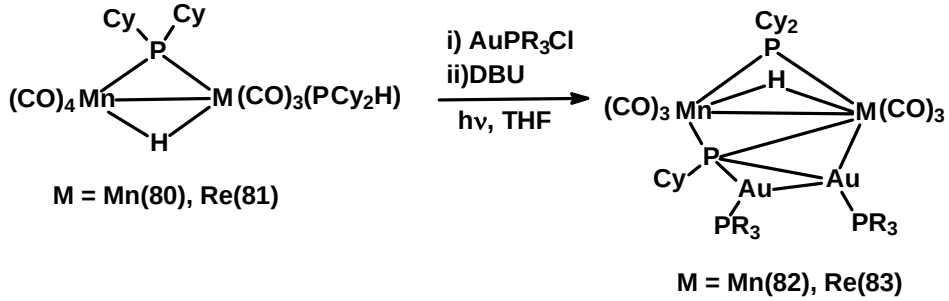


Scheme 21

The phosphido – bridged dimanganese complex, $[Mn_2(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(H_2PCy)]$ (**80**) or the monophosphido – bridged manganese – rhenium complex, $[MnRe(\mu\text{-}H)(\mu\text{-}PCy_2)(CO)_7(H_2PCy)]$ (**81**) react at room temperature with $[ClAuPR_3]$ (R = Ph, Et) in presence of DBU, under photochemical condition to give $[MnM(AuPR_3)_2(\mu\text{-}H)(\mu\text{-}PCy_2)(\mu_4\text{-}PCy)(CO)_6]$ (M = Mn (**82**) or Re (**83**), R = Ph, Et) (Scheme 22) [26].



Scheme 22

The dianionic $[\{Mn_2\{\mu\text{-}P(OEt)_2\}\{\mu\text{-}\eta^2\text{-}OP(OEt)_2\}(CO)_6\}]^{2-}$ (**84**) reacts with $[ZnCl_2(bpy)]$ at room temperature to afford a neutral Mn_2Zn cluster $[Mn_2Zn\{\mu\text{-}P(OEt)_2\}\{\mu\text{-}\eta^2\text{-}OP(OEt)_2\}(CO)_6(bpy)]$ (**85**) [27]. Complex **84** also reacts with Group 11 metal chloro complexes to form several higher nuclearity heterometallic clusters (Scheme

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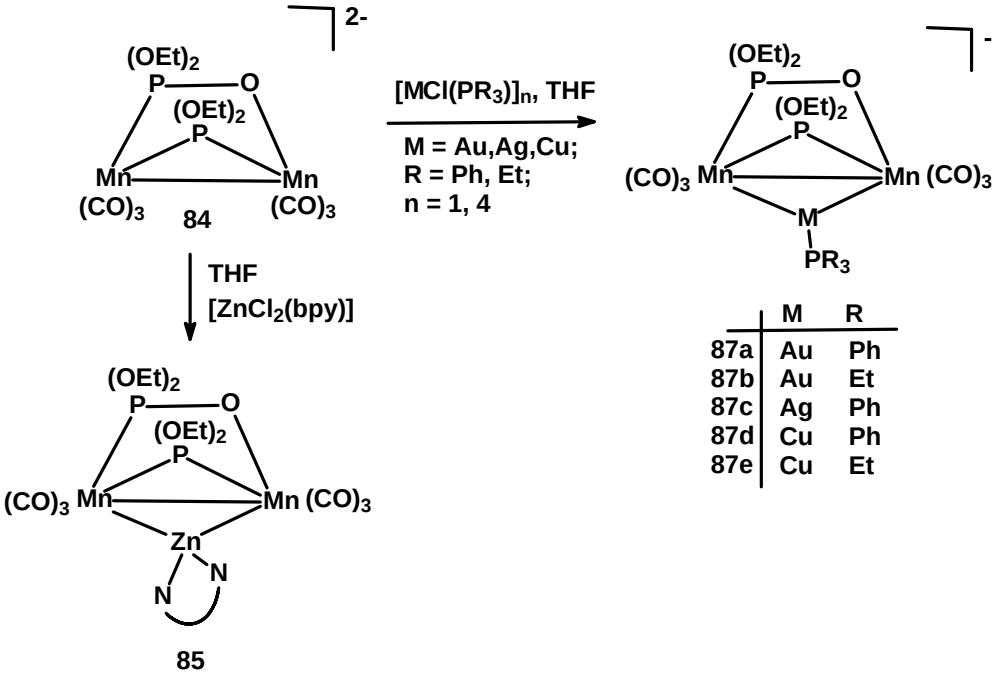
23). The silver and gold analogs of the anionic trinuclear complexes (**87a**, **87c**) react with a second molecule of $[MCl(PPh_3)]_n$ to yield the corresponding neutral tetranuclear clusters $[Mn_2M_2\{\mu\text{-}P(OEt)_2\}\{\mu\text{-}\eta^2\text{-}OP(OEt)_2(CO)_6(PPh_3)_2]$ (M = Ag (**88a**), Au (**88b**). Pentanuclear Mn-Au clusters (**89 a, b**) have been obtained when $[Mn_2Au\{\mu\text{-}P(OEt)_2\}\{\mu\text{-}\eta^2\text{-}OP(OEt)_2\}(CO)_6(PR_3)]^-$ (**87 a, b**) are exposed to UV light in presence of $[AuClPR_3]$ (R = Ph, Et) (Figure 3) [27]. Like in **79 a**/**b**, in **89 a**/**b** too the two manganese atoms occupy the equatorial positions of a Mn_2Au_3 trigonal bipyramidal core.



Scheme 23

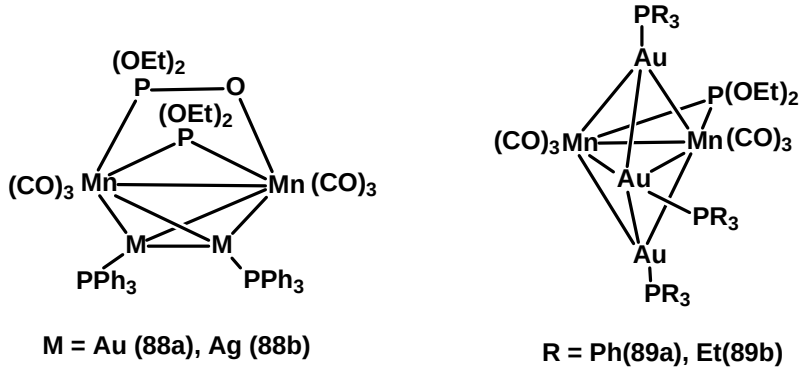


Figure 3

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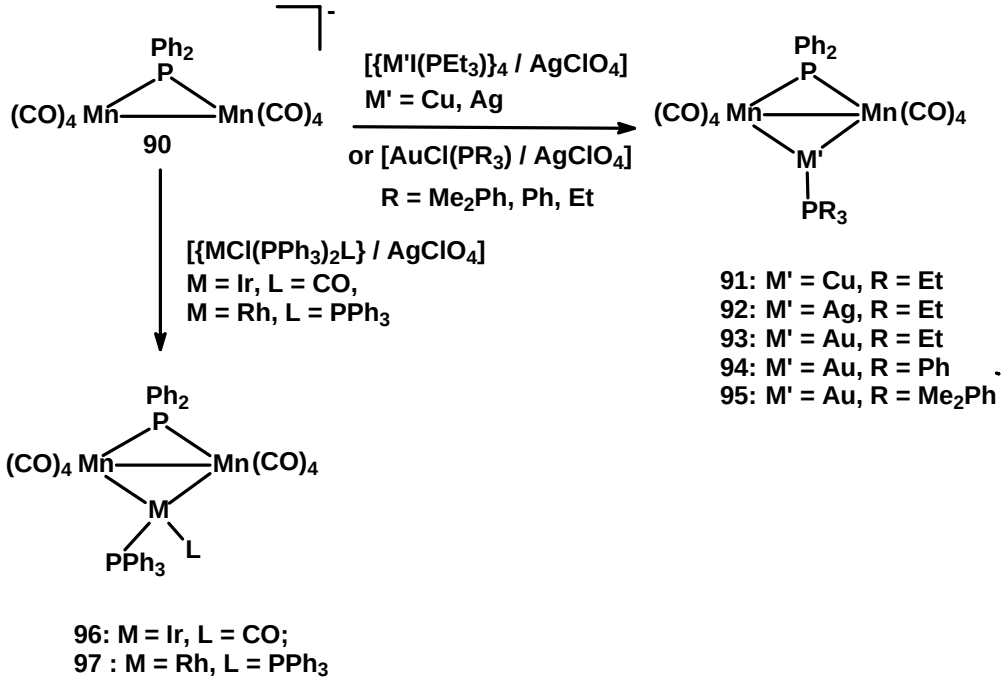
The monophosphido – bridged anionic complex $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$ (**90**) reacts with Group 11 metal complexes, derived from the mixture of $[\{M'I(PEt_3)\}_4]$ (M' = Cu, Ag) or $[AuCl(PR_3)]$ (R = Et, Ph, Me_2Ph) and $AgClO_4$, to give trinuclear clusters $[Mn_2\{\mu\text{-}M'(PR_3)(\mu\text{-}PPh_2)(CO)_8]$ (M' = Cu, R = Et (**91**); M' = Ag, R = Et (**92**); M' = Au, R = Et (**93**) or Ph (**94**) or Me_2Ph (**95**)). Reaction of $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$ with a mixture of $[MCl(PPh_3)L]$ (M = Rh, L = PPh_3; M = Ir, L = CO) and $AgClO_4$ leads to manganese-iridium (**96**) or manganese-rhodium trinuclear clusters (**97**) (Scheme 24) [27].



Scheme 24

Mixed Mn/Hg clusters, $[Mn_2Hg(L)(\mu\text{-}PPh_2)(CO)_8]$ (L = Ph (**98**), Cl (**99**)) and $[Mn_4Hg(\mu\text{-}PPh_2)_2(CO)_{16}]$ (**100**) have been obtained from the reaction of $[N(PPh_3)_2][Mn_2(\mu\text{-}PPh_2)(CO)_8]$ with [HgPhCl], $[HgCl_2]$ and $[Hg(CN)_2]$ respectively (Scheme 25) [28].

