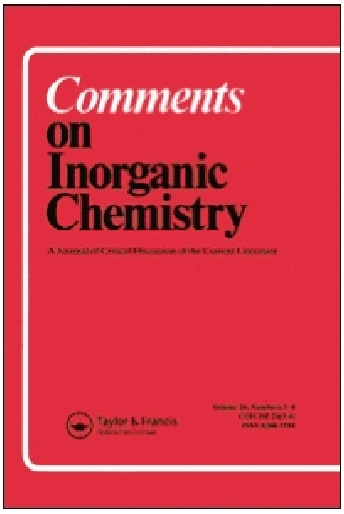

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OXO INCORPORATED METAL ACETYLIDE COMPLEXES

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OXO INCORPORATED METAL ACETYLIDE COMPLEXES

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Studies on organometallic oxo complexes have intensified in recent years due to their implications in catalytic oxidations or as reagents in the oxidation of organic molecules. Synthesis of such complexes containing a hydrocarbon ligand besides the carbonyl and oxo provides an opportunity to obtain complexes with both low oxidation state metal carbonyl fragment and high oxidation state metal oxide fragment in the same molecule. Our attention has been focused on oxo incorporated metal acetylide complexes, in particular, to understand how oxo ligands bond to the metal atoms. Synthetic strategy, structural behavior and reactivity of oxo acetylide metal complexes and clusters are reviewed.

Keywords: acetylide, oxo, organometallic, metal

INTRODUCTION

Organometallic oxo complexes have been of considerable interest in recent years as a result of their implications in catalytic oxidations or as reagents in oxidation of organic molecules.[1] Oxo complexes containing hydrocarbyl ligands serve as realistic models for metal-mediated oxidations and other homogeneous and heterogeneous reactions with high valent metal species as catalysts.[2] Migration of an alkyl or aryl

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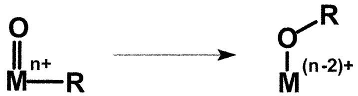


Scheme 1. Migration of alkyl or aryl group.

group to the oxo ligand (Scheme 1) has been proposed as an important step in the overall mechanism for oxidizing these fragments.

The oxide (=O) ligand is normally considered to be a hard ligand in organometallic chemistry, principally associated with early, high oxidation state metal fragments.[3] The most important generalization in metal-oxo chemistry is that M=O groups are stabilized at metal centers with an oxidation state of no less than 4+ and no more than four d electrons. Oxo-metal bonds are describable by the canonical forms, shown in Fig. 1, which show that the metal must be a π-acceptor and adequately electron deficient so as to induce charge distribution as in contribution Fig. 1(b).

Metal atoms with configurations d^{0-4} have vacant or half-filled π-acceptor orbitals necessary for this interaction. Scheme 2 shows different types of binuclear oxo metal groups containing both terminal and bridging oxo ligands.

Oxo-element groups are prevalent in the chemistry of groups 15–18, with the same restriction on oxidation state. Although complexes of high oxidation state "oxophilic" metals and low oxidation state metals with π-acid ligands are usually considered to be at the opposite extremes of the spectrum of transition metal organometallic complexes, recent developments suggest that oxides can play an important role as interfacial ligands, bridging early–high and late-low oxidation state metal centers to form mixed metal oxide clusters, which may serve as models for oxide-supported metal catalysts.[4,5] Several oxo metal complexes have been synthesized and their reactions with organic substrates have been studied. For instance, the dioxo Mo(VI) complex $[(\eta^5\text{-}C_5Me_5)Mo(O)_2Cl]$ has been invoked as a catalyst for the reaction of alkyl

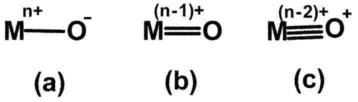
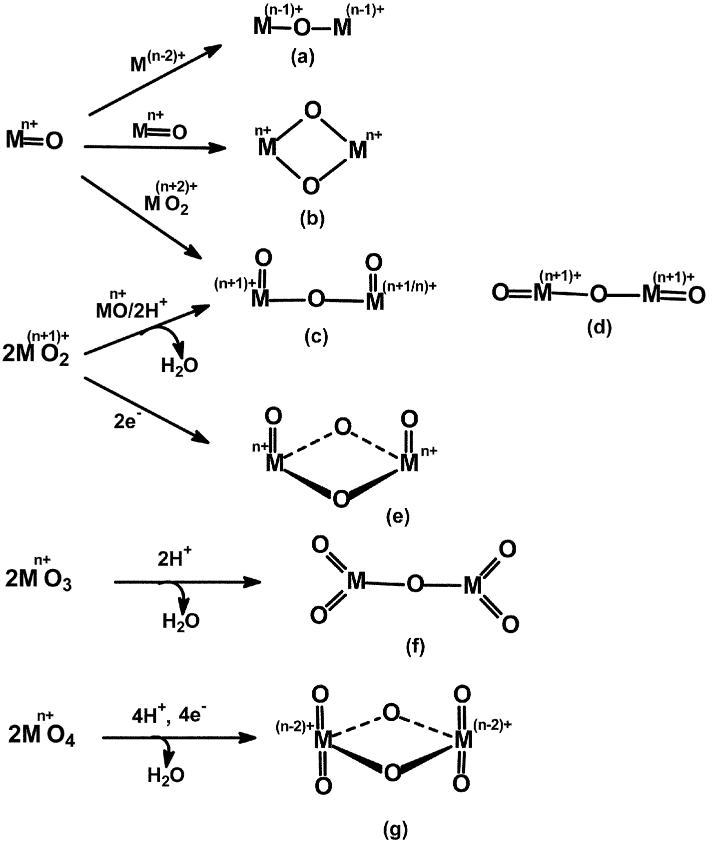


Figure 1. Canonical forms of MO (terminal).

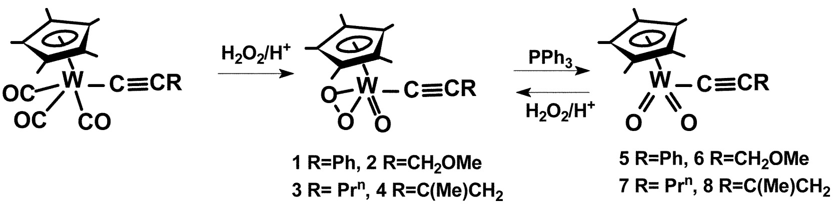


Scheme 2. $M_2(\mu\text{-O})$ (a), linear $M_2O_2(\mu\text{-O})$ (b), *syn*- or *anti*-$M_2O_2(\mu\text{-O})$ (c), $M_2O_4(\mu\text{-O})$ (d), $M_2(\mu\text{-O})_2$ (e), *cis*- or *trans*-$M_2O_2(\mu\text{-O})_2$ (f) and $M_2O_4(\mu\text{-O})_2$ (g).

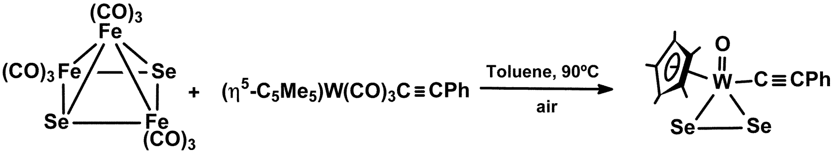
hydroperoxides with olefins to yield the epoxides and alcohols.[6] The related peroxo molybdenum or tungsten species also appear to be useful reagents in alcohol oxidation and other catalytic processes.[7] Metal-oxo species are also utilized in industrial processes involving homogeneous catalysis. For example, vanadium–oxo complexes catalyze the rearrangement of allylic or propargylic alcohols in the manufacture of terpene alcohols and vitamin-A.[8] Besides these, metal-oxo complexes are also present on the surface of industrially important heterogeneous catalysts, as in the use of iron molybdate catalysts for the oxidation of methanol to formaldehyde.[9] Molybdenum oxo complexes, $[Mo(O)_2L_n]$ ($L = S$, N-cys-OR; $n = 2$ and $L = SR_4$; $n = 4$), catalytically oxidize the conversion of benzoin to benzyl.[10] Elucidation of the reactivity and structural features of these oxo complexes or clusters is crucial to further understanding of how oxo ligands bond to the metal atoms and how they react with adjacent hydrocarbon ligands and serve as intimate reagents for oxygen transfer reactions.[1c] There exists substantial interest in the synthesis, structural characterization and reactivity of organometallic complexes bearing the oxo and hydrocarbon ligands. The conventional method of preparing organometallic oxo complexes from carbonyl complexes involves a thermally or photochemically induced reaction in the presence of air or oxygen. However, several other methods have been reported for obtaining a diverse array of organometallic complexes bearing oxo ligands. In this review we focus our discussion on complexes containing oxo and acetylide ligands of mononuclear and polynuclear metal systems.

MONONUCLEAR COMPLEXES

Two synthetic strategies have been used for obtaining mononuclear complexes containing the acetylide and oxo ligand. In one, hydrogen peroxide is the source of the oxo group, while in the other, aerobic conditions are used for formation of the oxo derivatives. The pentamethylcyclopentadienyl tungsten carbonyl acetylide complexes $[(\eta^5\text{-}C_5Me_5)W(CO)_3(CCR)]$, R = Ph, CH_2OMe, Pr^n and $C(Me){=}CH_2$ react with acidic solution of hydrogen peroxide at room temperature to form the oxo–peroxo acetylide complexes $[(\eta^5\text{-}C_5Me_5)W(O)(O)_2(CCR)]$ (**1–4**), which undergo loss of one oxygen atom on treatment with triphenylphosphine to afford the corresponding dioxo complexes $[(\eta^5\text{-}C_5Me_5)W(O)_2(CCR)]$ (**5–8**) (Scheme 3).[11] However, treatment of hydrogen peroxide with the analogous molybdenum complex $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3(CCR)]$ or the cyclopentadienyl compound



Scheme 3. Reaction of $[(\eta^5\text{-}C_5H_5)W(CO)_3(CCR)]$ with H_2O_2.