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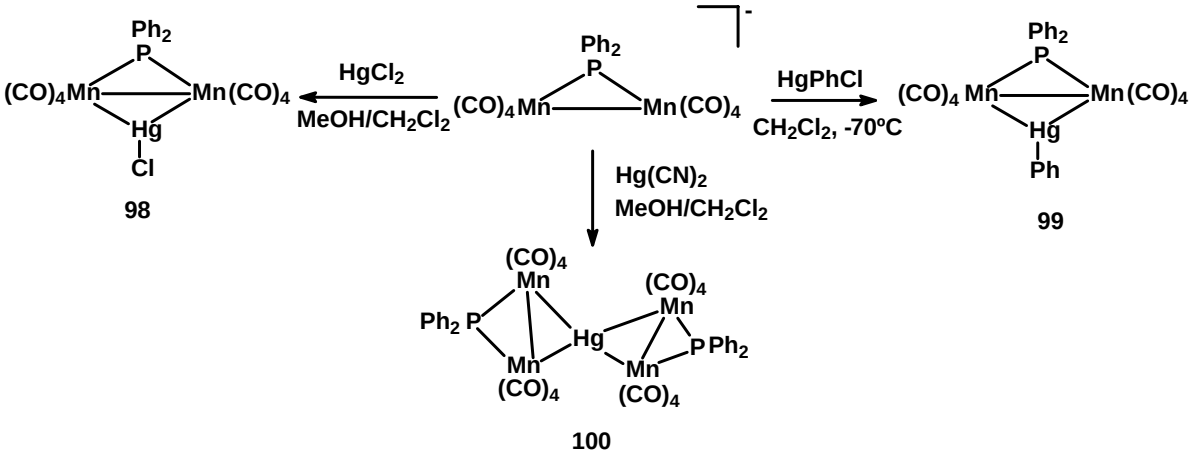
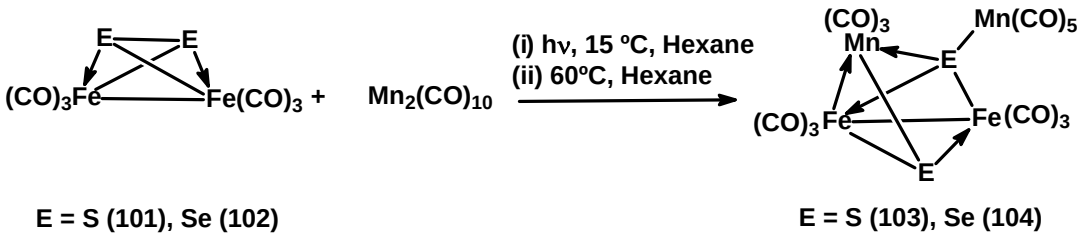


Scheme 25

Clusters containing ligands derived from Group 16 elements.

Chalcogen bridged tetranuclear Fe-E-Mn clusters (E = S (**103**), E = Se (**104**)) have been obtained by the reaction of $[Fe_2E_2(CO)_6]$ (E = S (**101**), Se (**102**)) with dimanganese decacarbonyl (Scheme 26) [29,30]. The formation of **101** or **102** can be considered to formally take place via an initial E-E bond cleavage and insertion of two $Mn(CO)_5$ fragments. Elimination of two CO ligands from one Mn atom and formation of E-Mn and Fe-Mn bonds would form **103** and **104**. The bond distances for Mn-Se bonds are 2.391(3) Å and 2.516(3) Å while donor – acceptor Fe-Mn bond is 2.709(3) Å.



Scheme 26

Room temperature reaction of $[Fe_3Te_2(CO)_9]$ (**105a**) with $[Et_4N][Mn(CO)_5]$ gives a $Mn(CO)_4$ bridging butterfly complex, $[Te_2Fe_2Mn(CO)_{10}]^-$ (**106a**), while treatment of $[Fe_3Se_2(CO)_9]$ (**105b**) with $[Et_4N][Mn(CO)_5]$ produces a square pyramidal complex,

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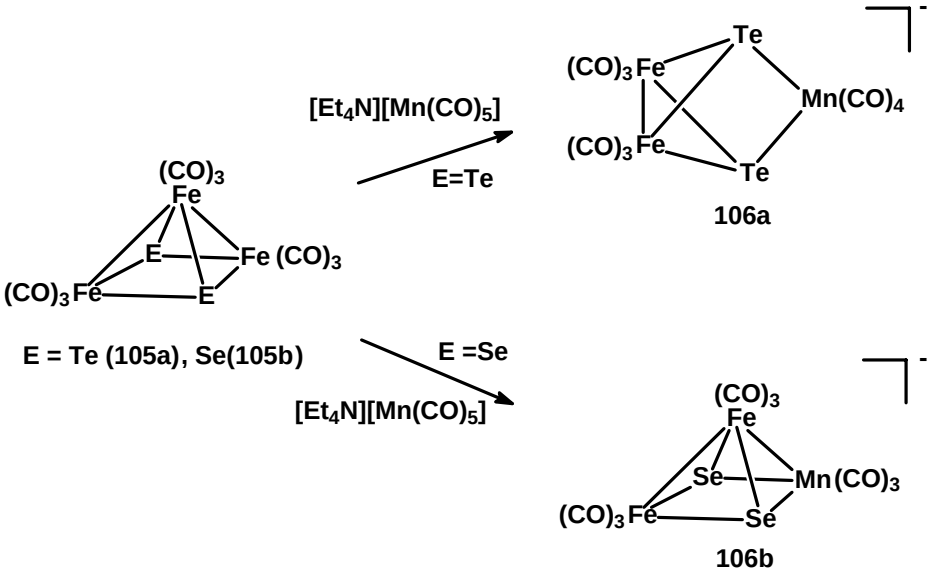
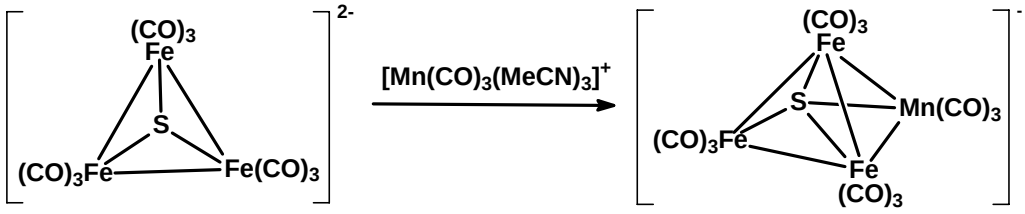
$[Se_2Fe_2Mn(CO)_9]^-$ (**106b**) (Scheme 27) [31]. The contrast between the Te – bridged and Se – bridged compounds seen in the reactions of $[Fe_3E_2(CO)_9]$ with $[Mn(CO)_5]^-$ is similar to that observed in reaction of $[Fe_3E_2(CO)_9]$ with PPh_3. For E = Te, the adduct, $[Fe_2(CO)_6(\mu_3\text{-}Te)_2Fe(CO)_3(PPh_3)]$ is isolable whereas for E = Se, the square – pyramidal, $[Fe_3(CO)_8(\mu_3\text{-}Se)_2(PPh_3)]$ is obtained [32]. The Te-Te bond distance of 3.207(2) Å in **106a** shows significant intramolecular interaction.



Scheme 27

A Fe_3Mn cluster containing quadruply bridging sulfido ligands $[PPN][Fe_3Mn(CO)_{12}(\mu_4\text{-}S)]$ (PPN = $(PPh_3)_2N^+$) (**107**) has been synthesized by a condensation reaction between $[PPN]_2[Fe_3(CO)_9(\mu_3\text{-}S)]$ and $[Mn(CO)_3(NCCH_3)_3][PF_6]$ (Scheme 28). The structure contains a Fe_3Mn butterfly metal core in which a sulfido ligand quadruply bridges all the four metal atoms. Each of the four metal atoms has three terminal carbonyl groups [33].



107

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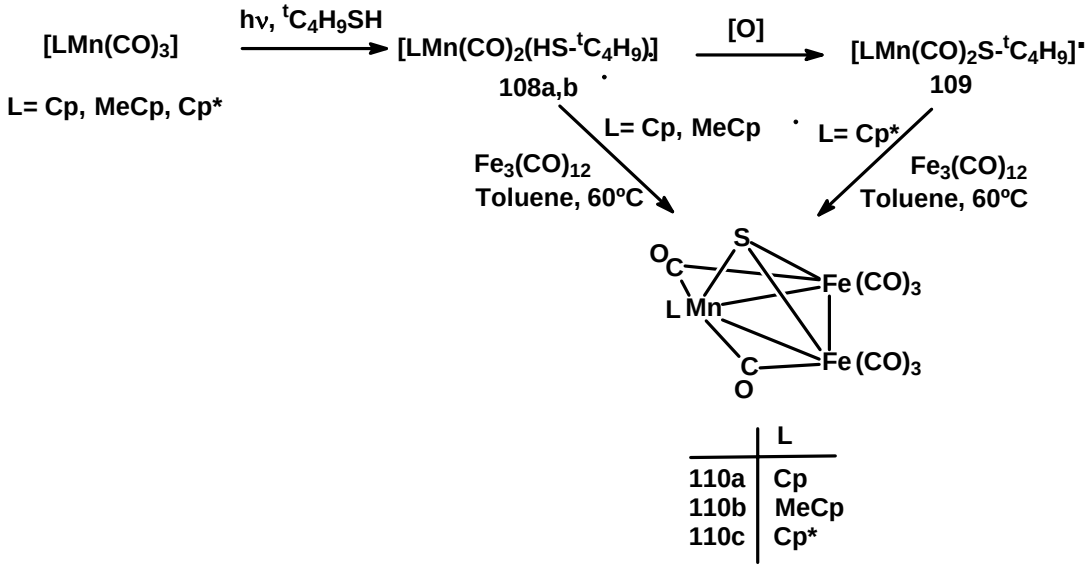
Scheme 28

Thermal reaction of $[LMn(CO)_2(HS\text{-}^tC_4H_9)]$ (L = Cp, MeCp) (**108 a,b**) or the radical $[Cp^*Mn(CO)_2S\text{-}^tC_4H_9]$ (**109**) with $[Fe_3(CO)_{12}]$ in toluene leads to the formation of a sulfide - bridged Fe_2Mn clusters $[Fe_2(CO)_6LMn(\mu\text{-}CO)_2(\mu_3\text{-}S)]$ (L = Cp (**110a**), MeCp (**110b**), Cp* (**110c**)) (Scheme 29) [34]. Structure of these contain a $MnFe_2$ metal core with a triply bridging sulfur atom. The two Mn-Fe bonds are bridged by a carbonyl group each and each of the two iron atoms bear three terminal carbonyl groups, while the manganese atom contains a pentahapto cyclopentadiene ligand (L).



Scheme 29

The much proven successful strategy of addition of electron poor metal units across the chalcogen-chalcogen bond of a dichalcogenide metal carbonyl complex as a first step in cluster growth reaction has been successfully employed in the synthesis of a number of Mn – containing mixed metal clusters. Reaction of $[Mn_2(CO)_7(\mu\text{-}S_2)]$ (**111**) with $[CpCo(CO)_2]$ and $[Cp^*Rh(CO)_2]$ results in the formation of CpCo and Cp*Rh inserted products, **112** and **113** [35, 36]. Room temperature reaction of a hexane solution of $[Mn_2(CO)_7(\mu\text{-}S_2)]$ with $[CpCo(CO)(PPh_3)]$ results in the formation of two mixed metal clusters, $[CpCoMn_2(CO)_6(\mu_3\text{-}S)_2]$ (**112**) and $[CpCoMn_2(PPh_3)(CO)_5(\mu_3\text{-}S)_2]$ (**114**) (Scheme 30).

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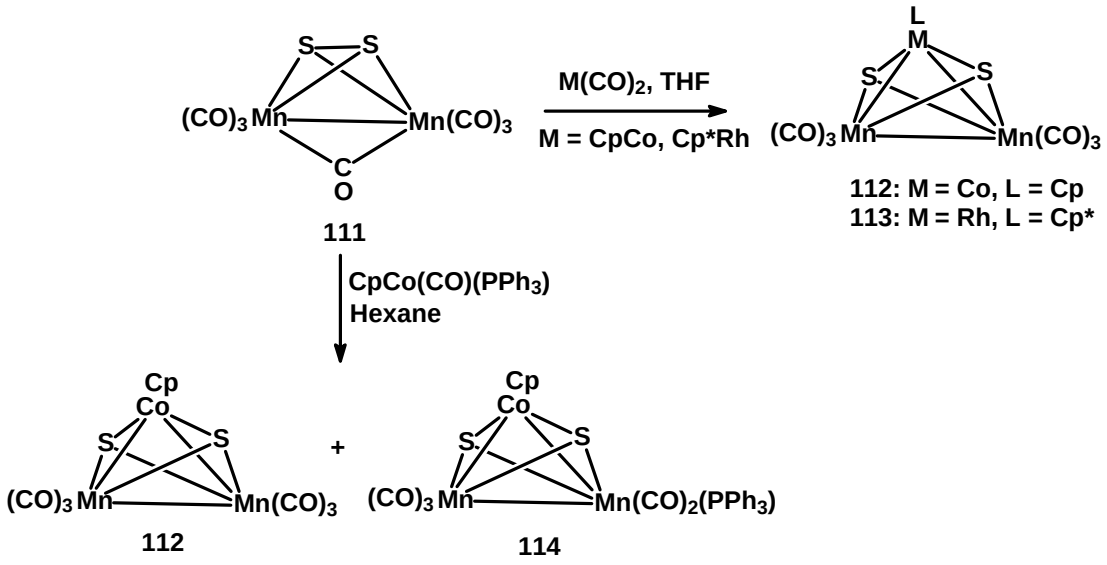
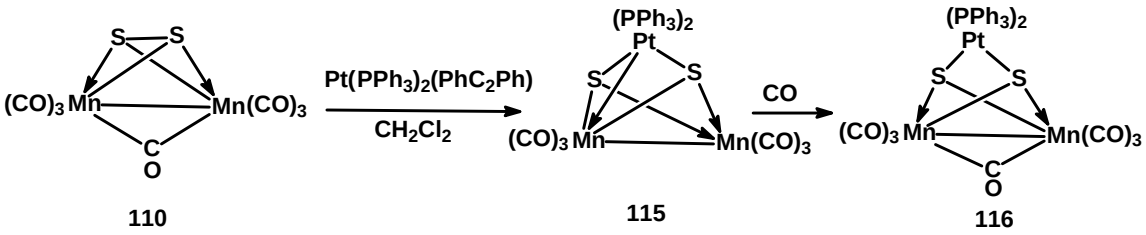


Scheme 30

Platinum-manganese mixed metal cluster, $[Mn_2(CO)_6Pt(PPh_3)_2(\mu_3\text{-}S)_2]$ (**115**) has been prepared by the reaction of $[Mn_2(CO)_7(\mu\text{-}S_2)]$ with $[P(PPh_3)_2(PhC_2Ph)]$ (Scheme 31) [37, 36]. Platinum atom has two PPh_3 groups and each manganese atom has three terminal carbonyl groups. A Pt→Mn donor – acceptor bond is proposed to satisfy the electron count around each Mn atom. Addition of CO to **115** cleaves the Pt-Mn bond and formation of a CO – bridged $[Mn_2(CO)_6(\mu\text{-}CO)Pt(PPh_3)_2(\mu_3\text{-}S)_2]$ (**116**).



Scheme 31

Reaction between $[Mn_2(CO)_7(\mu\text{-}S_2)]$ and $[CpNi(CO)]_2$ in benzene solution results in the formation of two nickel-manganese clusters, $[Cp_2Ni_2Mn(CO)_3(\mu_3\text{-}S)_2]$ (**117**) and $[Cp_2Ni_2Mn_4(CO)_{14}(\mu_6\text{-}S_2)(\mu_3\text{-}S)_2]$ (**118**) (Scheme 32). EPR and temperature dependent magnetic susceptibility measurements of **117** shows that the compound is one electron paramagnetic [38]. Both the clusters have been structurally characterized by X-ray diffraction analysis. Structure of cluster **117** consists of a $MnNi_2S_2$ square pyramidal

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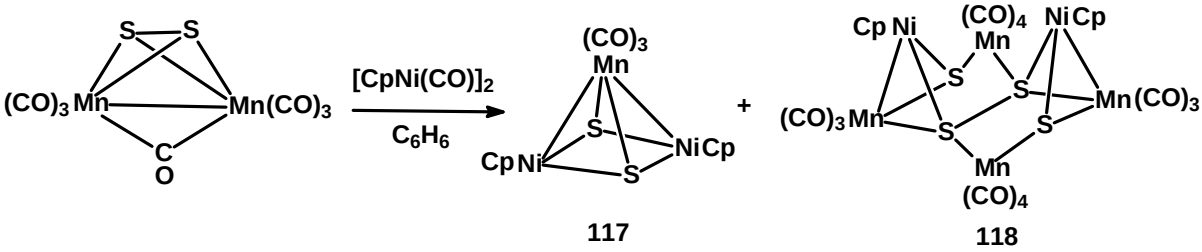
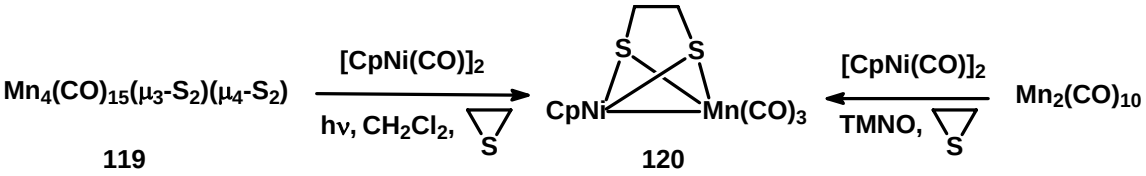
core with the manganese atom at the apical position. Cluster **118** contains two nickel and four manganese atoms linked by two triply bridging sulfido ligands and one μ_6-S_2 ligand. When $[Mn_4(CO)_{15}(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)]$ (**119**) is reacted with $[CpNi(CO)]_2$ and thiirane in presence of light, a ethanedithiolato bridged nickel-manganese compound (**120**) is obtained. The same compound can also be synthesized by a room temperature reaction of $[Mn_2(CO)_{10}]$ with $[CpNi(CO)]_2$, TMNO and thiirane (Scheme 33) [38]. Selenium - bridged mixed Mn/Ni cluster $[Cp_2Ni_2Mn(CO)_3(\mu_3\text{-}Se)_2]$ (**121**) has been obtained by the reaction of $[Mn_2(CO)_{10}]$ with $[CpNi(CO)]_2$ and selenium powder in presence of TMNO as a decarbonylating agent (Scheme 34) [38].



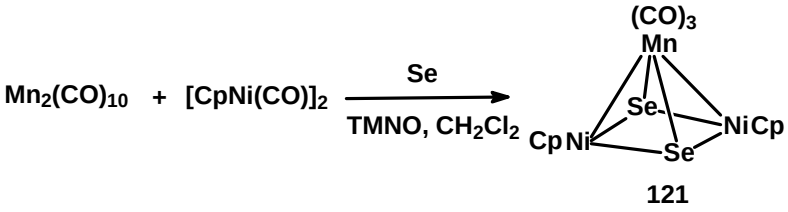
117 **118**

Scheme 32



119 **120**

Scheme 33



121

Scheme 34

The molybdenum-manganese disulfide complex $[LMoMn(CO)_5(\mu\text{-}S_2)]$ (L = Cp (**122a**), Cp*(**122b**)) can be synthesized by the treatment of $[Mn_2(CO)_7(\mu\text{-}S_2)]$ with $[LMo(CO)_3]_2$ in benzene or by the thermal reaction of a dichloromethane solution of $[LMoMn(CO)_8]$ with elemental sulfur in presence of trimethylamine-oxide (TMNO) [39,

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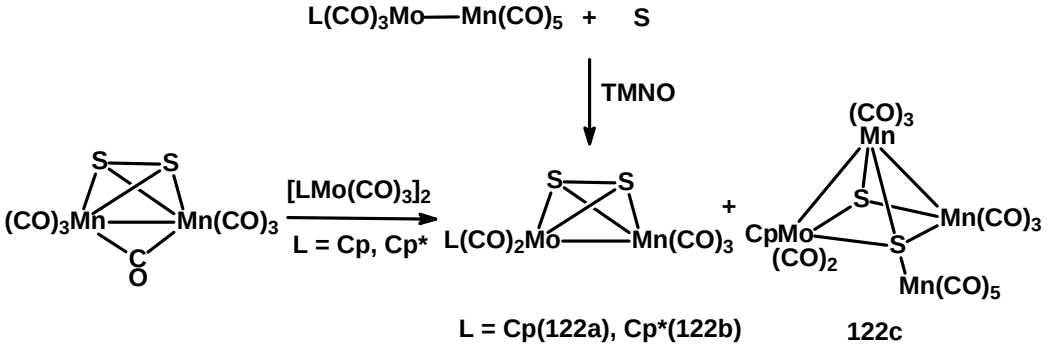
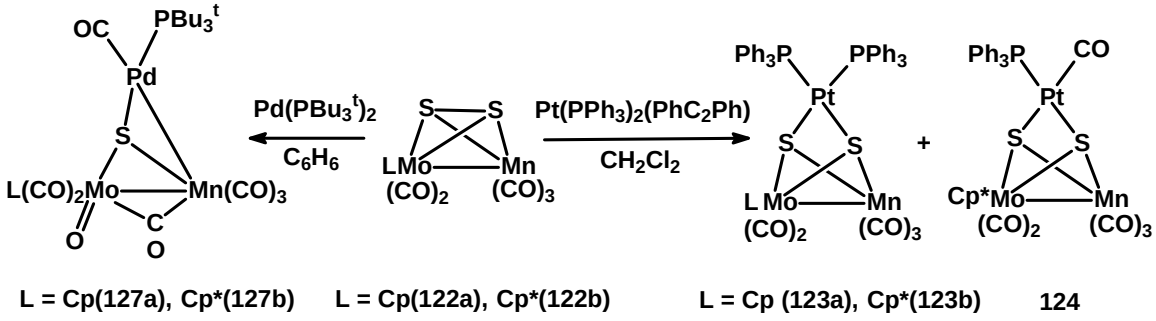
40]. From the first reaction, when L = Cp, a second product is isolable, $[CpMoMn_3(CO)_{13}(\mu_3\text{-}S)(\mu_4\text{-}S)]$ (**122c**) (Scheme 35) [40].