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Scheme 4. Thermolysis of [$Fe_3(CO)_9(\mu_3\text{-}Se)_2$] and [($\eta^5$-$C_5Me_5$)$W(CO)_3(CCPh)$] in air.

[(η^5-C_5H_5)$W(CO)_3(CCR)$] produces only decomposition, even at lower temperatures.

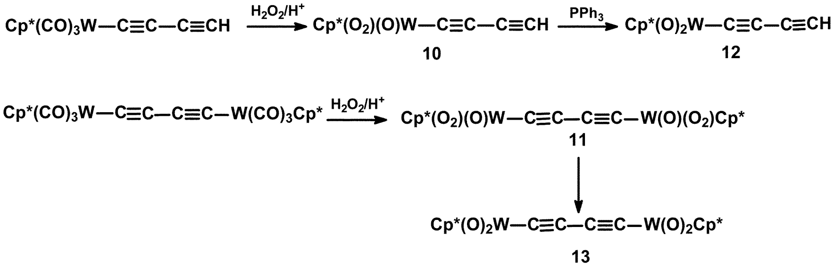
Formation of a mononuclear oxo acetylide metal complex [(η^5-C_5Me_5)$W(O)(Se)_2(CCPh)$] (9) is observed when a solution of [$Fe_3(CO)_9(\mu_3\text{-}Se)_2$] and [($\eta^5$-$C_5Me_5$)$W(CO)_3(CCPh)$] is heated at 90°C in presence of air (Scheme 4).[12]

The molecular structure of 9 consists of a (η^5-C_5Me_5)W(CCPh) unit, with oxo and side-on bonded Se_2 ligand attached to the W atom. The W-O bond distance of 1.702(4) Å infers a W-O (terminal) double bond character. The WSe_2 unit has a Se−Se bond distance of 2.316(2) Å, which is longer than the Se=Se double-bond distance of 2.19 Å but closer to the normal Se−Se single-bond distance of 2.336 Å.[13] It is comparable to the Se−Se bond distance for [$Fe_2(CO)_6(\mu\text{-}Se_2)$], 2.293(2) Å[14] but slightly shorter than in the $FeSe_2$ unit of [$CrFe_2(CO)_{10}Se_4$], 2.362(11) Å.[15,16] In contrast to the highly reactive Se−Se bond in [$Fe_2(\mu\text{-}Se_2)(CO)_6$], which is known to add numerous inorganic and organic moieties across it, the Se−Se bond in compound 9 is rather stable, much like the "picnic basket" compound [$CrFe_2(CO)_{10}Se_4$], which also features a very stable pair of Se−Se bonds.

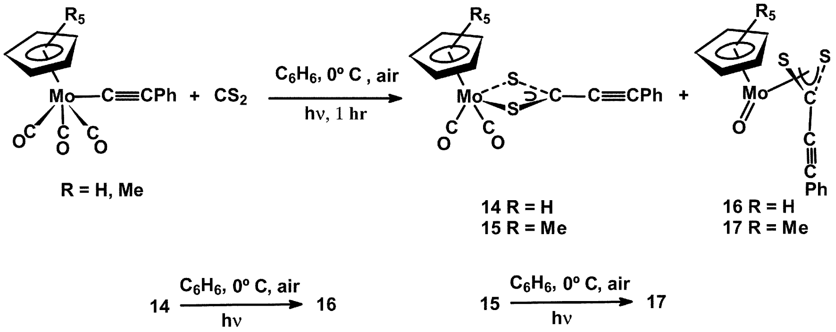
Carty and co-workers[17] have reported the preparation of an oxo–diynyl complex, [(η^5-C_5Me_5)$W(C{\equiv}CC{\equiv}CH)(O)_2$] (12) from the oxidation reaction of [(η^5-C_5Me_5)$W(C{\equiv}CC{\equiv}CH)(CO)_3$]. Formation of [($\eta^5$-$C_5Me_5$)$W(C{\equiv}CC{\equiv}CH)(O)_2$] occurs via an oxo-peroxo intermediate [(η^5-C_5Me_5)$W(C{\equiv}CC{\equiv}CH)(O_2)(O)$] (10) (Scheme 5).

The diyne diyl oxo derivative, [$\{W(O)_2(\eta^5\text{-}C_5Me_5)\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$] (13) has been obtained by oxidation of [$\{W(CO)_3(\eta^5\text{-}C_5Me_5)\}_2$ (μ-$C{\equiv}CC{\equiv}C$)] under identical conditions to those used for preparation of [$W(C{\equiv}CC{\equiv}CH)(O)_2(\eta^5\text{-}C_5Me_5)$].

Under aerobic condition, low temperature photolysis of benzene solution of [(η^5-C_5R_5)$Mo(CO)_3(CCPh)$] (R = H, Me) in presence of CS_2



Scheme 5. Reaction of [Cp*W(C≡CC≡CH)(CO)$_3$] and [{Cp*W(CO)$_3$}$_2$(μ-C≡CC≡C)] with H_2O_2, (Cp* = η^5-C_5Me_5).



Scheme 6. Reaction of [(η^5-C_5R_5)Mo(CO)$_3$(CCPh)] (R = H, Me) with CS_2.

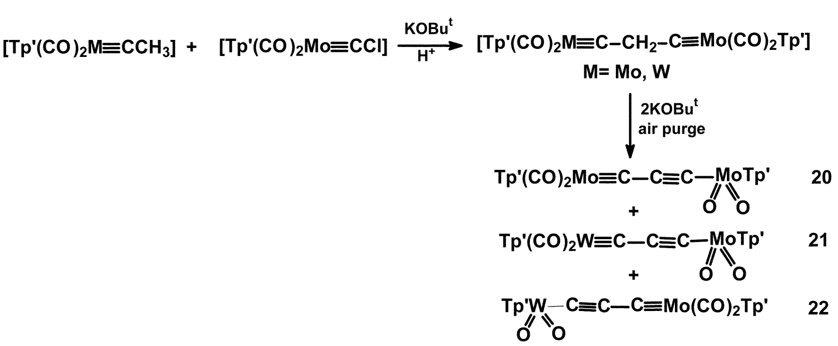
gives [(η^5-C_5R_5)Mo(CO)$_2$(η^2 – S_2CC≡CPh)] (R = H (**14**), Me (**15**)) and [(η^5-C_5R_5)Mo(O)(η^3-S_2CC≡CPh)] (R = H (**16**), Me (**17**)). Compounds **16** and **17** are also separately obtained in reasonable yields when a benzene solution of **14** or **15** is photolyzed in presence of air (Scheme 6). Compounds **16** and **17** are isostructural, the structure consists of a {(η^5-C_5Me_5)Mo(=O)} moiety and a (S_2CC≡CPh) ligand attached to the Mo atom in an unusual η^3-allylic fashion. The (C≡CPh) substituent and the oxo on the molybdenum atom are mutually endo in both **16** and **17**.[18]

POLYNUCLEAR COMPLEXES

Acetylide–bridged cluster compounds have attracted much attention, and in recent times there has been growing interest in polynuclear complexes bearing both the acetylide and oxo ligands. Although a variety of unusual acetylide bonding and acetylide coupling reactions have been observed on mixed metal clusters, there are relatively few metal clusters containing both the oxo and acetylide ligands. Such clusters, containing both oxo and acetylide ligands, are of special interest as they offer valuable insight into the coordination mode common for oxygen atoms bound to surfaces and the enhanced reactivity of cluster–bound hydrocarbon fragments mediated by an oxo ligand. Aerobic conditions are the most widely used strategy for obtaining such complexes; however, in some cases use of N_2O or of oxo and oxo-peroxo complexes has yielded the acetylide and oxo incorporated clusters.

Mo-Mo and W-Mo Complexes

Deprotonation of $[Tp'(CO)_2M{\equiv}CCH_3]$ (M = Mo, W) {Tp′ = hydridotri-(3,5-dimethylpyrazolylborate)} generates a vinylidene anion, which on treatment with $[Tp'(CO)_2Mo{\equiv}CCl]$ yields $[Tp'(CO)_2M{\equiv}CCH_2C{\equiv}Mo(CO)_2Tp']$ (M = Mo (**18**), W (**19**)). Treatment of **18** with 2 equivalents of $KOBu^t$, followed by exposure to air, yields the green mixed-metal dimer $[Tp'(CO)_2Mo{\equiv}CC{\equiv}CMo(O)_2Tp']$ (**20**) (Scheme 7). Similarly, in the presence of base, **19** can be oxidized with air to form two bimetallic complexes, $[Tp'(CO)_2W{\equiv}CC{\equiv}CMo(O)_2Tp']$ (**21**) and $[Tp'(O)_2W{\equiv}CC{\equiv}CMo(CO)_2Tp']$ (**22**).[19]



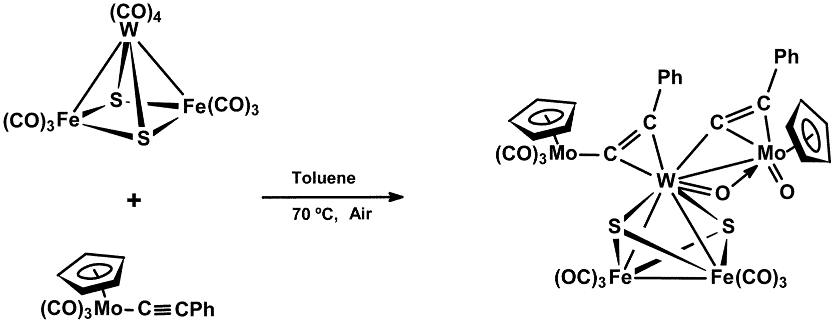
Scheme 7. Reaction of $[Tp'(CO)_2M{\equiv}CCH_3]$ (M = Mo, W) with $[Tp'(CO)_2Mo{\equiv}CCl]$ [Tp′ = hydridotri(3,5-dimethylpyrazolylborate)].