Scheme 35

At room temperature, $[LMoMn(CO)_5(\mu\text{-}S_2)]$ (L = Cp (**122a**), Cp*(**122b**)) undergoes addition reaction with $[Pt(PPh_3)_2(PhC_2Ph)]$ to give $[LMoMn(CO)_5Pt(PPh_3)_2(\mu_3\text{-}S)_2]$ (L = Cp (**123a**), Cp* (**123b**)) and $[Cp^*MoMn(CO)_6Pt(PPh_3)(\mu_3\text{-}S)_2]$ (**124**) (Scheme 35). The selenium – bridged cluster, $[CpMoMn(CO)_5Pt(PPh_3)_2(\mu_3\text{-}Se)_2]$ (**125**) has been obtained from the reaction of $[CpMoMn(CO)_5(\mu\text{-}Se_2)]$ (**126**) and $[Pt(PPh_3)_2(PhC_2Ph)]$ [44]. When $[LMoMn(CO)_5(\mu\text{-}S_2)]$ (L = Cp (**122a**), Cp*(**122b**)) is treated with $Pd(PBu_3^t)_2$, two oxo heterometallic clusters $[LMo(O)Mn(CO)_4(\mu\text{-}CO)Pd(PBu_3^t)(\mu_3\text{-}S)]$ (L = Cp (**127a**), Cp*(**127b**)) are obtained (Scheme 36) [39, 36].



Scheme 36

Sulfido – bridged trimetallic clusters $[Cp_2MoMnCo(CO)_5(\mu_3\text{-}S)_2]$ (**128**) and $[Cp_2Mo(O)MnCo(CO)_3(\mu_3\text{-}S)_2]$ (**129**) have been obtained by the reaction of

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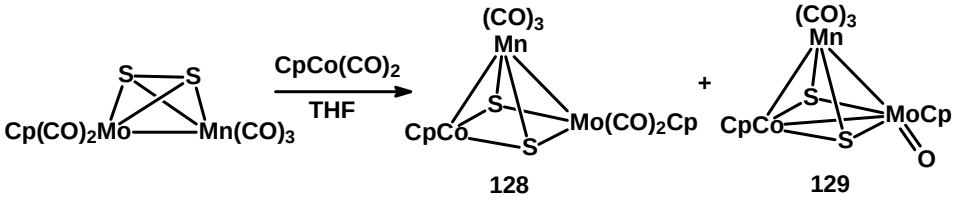
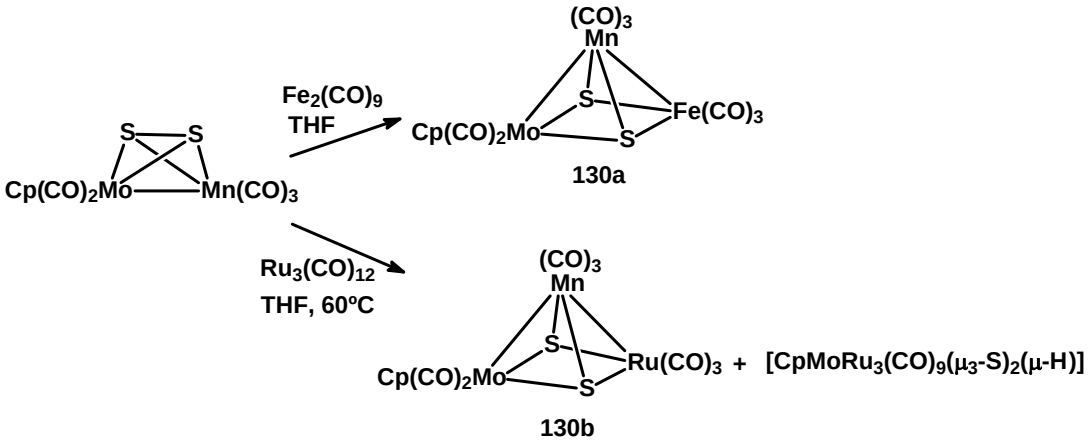
$[CpMoMn(CO)_5(\mu\text{-}S_2)]$ with $[CpCo(CO)_2]$ (Scheme 37) [41, 36]. The molecular structure of **128** consists of an open base square pyramidal $CoMnMoS_2$ framework with the manganese atom in the apical site. Two cyclopentadienyl groups on each of cobalt and molybdenum atom and three terminal carbonyl ligands on manganese and two carbonyl ligands on molybdenum satisfy the eighteen electron count of the cluster. The structure of **129** shows a closed base square pyramidal framework having two μ_3-S ligands, one Cp on cobalt, a Cp and an oxo group on molybdenum and three carbonyls on manganese atom.



Scheme 37

The disulfide compound $[CpMoMn(CO)_5(\mu\text{-}S_2)]$ also reacts with $[Fe_2(CO)_9]$ at room temperature and with $[Ru_3(CO)_{12}]$ in THF reflux condition to form trimetallic clusters $[CpMoMnFe(CO)_8(\mu_3\text{-}S)_2]$ (**130a**) and $[CpMoMnRu(CO)_8(\mu_3\text{-}S)_2]$ (**130b**) respectively. Both the compounds are structurally similar to the trimetallic **128** (Scheme 38) [41, 36].



Scheme 38

Addition reactions of $[CpMoMn(CO)_5(\mu\text{-}S_2)]$ have been extended to a variety of unsaturated small organic molecules resulting in insertion into the S-S bond at room

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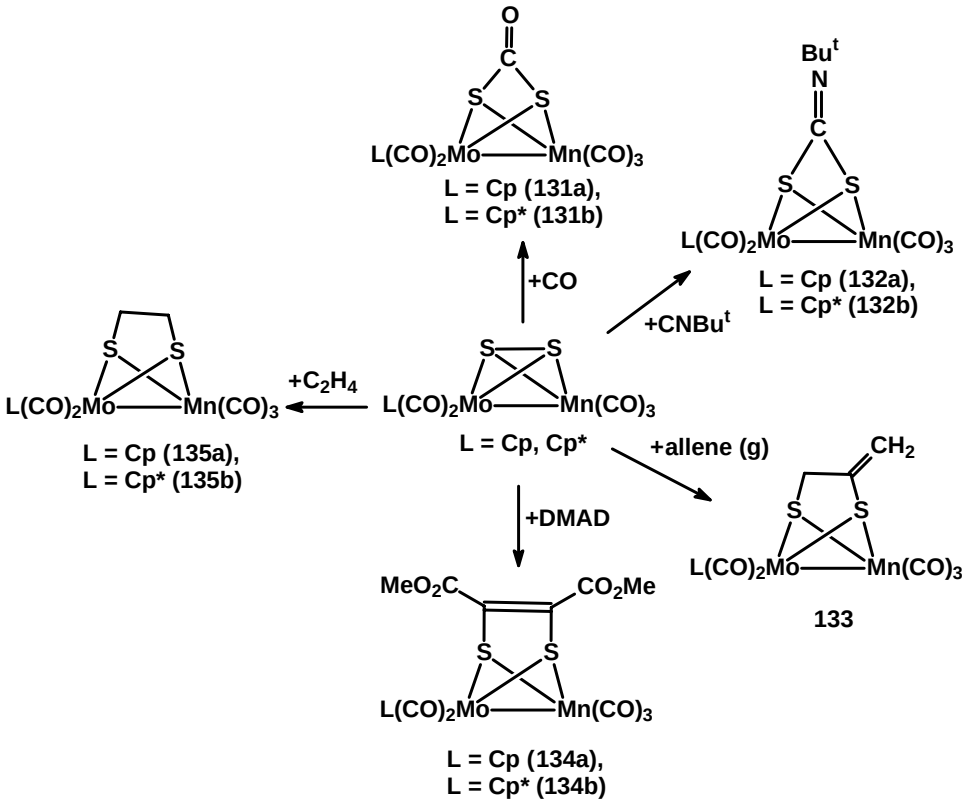
temperature and formation of a number of mixed Mo-Mn addition products (**131-135**) (Scheme 39) [40].



Scheme 39

Under photolytic conditions, $[CpMoMn(CO)_5(\mu\text{-}S_2)]$ adds alkenes to form adducts, **136-142** (Scheme 40) [42].

Quinone insertion products (**136a**,**b**) undergo reversible reduction to appropriate hydroquinones (**136c**,**d**) (Scheme 41) [43].

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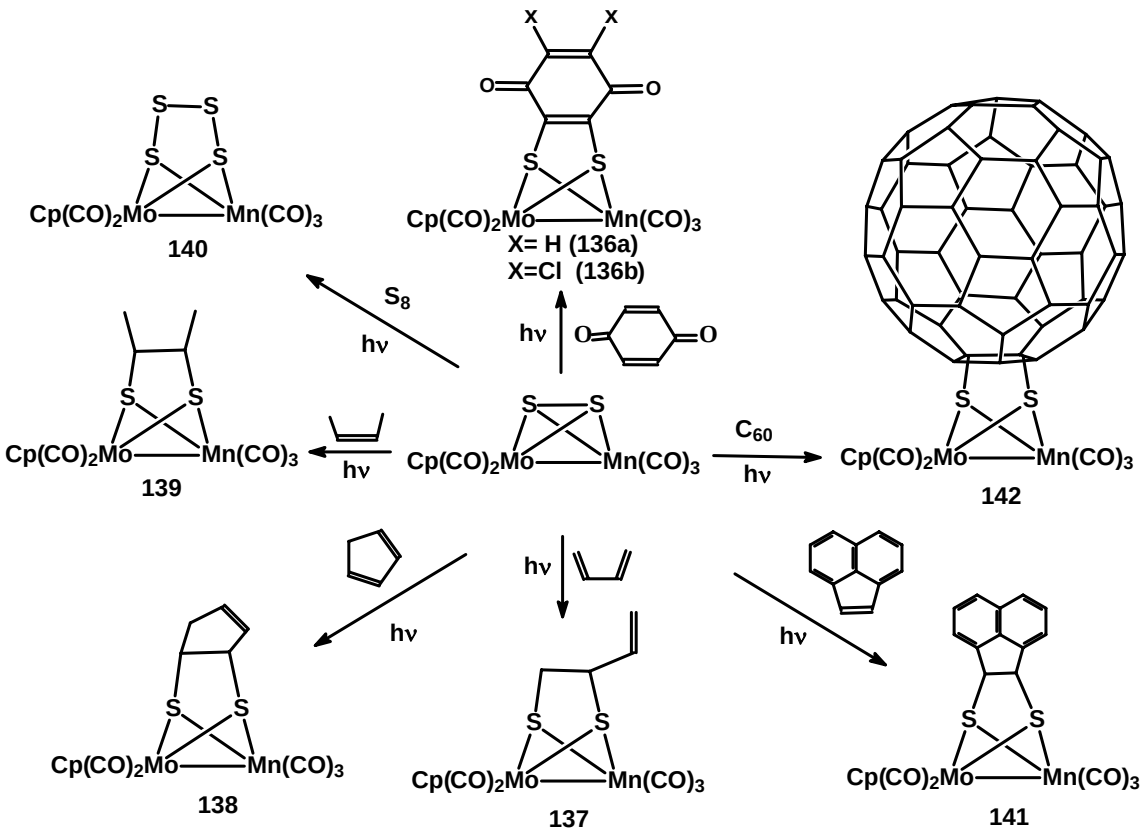
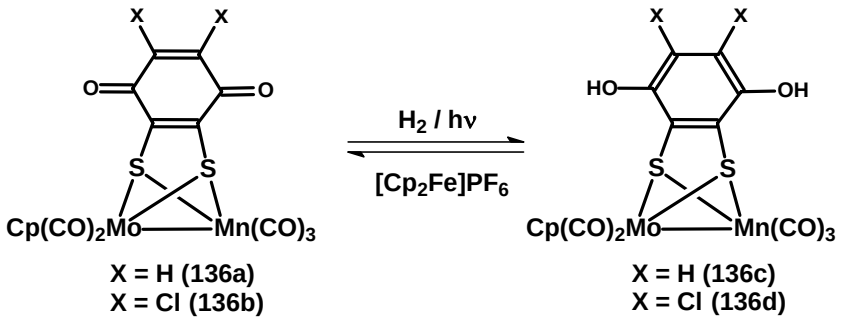


Scheme 40



Scheme 41

The diselenido – bridged Mo-Mn dimer, $[CpMoMn(CO)_5(\mu\text{-}Se_2)]$ (**126**) has been obtained from a mild thermolysis reaction between $[CpMoMn(CO)_8]$ and selenium powder in presence of $[Me_3NO]$. If the reaction is carried out under photolytic conditions, a tetranuclear cluster $[Cp_2Mo_2Mn_2(CO)_7(\mu_3\text{-}Se)_4]$ (**143**) is also obtained. Addition of various organic and inorganic moieties across the Se-Se bond of **126** are similar to those observed for **122** and $[Fe_2(CO)_6(\mu\text{-}E_2)]$ (E = S, Se or Te). The oxo

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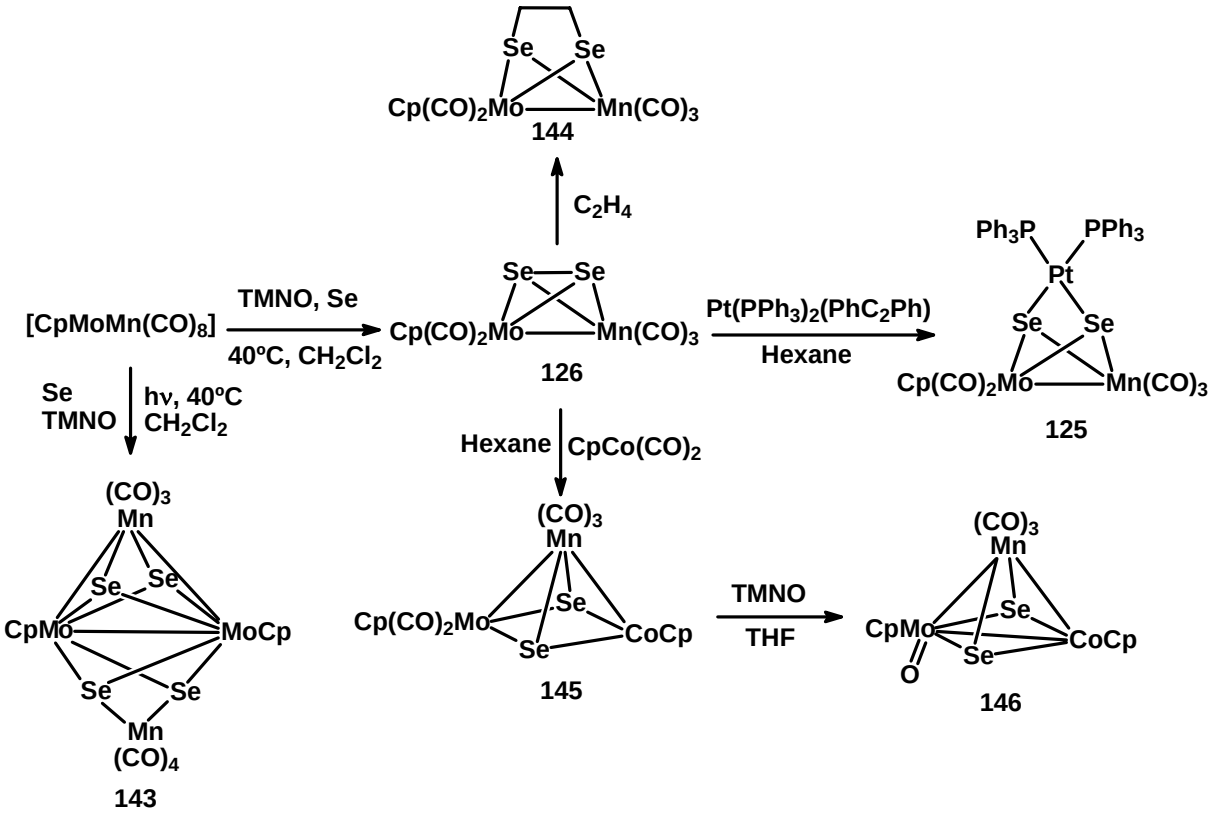
compound, $[Cp_2CoMo(O)Mn(CO)_5(\mu_3\text{-}Se)_2]$ (**146**) has been obtained from **145** by using $[Me_3NO]$ to decarbonylate the molybdenum carbonyls (Scheme 42) [44].



Scheme 42

A dimeric iron-manganese disulfide complex $[LFeMn(CO)_5(\mu\text{-}S_2)]_2$ (L = Cp (**148a**), Cp* (**148b**)) has been obtained from the reaction of $[LFeMn(CO)_7]$ (L = Cp, Cp*) (**147 a, b**) with thiirane in the presence of TMNO. When heated to 40 ºC, compound **148a** converts to a trimer, $[Cp_3Fe_3Mn_3(CO)_{15}(\mu_3\text{-}S)(\mu_4\text{-}S_2)_2]$ (**149**) (Scheme 43). The molecular structure of **148 a,b** consists of an open tetranuclear metal cluster having two triply bridging disulfide ligand bonded to two iron and two manganese atoms [45]. The central $Mn_2(\mu\text{-}S)_2$ square plane has one of the Mn-S edge bonded to $LFe(CO)_2S$ unit while the opposite Mn-S edge is bonded to a second unit of $LFe(CO)_2S$. In **148a**, both the $CpFe(CO)_2S$ fragments are on the opposite side of the central Mn_2S_2 plane while in compound **148b** the two $Cp^*Fe(CO)_2S$ fragments are on the same side of the plane and form a boat like conformation. Compound **149** contains three $Mn(CO)_3$