Fe-Mo and Fe-Mo-W Complexes

Investigations on developing new syntheses of acetylide incorporated, chalcogen-bridged clusters have shown that the reactions are strongly influenced by nature of chalcogen bridges present in the starting compounds, and reaction conditions used, in particular whether anaerobic or aerobic conditions are employed. Under anaerobic conditions, a number of mixed-metal clusters stabilized by chalcogens and containing C_4-ligands formed by head-to-head, head-to-tail or tail-to-tail coupling of acetylide ligands have been prepared. By contrast, under carefully controlled aerobic conditions, though acetylide coupling is not observed, chalcogen-bridged mixed metal clusters bearing one, two or three oxo, and one or two acetylide ligands are obtained.[12,20]

Thermolysis of a toluene solution of $[Fe_2W(CO)_{10}(\mu_3\text{-}S)_2]$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CCPh)]$ in the presence of air at 70°C yields the mixed–metal cluster $[(\eta^5\text{-}C_5H_5)_2Mo_2WFe_2(O)_2(S)_2(CO)_9(CCPh)_2]$ **(23)** (Scheme 8).[21] The core structure of **23** is a triangular Fe_2W unit, each face of which is capped by a sulfido ligand. The W atom is attached to two different Mo-containing moieties. It is π-bonded to the C≡C triple bond of a $(\eta^5\text{-}C_5H_5)Mo(CO)_3(CCPh)$ unit, and it is also bonded to a second Mo atom, and this bond is bridged by an oxo ligand and a μ_2, η^2-C≡CPh group. Also attached to this Mo atom is a terminal oxo ligand.

Electron count of the W–Mo portion of **23** shows 34 electrons, if one assumes that the bridging oxo ligand is a net 4-electron donor, of the type W=O→Mo. The short W–O (bridging) distance of 1.822(2) Å



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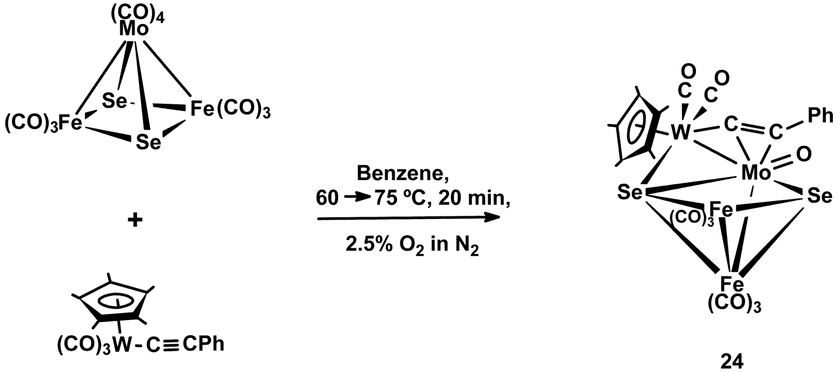
Scheme 8. Aerobic reaction of $[Fe_2W(CO)_{10}(\mu_3\text{-}S)_2]$ with $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(CCPh)]$.



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Scheme 9. Thermal reaction of $[Fe_2Mo(CO)_{10}(\mu_3\text{-}Se)_2]$ and $[(\eta^5\text{-}C_5Me_5)W(CO)_3CCPh]$.

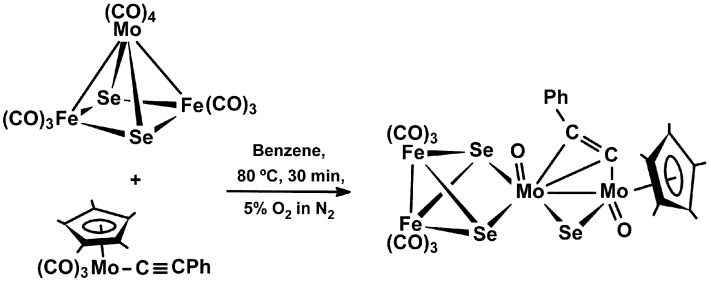
supports double bond character as observed in the fragments $W{=}O{\rightarrow}M$ (M = Ru, Os) in several $WOs_3(\mu\text{-}O)$, $WRu_4(\mu\text{-}O)$ and $WRu_5(\mu\text{-}O)$ clusters reported previously.[22,33] The W-Mo portion of **23** is therefore saturated and the W–Mo bond can be regarded as a single bond.

Thermolysis of a benzene solution of $[Fe_2Mo(CO)_{10}(\mu_3\text{-}Se)_2]$ and $[(\eta^5\text{-}C_5Me_5)W(CO)_3CCPh]$ under an optimum concentration of oxygen in the reaction medium yields the cluster $[(\eta^5\text{-}C_5Me_5)MoWFe_2(O)\text{-}(\mu_3\text{-}Se)(\mu_4\text{-}Se)(CO)_8(CCPh)]$ (**24**), containing a mono-oxygen metal center (Scheme 9).[23]

Its molecular structure consists of a distorted square pyramidal Fe_2MoSe_2 core in which the apical site is occupied by one of the iron atoms. The molybdenum atom has one terminal oxo ligand and one of the Mo-Se edges is bridged by a $(\eta^5\text{-}C_5Me_5)W(CO)_2$ group. The W-Mo bond is bridged by a $\eta^1,\eta^2\text{-}C{\equiv}CPh$ group. The Mo–O bond distance is comparable in length with the Mo=O double bond.

By contrast, reaction of $[Fe_2Mo(CO)_{10}(\mu_3\text{-}Se)_2]$ and $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3CCPh]$ at 80°C in an atmosphere of 5% O_2 in N_2 results in an acetylide bridged tetranuclear cluster $[(\eta^5\text{-}C_5Me_5)Mo_2Fe_2(O)_2(\mu_3\text{-}Se)_2(\mu\text{-}Se)(CO)_6(CCPh)]$ (**25**) containing a μ_2-bridging Se atom and two terminal oxo ligands (Scheme 10). There is no observable reaction between $[Fe_2Mo(CO)_{10}(\mu_3\text{-}Te)_2]$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3CCPh]$.[24]

Mild thermolysis of a benzene solution of $[Fe_2Mo(CO)_{10}(\mu_3\text{-}S)_2]$ with $[(\eta^5\text{-}C_5Me_5)W(CO)_3CCPh]$ and $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3CCPh]$ under 5% concentration of oxygen in the reaction medium yields clusters with two or three oxygen ligands, $[(\eta^5\text{-}C_5Me_5)WMo_2(\mu\text{-}O)_2(\mu\text{-}S)$



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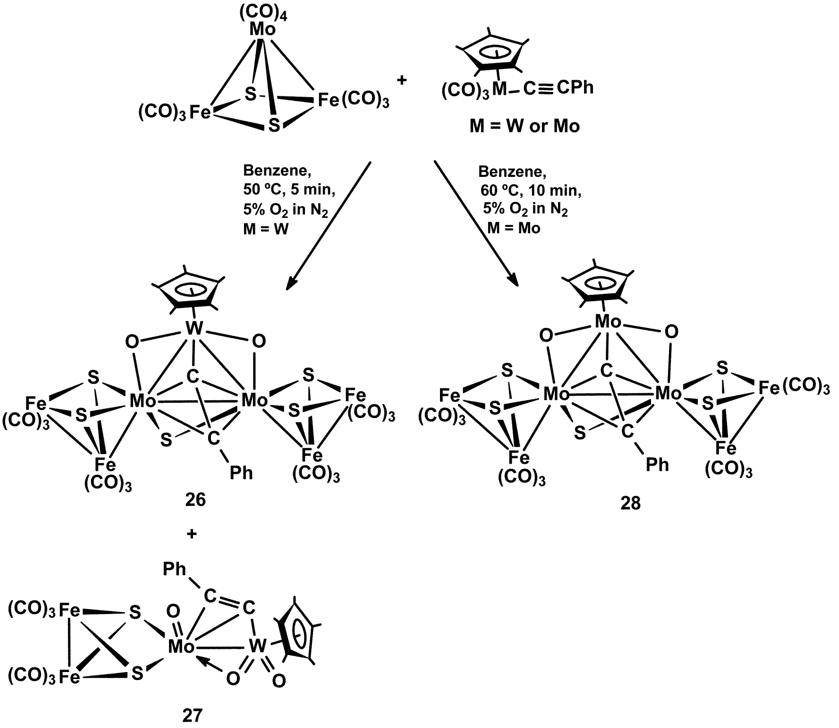
Scheme 10. Reaction of $[Fe_2Mo(CO)_{10}(\mu_3\text{-}Se)_2]$ with $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3CCPh]$.

$(\mu_3\text{-}CCPh)\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}_2]$ (**26**), $[(\eta^5\text{-}C_5Me_5)WMo(O)_2(\mu\text{-}O)(\mu\text{-}CCPh)\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}]$ (**27**) and $[(\eta^5\text{-}C_5Me_5)Mo_3(\mu\text{-}O)_2(\mu\text{-}S)(\mu_3\text{-}CCPh)\{Fe_2(CO)_6(\mu_3\text{-}S)_2\}_2]$ (**28**) (Scheme 11).[23] Molecular structures of **26** and **28** show an identical cluster core geometry consisting of two distorted $MoFe_2S_2$ square pyramid units joined via a Mo–Mo bond, which is bridged by a $(\eta^5\text{-}C_5Me_5)W$ group in **26** and by a $(\eta^5\text{-}C_5Me_5)Mo$ group in **28**. The edges of the Mo_2W triangle of **26** and Mo_3 triangle of **28** are bridged by a sulfido and two oxo ligands, and the face is capped by a phenylacetylide moiety.

The molecular structure of **27** consists of an open Fe_2S_2 butterfly unit in which S atoms are attached to the molybdenum atom of a $Mo(=O)W(=O)(\eta^5\text{-}C_5Me_5)(\mu\text{-}O)(\mu\text{-}C\equiv CPh)$ unit. The two terminal oxo ligands adopt the somewhat rare *trans* geometry, similar to the terminal oxo ligands in the Te-bridged $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}Te)]$.[25] The Mo–W bond is bridged unsymmetrically by a four electron oxo ligand: Mo–O(bridging) = 2.017(3) Å, W–O(bridging) = 1.873(3) Å. The terminal Mo=O bond distance of 1.673(3) Å is similar to that in **24** as well as in $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}Te)]$ (1.693(4) Å) and $[(\eta^5\text{-}C_5H_5)_2Mo_2(O)_2(\mu\text{-}O)(\mu\text{-}S)]$ (1.694(8) Å),[25] and the W–O(terminal) distance of 1.711(3) Å is close to that of a double bond between tungsten and an oxo ligand (1.711(6) Å), observed in $[(\eta^5\text{-}C_5Me_5)W(O)_2(CCPh)Ru_6(\mu_6\text{-}C)(CO)_{14}]$.[26]

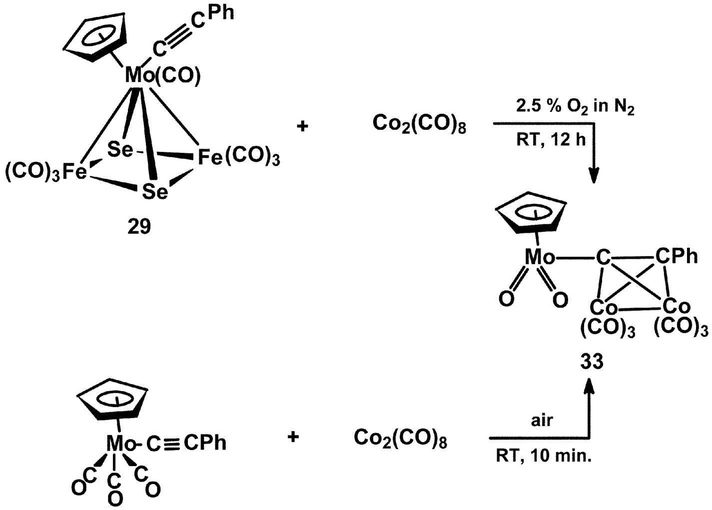
Mo-Co Complexes

Organometallic compounds containing free carbon chain ligands can provide a reaction site for the development of cluster multiplicity. In



Scheme 11. Reaction of $[Fe_2Mo(CO)_{10}(\mu_3\text{-}S)_2]$ with $[(\eta^5\text{-}C_5Me_5)W(CO)_3CCPh]$ and $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3CCPh]$.

principle, these compounds should resemble mononuclear η^1-acetylide in terms of reactivity. Much work has been reported with metal complexes using C_2, C_4 and longer chain units whereas metal cluster bound free carbon chains are much less common. The first example of a mixed–metal cluster bearing a η^1-bound acetylide group $[(\eta^5\text{-}C_5H_5)MFe_2(CO)_7(\mu_3\text{-}E)_2(\eta^1\text{-}CCPh)]$ (M = Mo, W; E = Se, Te), (**29–32**) in which the C≡C bond remains intact has been obtained from the reaction of $[(\eta^5\text{-}C_5H_5)M(CO)_3CCPh]$ (M = Mo, W) and $[Fe_3(CO)_9(\mu_3\text{-}E)_2]$ (E = Se, Te) in presence of trimethylamine-N-oxide.[27] The compound $[(\eta^5\text{-}C_5H_5)MoFe_2(CO)_7(\mu_3\text{-}Se)_2(\eta^1\text{-}CCPh)]$ (**29**) reacts with $Co_2(CO)_8$ under a limited concentration of O_2 at room temperature to yield a dioxo complex, $[(\eta^5\text{-}C_5H_5)Mo(O)_2Co_2(CO)_6(\mu\text{-}CCPh)]$ (**33**). However, compound **33** can also be isolated when the mononuclear metal acetylide

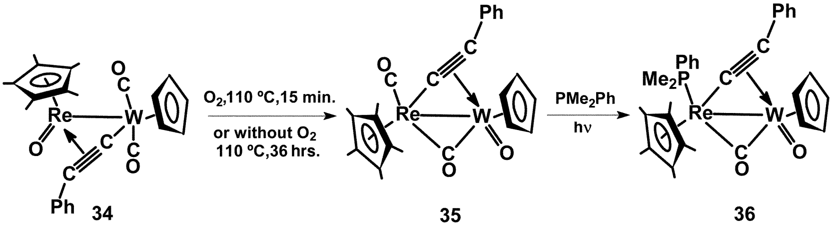


Scheme 12. Reaction of $[(\eta^5\text{-}C_5H_5)MoFe_2(CO)_7(\mu_3\text{-}Se)_2(\eta^1\text{-}CCPh)]$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3CCPh]$ with $Co_2(CO)_8$.

$[(\eta^5\text{-}C_5H_5)Mo(CO)_3CCPh]$ is treated with $Co_2(CO)_8$ in air at room temperature for 10 minutes (Scheme 12).[28]

W-Re Complexes

The rhenium dioxo dimer $[(\eta^5\text{-}C_5Me_5)Re(O)(\mu\text{-}O)]_2$, generated *in situ* by treatment of 1:1 molar equivalent of $[(\eta^5\text{-}C_5Me_5)Re(O)_3]$ and PPh_3, reacts with the tungsten acetylide complex $[(C_5H_5)W(CO)_3(CCPh)]$ in toluene at 110°C to afford a dark green oxo-acetylide compound $[(\eta^5\text{-}C_5Me_5)Re(O)(\mu\text{-}C_2Ph)W(CO)_2(\eta^5\text{-}C_5H_5)]$ (**34**) as the major product and an orange compound $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(\mu\text{-}C_2Ph)W(O)(\eta^5\text{-}C_5H_5)]$ (**35**) in smaller amount.[29] Heating a toluene solution of 34 under nitrogen at 110°C for 36 hrs. or under oxygen at 110°C for 15 minutes affords compound **35**. This reaction can be thought to proceed formally via a transfer of the oxo ligand from rhenium to tungsten, CO migration from W to Re atoms and a concomitant acetylide sigma-pi, pi-sigma rearrangement. Photolysis of a solution of **35** in presence of slight excess of PMe_2Ph leads to the formation of $[(\eta^5\text{-}C_5Me_5)Re(PMe_2Ph)(\mu\text{-}CO)(\mu\text{-}C_2Ph)W(O)(\eta^5\text{-}C_5H_5)]$ (**36**) (Scheme 13).

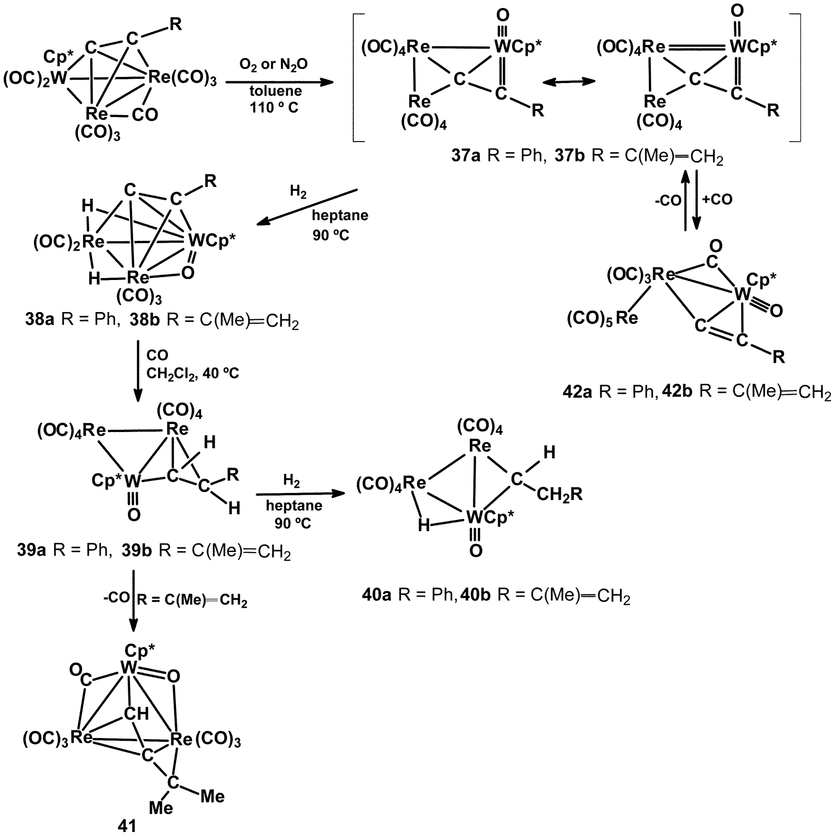


Scheme 13. Thermolysis of $[(\eta^5\text{-}C_5Me_5)Re(O)(\mu\text{-}C_2Ph)W(CO)_2(\eta^5\text{-}C_5H_5)]$.