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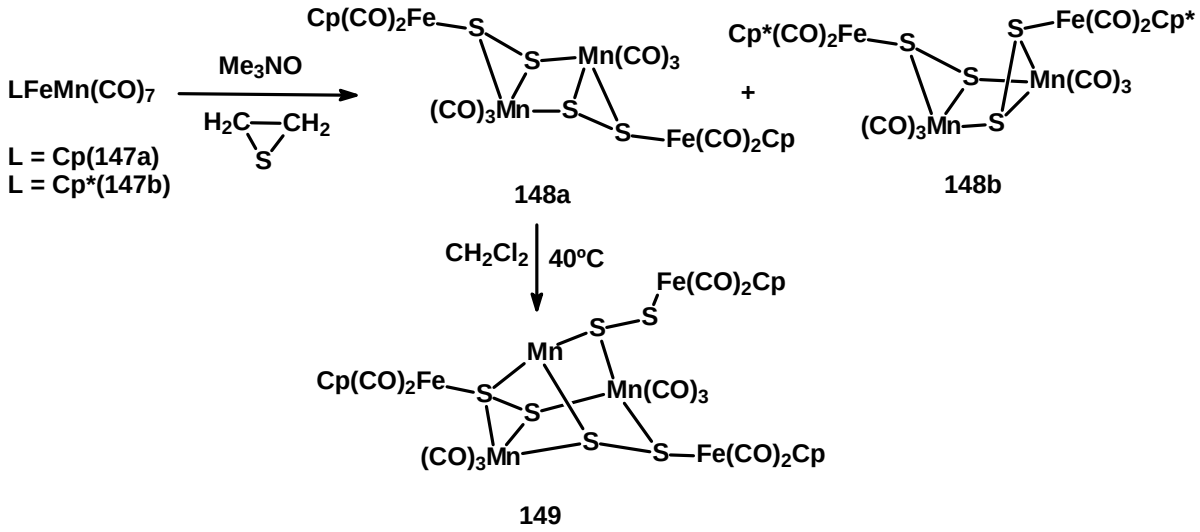
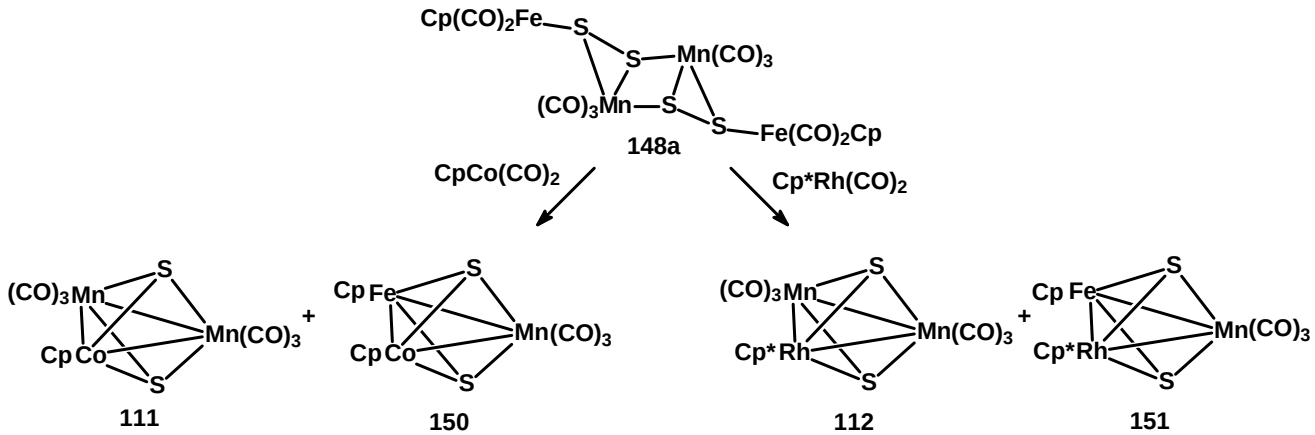
groups bonded by three bridging disulfide ligands with each of the disulfide ligand containing one $CpFe(CO)_2$ unit. Two of the disulfido ligands are quadruply bridging while one is triply bridging. Compound **148a** reacts at room temperature with $[LCo(CO)_2]$ (L = Cp, M = Mo; L = Cp*, M = Rh) to form two types of μ_3 – S bridged clusters : the trimetallic $[LCpFeMnM(CO)_3(\mu_3\text{-}S)_2]$ (L = Cp, M = Co (**150**); L = Cp*, M = Rh (**151**)) and the bimetallic clusters $[LMMn_2(CO)_6(\mu_3\text{-}S)_2]$ (L = Cp, M = Co (**111**); L = Cp*, M = Rh (**112**)) (Scheme 44) [46]**.**



Scheme 43



Scheme 44

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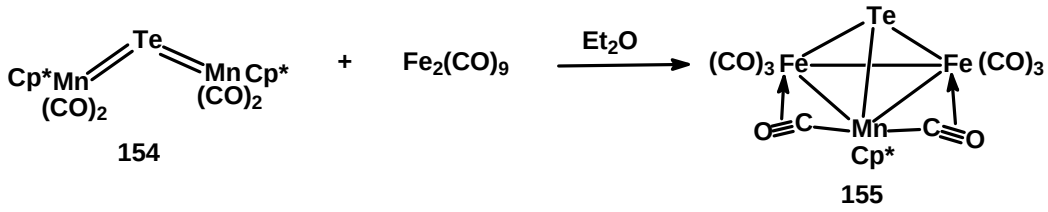
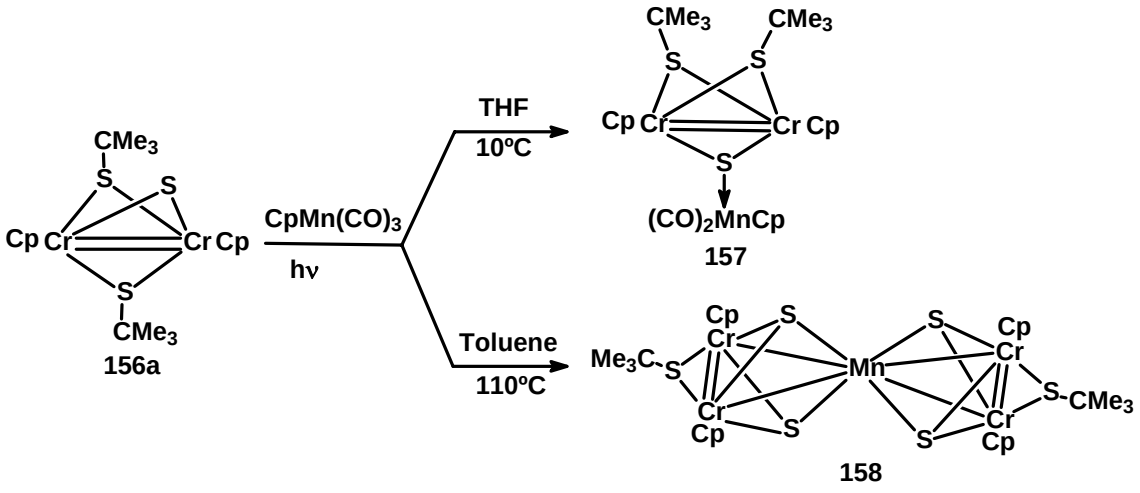
Treatment of the tellurium – bridged complex $[(\mu\text{-Te})[(\eta^5\text{-}C_5Me_5)Mn(CO)_2]_2$ (**154**) with $[Fe_2(CO)_9]$ yields a $MnFe_2$ cluster $[(\eta^5\text{-}C_5Me_5)MnFe_2Te(CO)_8]$ (**155**) (Scheme 45) [47].



Scheme 45

Photochemical reaction of a THF solution of $[CpCr(\mu\text{-}SCMe_3)]_2(\mu\text{-S})$ (**156a**) with $[CpMn(CO)_3]$ results in the formation of a trimetallic cluster $[CpCr(\mu\text{-}SCMe_3)]_2(\mu_3\text{-S})Mn(CO)_2Cp]$ (**157**) [48]. In contrast, photochemical reaction of $[CpCr(\mu\text{-}SCMe_3)]_2(\mu\text{-S})$ and $[CpMn(CO)_3]$ in 2:1 molar ratio in boiling toluene yields a pentametallic cluster $[Cp_2Cr_2(SCMe_3)(\mu_3\text{-S})_2)_2Mn]$ (**158**) (Scheme 46) [49]. X-ray structure analysis of **157** reveals that the binuclear fragment $[CpCr(\mu\text{-}SCMe_3)]_2(\mu\text{-S})$ is linked to $[CpMn(CO)_2]$ unit via a Mn-S bond (2.334(2) Å). The Cr-Cr bond (2.704(1) Å) is bridged by two $SCMe_3$ groups and one sulfide ligand. The structure of **158** has two $[Cp_2Cr_2(\mu\text{-}SCMe_3)](\mu_3\text{-}S)_2]$ fragments linked to each other via a manganese atom and forms a bow-tie Cr_4Mn metal framework.



Scheme 46

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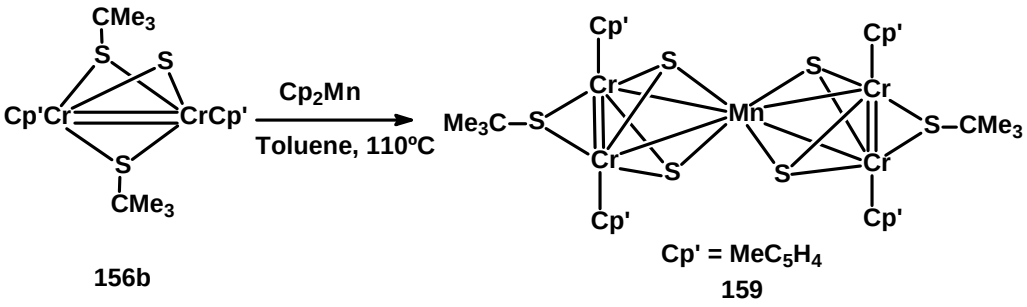
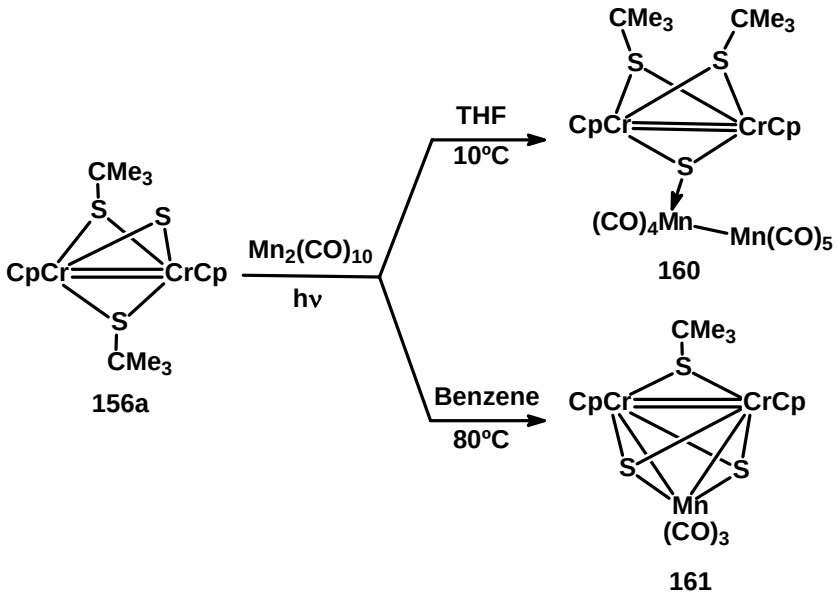
Formation of **159** can be considered as a formal substitution of each Cp ligand of Cp_2Mn by the isolobal $\{(Cp'Cr)_2(\mu\text{-}SCMe_3)(\mu\text{-}S)_2\}$ ($Cp' = MeC_5H_4$) (Scheme 47) [50]. Similarly the Cr/Mn compound $[CpCr(\mu\text{-}SCMe_3)]_2(\mu_3\text{-}S)_2Mn(CO)_3$ (**161**), formed from the photochemical reaction of $[CpCr(\mu\text{-}SCMe_3)]_2S$ and $Mn_2(CO)_{10}$, can be easily understood as a derivative of $CpMn(CO)_3$ obtained by a formal substitution of Cp by the isolobal $\{(CpCr)_2(\mu\text{-}SCMe_3)(\mu\text{-}S)_2\}$. Interestingly, the electrochemical studies of **161** and $CpMn(CO)_3$ show very similar oxidation potentials (Scheme 48) [51]. Compound **160** has been obtained on changing the reaction condition to low temperature photoreaction between $[CpCr(\mu\text{-}SCMe_3)]_2S$ and $[Mn_2(CO)_{10}]$.



156b 159

Scheme 47



156a 160 161

Scheme 48

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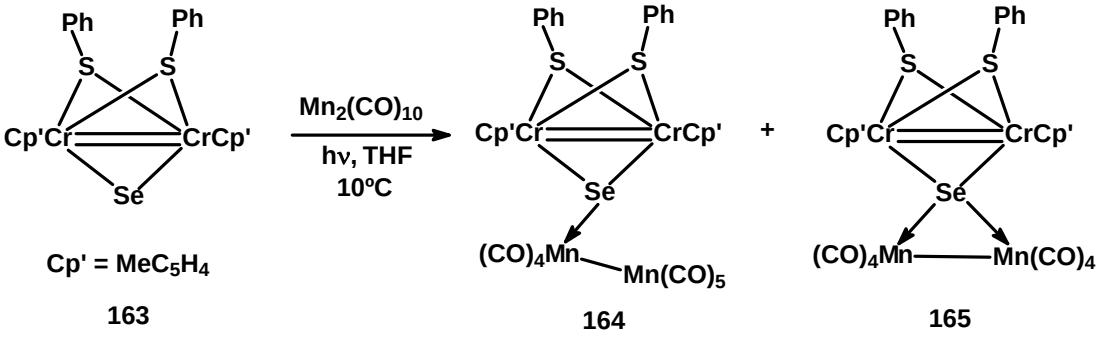
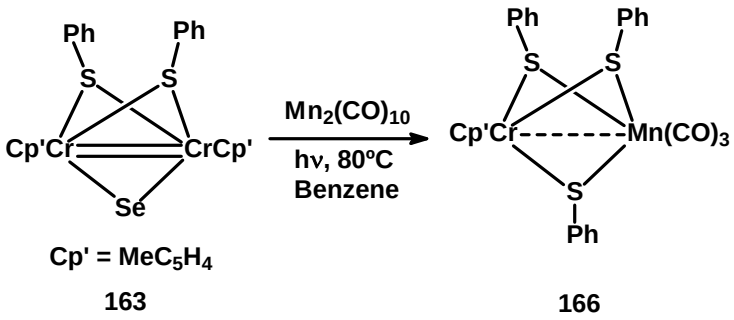
Photolysis of a thf solution containing $[CpCr(\mu\text{-}SCMe_3)]_2(\mu\text{-}S)$ and $[Mn_2(CO)_{10}]$ yields a single stable product, $[(Cp)Cr(\mu\text{-}SCMe_3)]_2(\mu_3\text{-}S)Mn_2(CO)_9$ (**160**) (Scheme 48) [52]. On the other hand, the selenium – bridged, $[(CH_3Cp)Cr(\mu\text{-}SPh)]_2(\mu\text{-}Se)$ (**163**) reacts with $[Mn_2(CO)_{10}]$ under photolytic condition to form two mixed metal clusters, $[(CH_3Cp)Cr(\mu\text{-}SPh)]_2(\mu_3\text{-}Se)Mn_2(CO)_9$ (**164**) and $[(CH_3Cp)Cr(\mu\text{-}SPh)]_2(\mu_4\text{-}Se)Mn_2(CO)_8$ (**165**) (Scheme 49), and in boiling benzene to give the bimetallic $[(CH_3Cp)Cr(\mu\text{-}SPh)_3Mn(CO)_3]$ (**166**) (Scheme 50) [53]. The Cr-Mn bond distance of 3.0239(7) Å is long for a single bond in **159** (2.839(4) Å, 2.967(3) Å, 3.019(3) Å and 3.104(4) Å) and in **161** (2.828(2) Å and 2.716(2) Å), but a slight interaction between the metal atoms has been suggested in accordance with the paramagnetic behaviour (3.67 μ_B) of the compound.



Scheme 49



Scheme 50

Compound **166** exhibits paramagnetic behaviour while all other derivatives of $[(RCp)Cr(\mu\text{-}SR')]_2(\mu\text{-}X)$ (**157-165**) show antiferromagnetism, which varies in a fairly wide range ($-2J$= 400-700cm^{-1}) depending on the type of Mn-containing fragment, presence or absence of Cr-Mn bonds and nature of chalcogen bridge [53].

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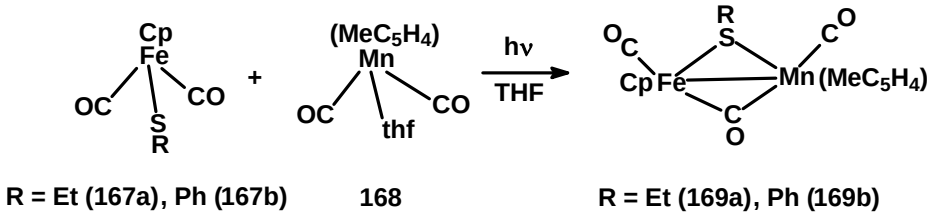
Photolysis of a thf solution of $[CpFe(CO)_2(SR)]$ (R = Et (**167a**), Ph (**167b**)) and $[(CH_3C_5H_4)Mn(CO)_2(THF)]$ (**168**) results in the formation of a SR bridged Fe-Mn compound $[CpFeMn(CH_3C_5H_4)(\mu\text{-}SR)(\mu\text{-}CO)(CO)_2]$ (R = Et (**169a**), Ph (**169b**)) (Scheme 51) [54]. It has been shown by variable temperature NMR spectroscopy that in solution it consists of an interconvertable mixture of *cis*- and *trans*- isomers in equilibrium with each other, confirmed by variable temperature NMR spectroscopy.



R = Et (167a), Ph (167b) **168** **R = Et (169a), Ph (169b)**

Scheme 51

Reactions of either $[Mn(CO)_3(S_2CPCy_3)(Br)]$ with Na $[Re(CO)_5]$ or $[Re(CO)_3(S_2CPCy_3)(Br)]$ with Na$[Mn(CO)_5]$ produce selectively the heterobimetallic complex $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$ (**170b**) which contains an unsymmetrical S_2CPCy_3 bridge between the Mn-Re bond giving eight electrons to the metal atoms. Reaction of $[MnRe(CO)_6(\mu\text{-}S_2CPCy_3)]$ (**170b**) with $[Li\{BHEt_3\}]$ forms an anionic complex $[\{MnRe(CO)_6(\mu\text{-}H)(\mu\text{-}S_2CPCy_3)\}^-Li^+]$ (**171**), which reacts with CS_2 to form $[MnRe(CO)_6\{\mu\text{-}S_2C{=}CPCy_3(SLi(THF)_3)\}]$ (**172**) where the $S_2C{=}C(S)PCy_3$ ligand acts as a bridge between the Mn-Re bond. Further reaction with various halides (RX) gives $[MnRe(CO)_6\{\mu\text{-}S_2C{=}CPCy_3(SR)\}]$ (R = Bu_3Sn (**173a**), Ph_3Sn (**173b**), Cy_3Sn (**173c**), $AuPPh_3$ (**173d**), $CH_2CH{=}CH_2$ (**173e**), CH_2CCH (**173f**)) (Scheme 52) [55].

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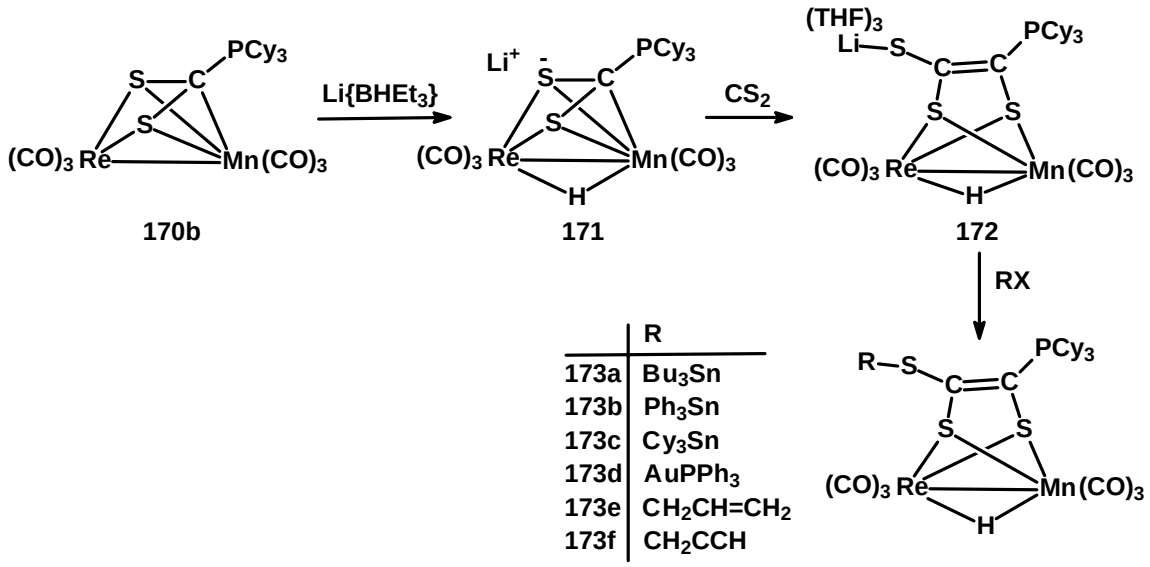

170b 171 172

Scheme 52

The dinuclear complexes, $[MnRe(CO)_6(\mu\text{-}S_2CPR_3)]$ (R = ^{i}Pr (**170a**), Cy (**170b**)) also react with sodium amalgum to form dianionic species $Na_2[MnRe(CO)_6(S_2CPR_3)]$ (**174a,b**) which on treatment with $[Pt(COD)Cl_2]$ in thf results in the formation of a hetero-trinuclear cluster $[(COD)PtMnRe(CO)_6(\mu_3\text{-}SC(PR_3))(\mu_3\text{-}S)]$ (R = ^{i}Pr (**175a**), Cy (**175b**)). Its structure, confirmed by X-ray crystallography, contains a five membered planar Pt-S-C-Re-S ring, in which all the five atoms of the ring are bonded to the manganese atom. Three carbonyl groups are attached to each of rhenium and manganese atoms and COD group is linked to platinum atom. The Pt-S-C-Re-S ring is isolobal with Cp, and the five metal atoms are able to donate a total of five electrons to the $Mn(CO)_3$ fragment to fulfil the 18-electron rule. The dianion (**174a,b**) reacts with two equivalent of MeI to give complex **176a,b** which on treatment with PEt_3 at 40 ºC gives rhenium-manganese dinuclear complexes containing a thiocarbonyl phosphorane ligand ($SCPR_3$) (**177a,b**) (Scheme 53) [56].