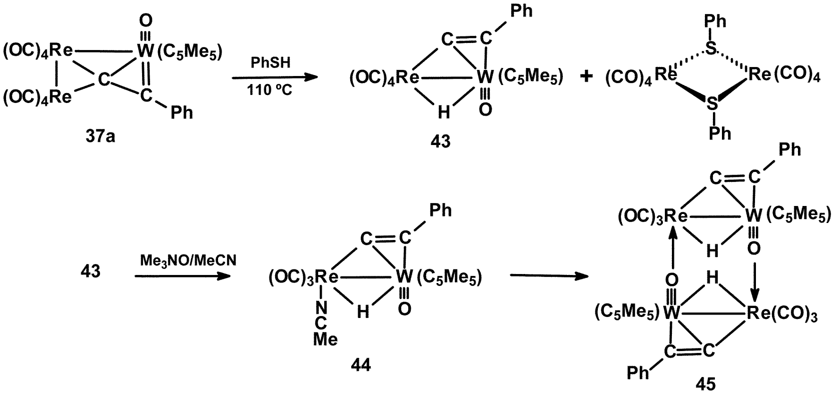
A trinuclear oxo acetylide complex $[WRe_2(C_5Me_5)(O)(CO)_8(CCR)]$, {R = Ph (**37a**), C(Me) = CH_2 (**37b**)} has been obtained when the acetylide cluster $[WRe_2(C_5Me_5)(CO)_9(CCR)]$, isolated from the reaction of $[Re_2(CO)_8(NCMe)_2]$ and $[(C_5Me_5)W(CO)_3(CCR)]$, is treated with O_2 or N_2O. Hydrogenation of **37a** affords three clusters, **38a**, **39a**, **40a**, whereas compound **37b** reacts with dihydrogen under similar conditions to furnish a mixture of **38b**, **39b** and **40b**, together with an allenyl cluster, $[(\eta^5\text{-}C_5Me_5)WRe_2(\mu\text{-}O)(CO)_7(CHCCMe_2)]$ (**41**). Treatment of **37a**/**b** with CO at 110°C provides the clusters $[(\eta^5\text{-}C_5Me_5)W(O)Re_2(CO)_9(CCR)]$ **42a**/**b**, which on thermolytic decarbonylation form **37a**/**b** (Scheme 14).[30]

Experimental evidence suggests that **38** is the initial product; it couples with free CO in solution to afford **39**, followed by addition of another H_2 molecule to produce **40**. Molecular structure of **37** consists of an open triangular core arrangement with eight CO ligands; the acetylide ligand adopts an unused μ_3, η^1, η^1, η^2-mode, in which the α-carbon is linked to all three metal atoms, but the β-carbon is bonded only to the W atom, with substantial carbenic character. The oxo ligand adopts a terminal bonding mode with a W–O bond distance of 1.699(6) Å, which the author illustrates to involve two resonance forms, one possessing W=Re and W=O double bonds, while the second contains a W–Re and a W≡O triple bond.

Compound **37a** reacts with thiophenol to afford $[(\eta^5\text{-}C_5Me_5)W(O)Re(CO)_4(\mu\text{-}H)(\mu\text{-}CCPh)]$ (**43**) and $[Re(CO)_4(\mu\text{-}SPh)]_2$ (Scheme 15).[31] Upon treatment with Me_3NO in acetonitrile, **43** loses one CO ligand and is converted to $[(\eta^5\text{-}C_5Me_5)W(O)Re(CO)_3(NCMe)(\mu\text{-}H)(\mu\text{-}CCPh)]$ (**44**). A head-to-tail dimerization of **44** occurs at room temperature to yield $[(\eta^5\text{-}C_5Me_5)WRe(CO)_3(\mu\text{-}O)(\mu\text{-}H)(\mu\text{-}CCPh)]_2$ (**45**).

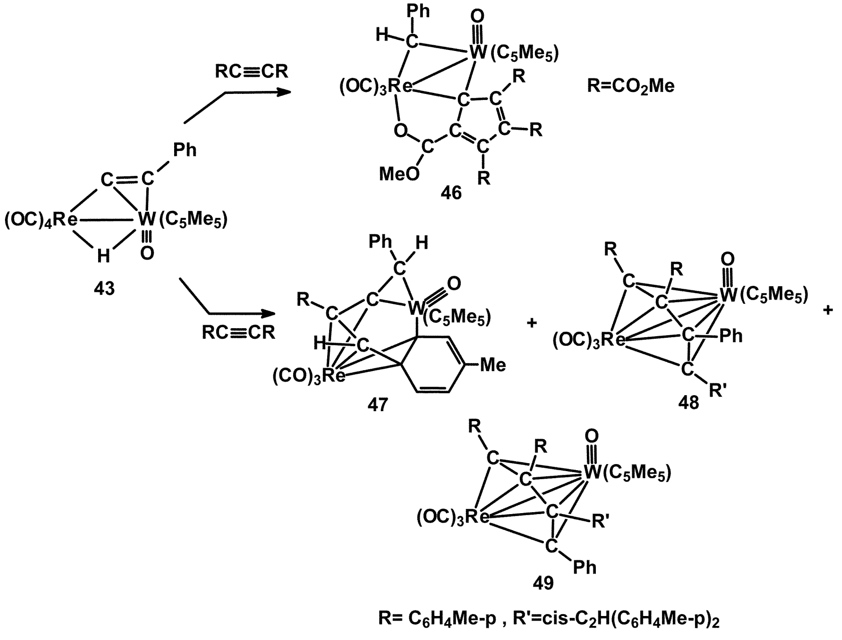


Scheme 14. Reaction pathway for WRe$_2$ acetylide cluster, (Cp* = η^5-C_5Me_5).



Scheme 15. Reaction of [WRe$_2$(C_5Me_5)(O)(CO)$_8$(CCPh)] with PhSH.

In an attempt to elucidate the reactivity and structural features of these complexes for a further understanding of how oxide ligands bond to the metal atoms, Chi and co-workers[32] have reported the reactions of **43** with disubstituted alkynes, such as dimethyl acetylene dicarboxylate and di-p-tolylacetylene. Thermolysis of the dinuclear oxo acetylide complex **43** with dimethyl acetylene dicarboxylate affords the bis(alkylidene) complex $[WRe(\eta^5\text{-}C_5Me_5)O(CO)_3(\mu\text{-}CHPh)]$ (**46**). In contrast, treatment of **43** with an excess of di-p-tolylacetylene in refluxing toluene produces three complexes $[WRe(\eta^5\text{-}C_5Me_5)O(CO)_3\{CH(Ph)CC(C_6H_4Me\text{-}p)CH(\mu\text{-}\eta^2\text{-}C_6H_3Me)\}]$ (**47**), $[WRe(\eta^5\text{-}C_5Me_5)O(CO)_3\{\mu\text{-}C_4Ph[C_2H(C_6H_4Me\text{-}p)_2](C_6H_4Me\text{-}p)_2\}]$ (**48**) and $[WRe(\eta^5\text{-}C_5Me_5)O(CO)_3\{\mu\text{-}C_4[C_2H(C_6H_4Me\text{-}p)_2]Ph(C_6H_4Me\text{-}p)_2\}]$ (**49**) (Scheme 16). Complex **46** is produced by the addition of two alkynes and cleavage of the acetylide C–C bond. On the other hand, formation of **47** involves ortho-metallation of a tolyl substituent on the incoming alkyne, while **48** and **49** are each produced by sequential coupling with two alkynes, forming the highly distorted metallacyclopentadienyl framework.

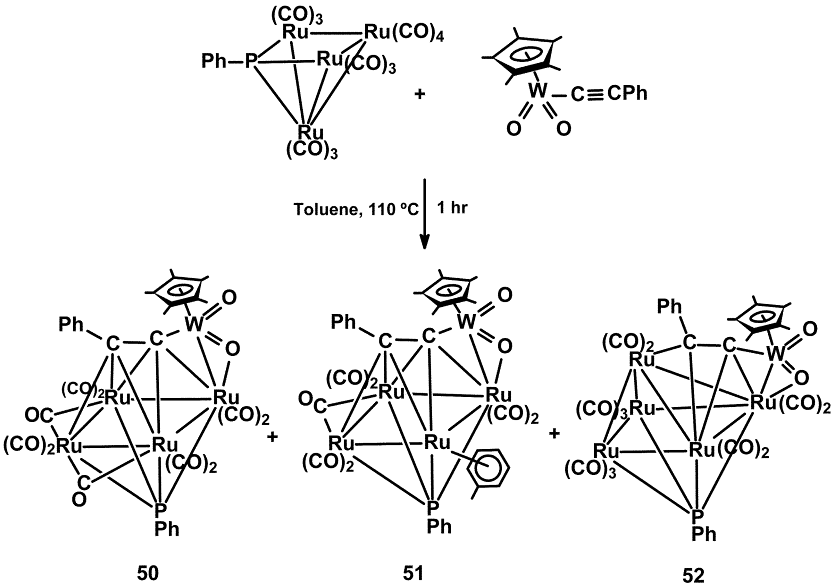


Scheme 16. Reactions of $[(\eta^5\text{-}C_5Me_5)W(O)Re(CO)_4(\mu\text{-}H)(\mu\text{-}CCPh)]$ with dimethyl acetylene dicarboxylate and di-p-tolylacetylene.

W-Ru Complexes

The strategy of utilizing the strong π-coordinating ability of an acetylide ligand to deliver a high oxidation state early-metal oxo fragment to a late–metal, low oxidation state carbonyl center has allowed the synthesis of mixed-metal clusters with oxo-bridged tungsten-ruthenium bonds. When a toluene solution of $[Ru_4(CO)_{13}(\mu_3\text{-}PPh)]$ and $[(C_5Me_5)W(O)_2(CCPh)]$ in a 1:1 ratio is heated to reflux, a pentanuclear complex $[(C_5Me_5)W(O)_2Ru_4(CO)_{10}(\mu_4\text{-}PPh)(CCPh)]$ **(50)** is obtained together with small amounts of $[(C_5Me_5)W(O)_2Ru_4(CO)_7(C_7H_8)(\mu_4\text{-}PPh)(CCPh)]$ **(51)** and $[(C_5Me_5)W(O)_2Ru_5(CO)_{12}(\mu_4\text{-}PPh)(CCPh)]$ **(52)** (Scheme 17).[33]

The molecular structure of **50** consists of a distorted square of Ru atoms capped on one side by a quadruply bridging phosphinidene ligand and on the other by a tungsten dioxo acetylide fragment $(C_5Me_5)W(O)_2(CCPh)$. The latter is attached to the Ru_4 fragment via the oxo-bridged W–Ru bond (2.806(1) Å) and by a μ_4-η^2-bound acetylide ligand. Structural data and electron counting suggest that both the bridging and the terminal oxo ligand possess W=O double bonds, which is in contrast to related monooxotungsten-containing cluster complexes in

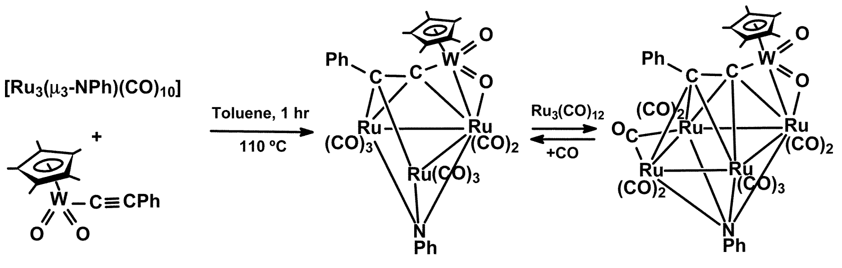


Scheme 17. Thermal reaction of $[Ru_4(CO)_{13}(\mu_3\text{-}PPh)]$ with $[(C_5Me_5)W(O)_2(CCPh)]$.

which the terminal oxo ligand instead adopts a formal W≡O triple bond. This unusual description of bonding is associated with the availability of only two valence orbitals on tungsten, which can be utilized to accept π-electrons from the oxo ligands. The toluene-substituted derivative $[(C_5Me_5)W(O)_2Ru_4(CO)_7(C_7H_8)(\mu_4\text{-PPh})(CCPh)]$ **(51)** and the hexametallic complex $[(C_5Me_5)W(O)_2Ru_5(CO)_{12}(\mu_4\text{-PPh})(CCPh)]$ **(52)** are prepared from the direct reaction of **50** with toluene (110°C, 1 h) and with excess $Ru_3(CO)_{12}$ in toluene (110°C, 15 min), respectively.[33]

Reaction of the corresponding imido cluster $[Ru_3(\mu_3\text{-NPh})(CO)_{10}]$ with $[(C_5Me_5)W(O)_2(CCPh)]$ in stoichiometric amount under toluene reflux for 1 h results in a tetrametallic complex $[(C_5Me_5)W(O)(\mu\text{-O})Ru_3(\mu_3\text{-NPh})(CCPh)(CO)_{10}]$ **(53)** and a small amount of a pentanuclear complex $[(C_5Me_5)W(O)(\mu\text{-O})Ru_4(\mu_4\text{-NPh})(CCPh)(CO)_{10}]$ **(54)**, a N-analogue of the phosphidine cluster compound **50**. Complex **53** consists of an open triangular Ru_3 metal framework, which is coordinated by a triply bridging imido ligand and by a bridging acetylide ligand on the opposite side of the Ru_3 plane. Moreover, the tungsten atom is connected to the central Ru atom, C_α atom of the acetylide ligand, a terminal oxo ligand and a bridging oxo ligand. Treatment of **53** with $Ru_3(CO)_{12}$ in refluxing toluene forms **54**, while heating a solution of **54** under CO atmosphere leads to the regeneration of **53** (Scheme 18).[34]

When the vinyl acetylide complex $[(C_5Me_5)W(O)_2(CCMe{=}CH_2)]$ is selected as an alternative precursor, treatment with $[Ru_3(\mu_3\text{-NPh})(CO)_{10}]$ in toluene affords two tetrametallic clusters: $[(C_5Me_5)W(O)(\mu\text{-O})Ru_3(\mu_3\text{-NPh})(CCCMe{=}CH_2)(CO)_8]$ **(55)** and $[(C_5Me_5)W(\mu\text{-O})_2Ru_3(\mu_3\text{-NPh})(CCCMe{=}CH_2)(CO)_6]$ **(56)**. Reaction of **56** with CO in refluxing toluene solution regenerates **55** in nearly quantitative yield. Two



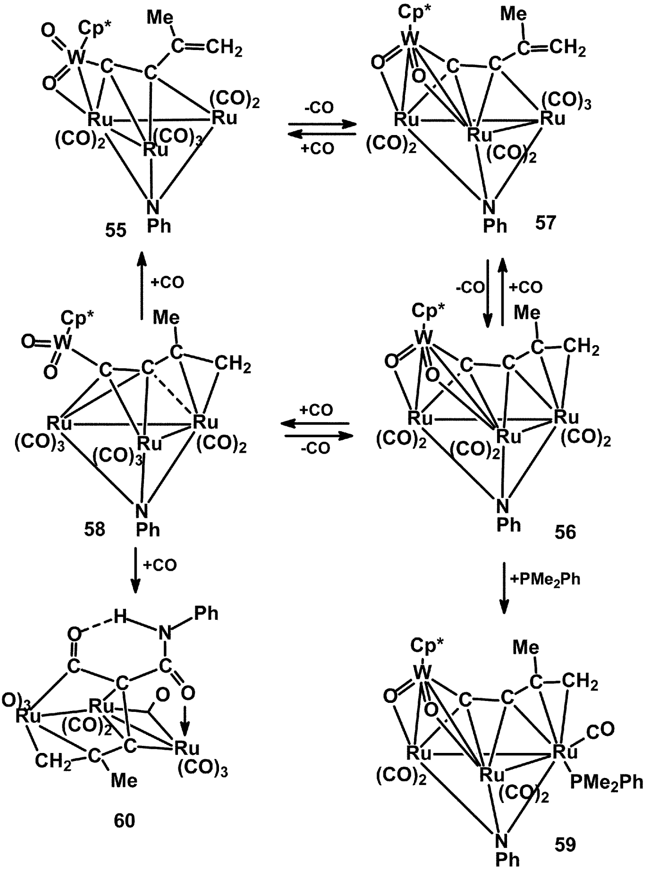
53

54

Scheme 18. Reaction of $[Ru_3(\mu_3\text{-NPh})(CO)_{10}]$ with $[(C_5Me_5)W(O)_2(CCPh)]$.

intermediate compounds $[(C_5Me_5)W(\mu\text{-}O)_2Ru_3(\mu_3\text{-}NPh)(CCCMe{=}CH_2)(CO)_7]$ (**57**) and $[(C_5Me_5)W(O)_2Ru_3(\mu_3\text{-}NPh)(CCCMe{=}CH_2)(CO)_8]$ (**58**) are isolated when **56** is exposed to CO at room temperature for 30 minutes. One carbonyl group is substituted and **59** is formed when thermolysis of **56** with 1 equivalent of PMe_2Ph is carried out. Removal of $(C_5Me_5)W(O)_2$ fragment and formation of $[Ru_3(CO)_9[C_6H_5O(CONHPh)]$ (**60**) is observed when complex **58** is exposed to CO atmosphere (40 psi) (Scheme 19).[34]

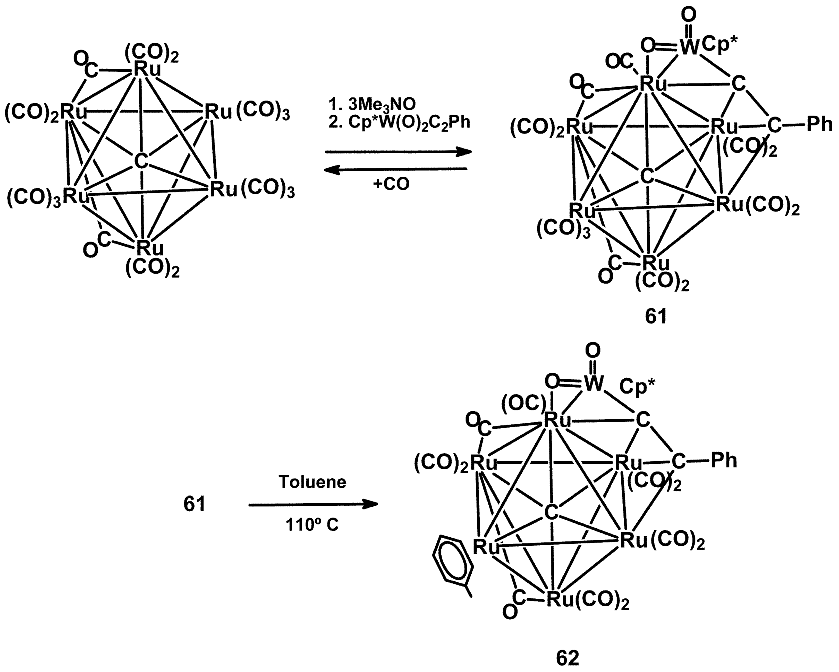
A mixed W/Ru cluster containing oxo and acetylide ligands $[(C_5Me_5)W(O)_2(CCPh)Ru_6(\mu_6\text{-}C)(CO)_{14}]$ (**61**) has been obtained on