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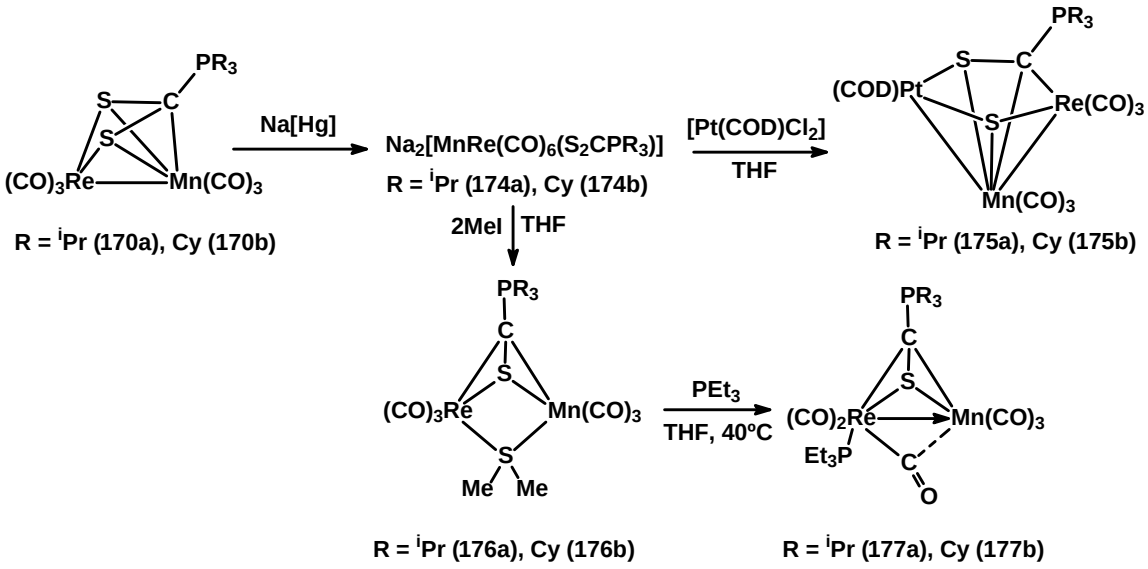
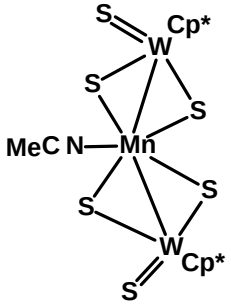


Scheme 53

When an acetonitrile solution of $[PPh_4][Cp^*WS_3]$ (**178**) is added to a solution of $[\{Mn(CH_3CN)_6\}(ClO_4\}_2]$ (**179**) (2:1 molar ratio) and stirred for 24 hrs, a trinuclear tungsten-manganese cluster $[\{Cp^*WS_3\}_2Mn(CH_3CN)]$ (**180**) is isolated (Figure 4) [57]. The cluster has been characterized by X-ray crystallography and reveals the presence of a slightly bent W-Mn-W (W-Mn-W = 158.94(2) Å) metal core having two sulfur bridges on each W-Mn bond (2.9451(1) Å av.). The other ligands include one terminal sulfur atom and a pentamethylcyclopentadiene group on each tungsten atom and a MeCN ligand on the manganese atom.



180

Figure 4

The reaction of $[Mn_2(CO)_6(pyS)_2]$ (**181**) with $[CpMo(CO)_3]_2$ (**182**) in refluxing toluene gives the heterodinuclear $[CpMoMn(CO)_3(\mu\text{-}CO)(\mu\text{-}\eta^2\text{-}pyS)(\mu\text{-}\eta^1\text{-}pyS)]$ (**183**).

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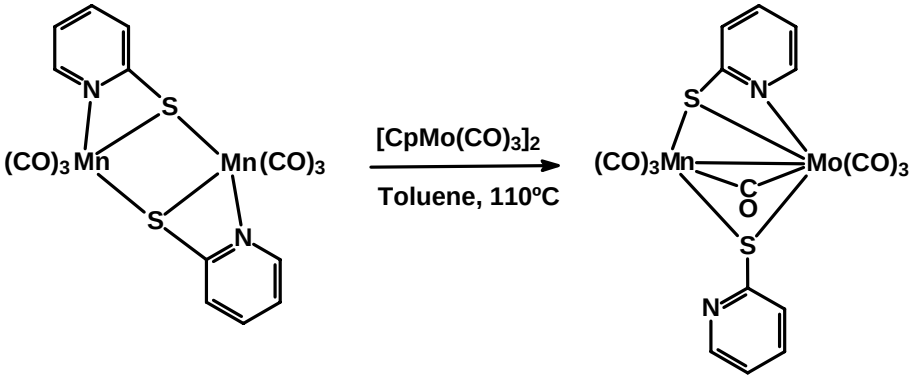
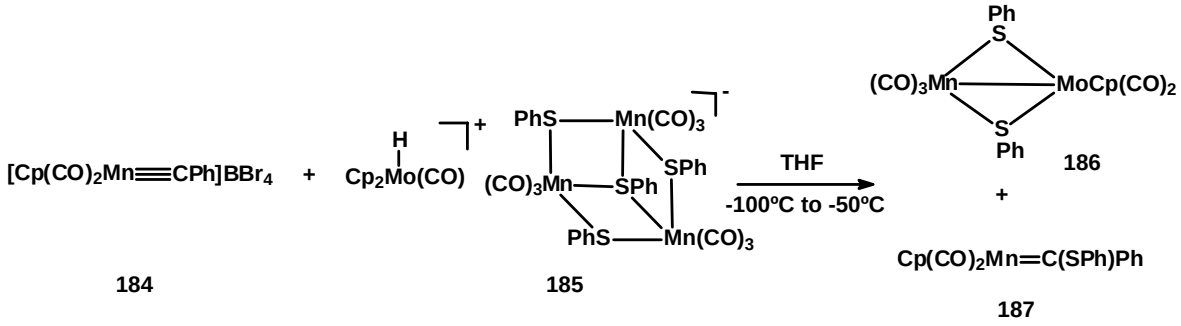
It contains a μ-η^2-pyridine-2-thiolato, a μ-η^1-pyridine-2-thiolato groups bridging the Mn-Mo bond (2.7316(7) Å) (Scheme 54) [58]. X-ray crystallography also reveals the presence of three terminal carbonyl groups bonded to manganese and a Cp ligand linked to molybdenum atom and a bridging CO group attached to both the metals.



181 **183**

Scheme 54

Low temperature reaction between the manganese carbyne complex $[Cp(CO)_2Mn{\equiv}CPh]BBr_4$ (**184**) and the thiolato – bridged $[\{Cp_2Mo(H)CO\}\{Mn_3(CO)_9(\mu\text{-}SPh)_4\}]$ (**185**) leads to formation of a Mo/Mn complex, $[CpMoMn(CO)_5(\mu\text{-}SPh)_2]$ (**186**) and a manganese-carbene complex, $[Cp(CO)_2Mn{=}C(SPh)Ph]$ (**187**) (Scheme 55) [59]. Structural analysis of **186** reveals two thiolato groups doubly bridging between the molybdenum –manganese bond. Three carbonyl groups are attached to manganese and one cyclopentadienyl and two carbonyl ligands are bonded to molybdenum atom.



184 **185** **187**

Scheme 55

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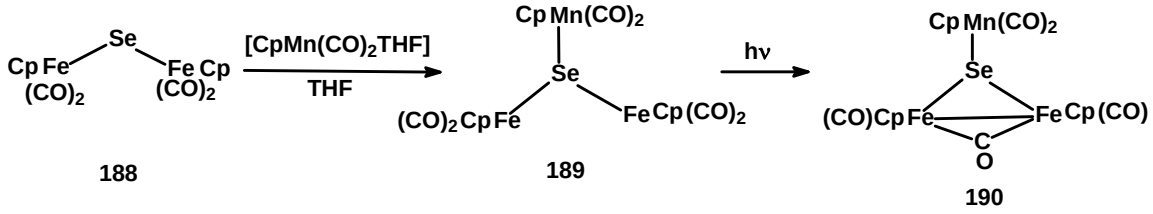
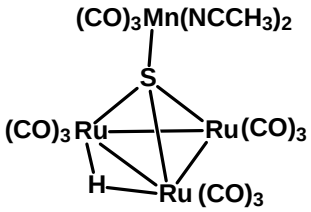
The iron complex $[CpFe(CO)_2(\mu\text{-}Se)Fe(CO)_2Cp]$ (**188**) reacts with the coordinatively unsaturated species formed from $[CpMn(CO)_2(THF)]$ to form a trinuclear $[\{CpFe(CO)_2\}_2\{CpMn(CO)_2\}(\mu_3\text{-}Se)]$ (**189**) with no metal –metal bond formation. In presence of light, **189** converts to the stable compound $[\{Cp_2Fe_2(\mu\text{-}CO)(CO)_2\{CpMn(CO)_2\}(\mu_3\text{-}Se)]$ (**190**) by losing one carbonyl group and by the formation of a Fe-Fe bond (Scheme 56). No metal-metal bond has been observed between the Mn and Fe atoms. The selenium atom is triply bridged to two iron and a manganese atoms [60].



188 **189** **190**

Scheme 56

The sulfido – bridged anionic $[Ru_3(CO)_9(\mu_3\text{-}S)]^{2-}$ (**191**) reacts with the cation $[Mn(CO)_3(NCCH_3)_3]^+$ (**192**) to form $[HRu_3(CO)_9(\mu_4\text{-}S)Mn(CO)_3(NCCH_3)_2]$ (**193**) (Figure 5) [61].



193

Figure 5

SUMMARY

Although manganese is found less frequently than some other metals in metal cluster chemistry, compounds reported in this review shows that a variety of manganese containing mixed metal clusters have been prepared by using bridging ligands derived from Groups 15 and 16. Still several more exist which have been obtained by other

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methods but are outside the scope of this review. The new manganese containing clusters will contribute to the burgeoning fields of activation of small organic molecules, non – linear optics and as reagents for the synthesis of novel nanomaterials.

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