Scheme 19. Carbonylation and decarbonylation reaction pathways for mixed W/Ru cluster.

treatment of carbide cluster [$Ru_6(\mu_6\text{-}C)(CO)_{17}$] with 3 equivalents of Me_3NO, followed by addition of high-valent acetylide complex [$(C_5Me_5)W(O)_2(CCPh)$]. The molecular structure of **61** depicts six ruthenium metal atoms forming an octahedral arrangement with an encapsulated carbide carbon. The $(C_5Me_5)W(O)_2(CCPh)$ fragment is found to reside on a Ru_3 metal triangle of central $Ru_6(\mu_6\text{-}C)$ framework with the W atom and one of its oxo ligands linked to a Ru atom, resembling the bonding pattern observed in **52**. Treatment of **61** with CO affords the carbido cluster [$Ru_6(\mu_6\text{-}C)(CO)_{17}$] and the free acetylide complex [$(C_5Me_5)W(O)_2(CCPh)$]. Thermolysis of a toluene solution of **61** (110°C, 8 hrs. under nitrogen) forms the cluster [$(C_5Me_5)W(O)_2(CCPh)Ru_6(\mu_6\text{-}C)(CO)_{11}(C_7H_8)$] (**62**) (Scheme 20).[26]

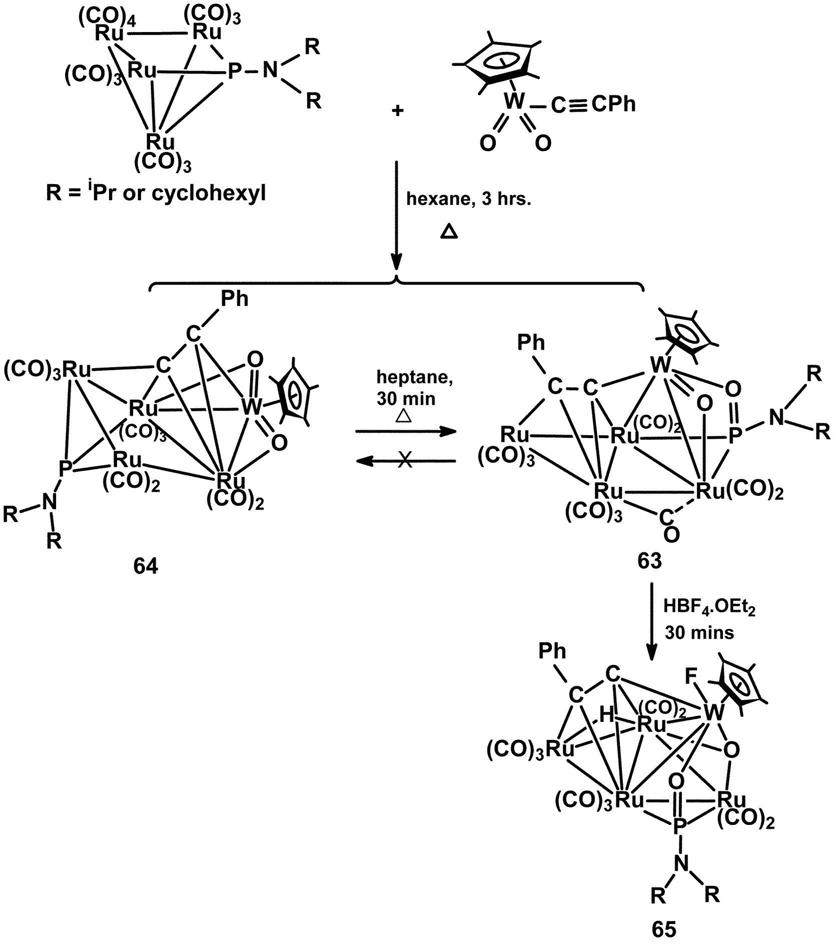
A useful strategy of constructing oxide bridged mixed metal clusters is by delivering an early metal oxo compound bearing an unsaturated hydrocarbyl ligand to a late metal, which has a high affinity for unsaturated hydrocarbyl group. The reaction of [$(\eta^5\text{-}C_5Me_5)W(O)_2CCPh$] in



Scheme 20. Addition of [$Cp^*W(O)_2(CCPh)$] to [$Ru_6(\mu_6\text{-}C)(CO)_{17}$] ($Cp^* = \eta^5\text{-}C_5Me_5$).

refluxing hexane for 3 hrs with the *nido* 62-electron phosphinidene cluster $Ru_4(CO)_{13}[PN(^iPr)_2]$ affords two complexes $[(\eta^5\text{-}C_5Me_5)W(\mu\text{-}O)Ru_4(CO)_9(\mu\text{-}CO)[\mu_3\text{-}\eta^2\text{-}OPN(^iPr)_2](\mu_4\text{-}\eta^2\text{-}CCPh)]$ (**63**) and $[(\eta^5\text{-}C_5Me_5)W(\mu\text{-}O)_2Ru_4(CO)_{10}[\mu_3\text{-}PN(^iPr)_2](\mu_5\text{-}\eta^2\text{-}CCPh)]$ (**64**) (Scheme 21).[35]

The molecular structure of **63** consists of an almost planar Ru_4 butterfly (dihedral angle of 177.43°) with the $(\eta^5\text{-}C_5Me_5)WC_2Ph$ fragment coordinated as a 6-electron donor to the Ru-Ru-Ru triangle as a $\mu_3\text{-}\eta^2\text{-}\|$-acetylene and with the tungsten atom asymmetrically bridging



Scheme 21. Reaction of $[(\eta^5\text{-}C_5Me_5)W(O)_2CCPh]$ with $Ru_4(CO)_{13}[PN(^iPr)_2]$.

the Ru—Ru bond. One oxygen atom acts as a bridge between tungsten and the phosphorus atom of the phosphinidene ligand with a P=O→W interaction. Another oxo ligand is bridged between tungsten and ruthenium atom in which the oxide is double bonded to the tungsten atom, the interaction being best described as W=O→Ru. In **64** the $(\eta^5\text{-}C_5Me_5)W(O)_2C_2Ph$ fragment is attached to a non-planar arrangement of four ruthenium atoms via a μ_5-acetylide, two W-Ru bonds and two W-O-Ru oxide bridges. The metal oxide interactions are best represented as W=O→Ru in both cases.

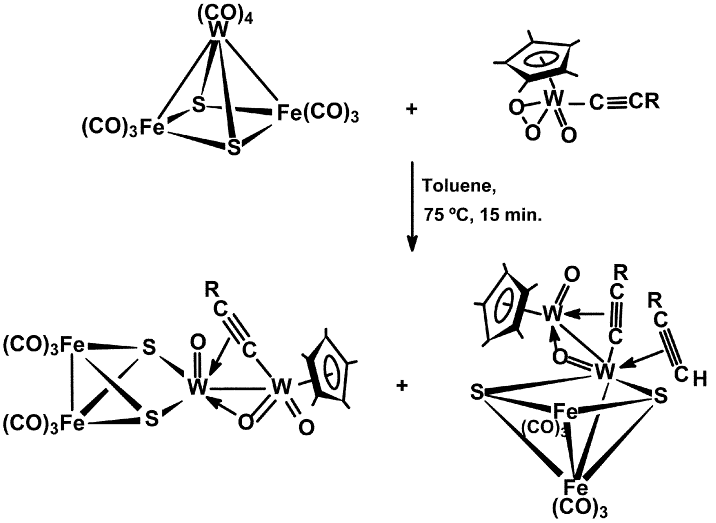
On refluxing a heptane solution of **64**, cluster **63** is obtained, which itself is stable to extended thermolysis. Thus, **64** with two W-O-Ru bridges appear to be an intermediate and cluster **63** as the final thermodynamic product. The rearrangement of **64** to **63** is accomplished by a formal rotation of the acetylide ligand on the WRu_4 framework of **64** such that the tungsten atom, which is bonded to the tail [C(2)Ph] of the acetylide in **64** (unlike that in $(\eta^5\text{-}C_5Me_5)W(O)_2CCPh$), is attached in a η^1-fashion to the head [C(1)] in **63**. However, acetylide bond isomerization and structural rearrangements have been observed previously in mixed metal systems and such transformations are more likely than the alternative of phenyl group transfer between acetylide carbon atoms.[36]

Addition of $HBF_4 \cdot OEt_2$ to **63** results in formation of $[(\eta^5\text{-}C_5Me_5)WF(\mu_3\text{-}O)HRu_4(CO)_9\{\mu_3\text{-}\eta^2\text{-}P(O)N(^iPr)_2\}(\mu_4\text{-}\eta^2\text{-}CCPh)]$ **(65)**, which features an oxo ligand in a triply bridging mode in much the same manner as found in some other mixed metal systems.[37,38]

Though it is not unusual for an organometallic tungsten center in a high oxidation state to react with a fluorinating reagent,[39] complex **65** is the first organometallic mixed metal cluster to contain a fluoride ligand.

Fe-W Complexes

The methodology of using mononuclear metal oxo complexes as one of the synthons to obtain polynuclear metal-oxo complexes has been extended in the use of mononuclear oxo-peroxo metal acetylides to synthesize some interesting polynuclear oxo complexes with coordinated acetylide unit. Thus, the thermolysis of a toluene solution containing $[Fe_2W(CO)_{10}(\mu_3\text{-}S)_2]$ and $[(\eta^5\text{-}C_5Me_5)W(O)(O)_2(\eta^1\text{-}CCR)]$ (R = Ph, (Me)C=CH$_2$) affords two new clusters, $[(\eta^5\text{-}C_5Me_5)W_2Fe_2(CO)_6(O)(\mu\text{-}O)_2(\mu_3\text{-}S)_2(\eta^2\text{-}CCR)]$ (**66**, **67**) and $[(\eta^5\text{-}C_5Me_5)W_2Fe_2(CO)_6(O)(\mu\text{-}O)(\mu_3\text{-}S)_2(\eta^2\text{-}CCR)(\eta^2\text{-}C(H)CR)]$ (**68**, **69**) (Scheme 22), whereas that



66 R= Ph
67 R= (Me)C=CH$_2$

68 R= Ph
69 R= (Me)C=CH$_2$

Scheme 22. Thermal reaction of [Fe$_2$W(CO)$_{10}$(μ_3-S)$_2$] and [(η^5-C$_5$Me$_5$)W(O)(O)$_2$(η^1-CCR)] (R = Ph, (Me)C=CH$_2$).

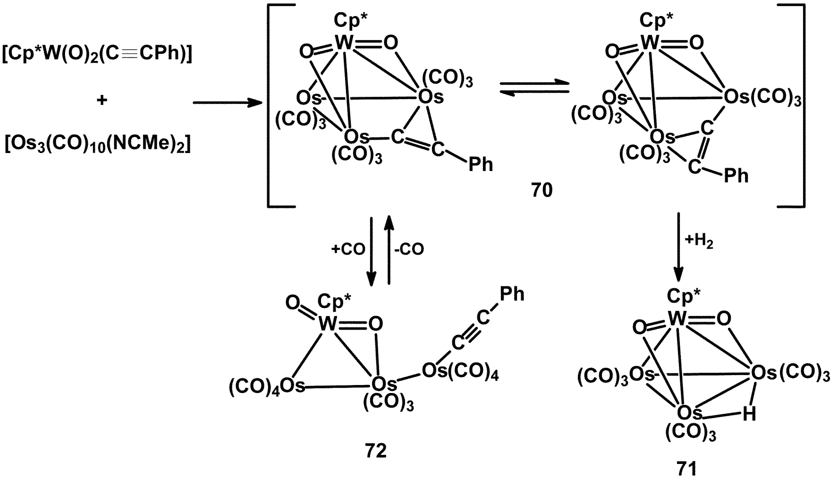
of a toluene solution of [Fe$_2$W(CO)$_{10}$(μ_3-S)$_2$] and [(η^5-C$_5$Me$_5$)W(O)(O)$_2$(η^1-CCR)] (R = Ph, (Me)C=CH$_2$) and RC≡CH (R = Ph, (Me)C=CH$_2$) also yields compounds **68** and **69**, respectively. Under the same conditions, Se- and Te-analogues of [Fe$_2$W(CO)$_{10}$(μ_3-S)$_2$] do not show any reactivity towards [(η^5-C$_5$Me$_5$)W(O)(O)$_2$(η^1-CCR)] (R = Ph, (Me)C=CH$_2$).[40]

In **66**/**67**, one of the oxo ligands that formally acts as a four electron bridge retains its double bond character to the {(η^5-C$_5$Me$_5$)W} unit while forming a coordinate bond to the W atom of the {Fe$_2$S$_2$W} core. In **68**/**69**, however, the bridging oxo is formally double-bonded with the W atom of the {Fe$_2$S$_2$W} core and it forms a coordinate bond to the {(η^5-C$_5$Me$_5$)W} unit.

W-Os Complexes

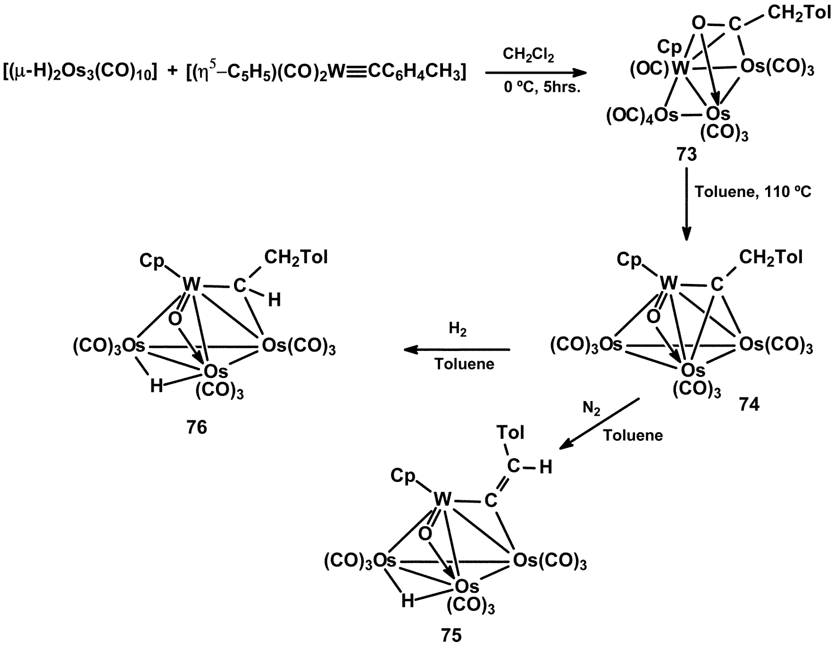
A heterometallic cluster compound [(C$_5$Me$_5$)W(μ-O)$_2$Os$_3$(μ-CCPh)(CO)$_9$] (**70**), which possess two edge-bridging oxo groups and an acetylide ligand in a μ-η^2 mode, has been obtained by addition of

$[(C_5Me_5)W(O)_2(CCPh)]$ to $[Os_3(CO)_{10}(NCMe)_2]$.[41] The electron withdrawing effect of the $(C_5Me_5)W(O)_2$ fragment decreases the relative energy of the π^*-orbitals and therefore increases the metal to acetylide ligand π-back bonding, improving the yields in contrast to the poor yields for the similar cluster building reactions using $[(C_5Me_5)W(CO)_3(CCPh)]$ and $[Os_3(CO)_{10}(NCMe)_2]$.[42] The possibility of the oxo ligand lone pair coordinating with the triosmium framework may also be the initial step to induce subsequent capping of the acetylide ligand. The molecule contains a WOs_3 butterfly core in which the tungsten atom is capped by a C_5Me_5 functional group and unusual bridging oxo ligands, which are located on the two W–Os bonds of nearly equal length (2.981(2) and 3.014(2) Å). The bond lengths to the oxo ligands (average W–O = 1.76(3) Å, Os–O = 2.13(3) Å) are consistent with a W=O→Os bonding mode. The acetylide ligand is linked to two Os atoms via σ-bonding and π-interaction. Upon addition of dihydrogen to 70, loss of acetylide ligand occurred to give $[(C_5Me_5)W(\mu\text{-}O)_2Os_3(\mu\text{-}H)(CO)_9]$ (71), while reaction with CO afforded the spiked triangular complex $[(C_5Me_5)W(O)(\mu\text{-}O)Os_3(CCPh)(CO)_{11}]$ (72). The transformation involves the formation of terminal acetylide group on Os atom and the shifting of one edge-bridging oxo ligand to the terminal mode. Thermolysis of 72 in toluene affords 70 in high yield (Scheme 23).



Scheme 23. Addition reaction of $[(Cp^*)W(O)_2(CCPh)]$ to $[Os_3(CO)_{10}(NCMe)_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$).

The bridging dihapto acyl ligand in $[(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}\{\mu_3\text{-}\eta^2\text{-}C(O)CH_2(C_7H_7)\}]$ (**73**) shows an "activated" C–O bond (d(C–O) = 1.372(20) Å).[43] On thermolysis scission of the acyl C–O bond occurs and the oxo-alkylidyne complex $[(\eta^5\text{-}C_5H_5)WOs_3(CO)_6(\mu\text{-}O)(\mu_3\text{-}CCH_2(C_7H_7))]$ (**74**) forms.[44] The oxo ligand in **74** forms a markedly unsymmetrical bridge that overall provides four electrons to the cluster. It can be viewed as forming a double bond to the tungsten atom and acting as a donor to the adjacent osmium atom, i.e., W=O→Os. This donation leads to ca. 0.1 Å lengthening of the W=O bond in comparison with terminal W=O bonds in related compounds. Pyrolysis of **74** in toluene under N_2 results in its conversion to $[(\eta^5\text{-}C_5H_5)WOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}C{=}CH(C_7H_7))(\mu\text{-}H)]$ (**75**), whereas bubbling H_2 through the solution provides $[(\eta^5\text{-}C_5H_5)WOs_3(CO)_9(\mu\text{-}O)(\mu\text{-}CHCH_2(C_7H_7))(\mu\text{-}H)]$ (**76**) quantitatively (Scheme 24).



Scheme 24. Reaction of $[(\mu\text{-}H)_2Os_3(CO)_{10}]$ with $[(Cp)(CO)_2W{\equiv}CC_6H_4CH_3]$, (Cp = $\eta^5\text{-}C_5H_5$).

CONCLUSIONS

A variety of synthetic methods have been developed to prepare oxo incorporated homonuclear as well as heteronuclear acetylide metal complexes. Among them, the oxidation reaction in presence of hydrogen peroxide, N_2O or air generally leads to mononuclear metal complexes and, in some cases, polynuclear complexes with both oxo and acetylide ligands. A number of such polynuclear complexes have also been isolated under limited concentration of oxygen in the reaction medium. Early metal oxo compounds bearing an acetylide ligand have been used as reagents to react with several metal clusters, which lead to oxo and acetylide containing metal clusters with different types of bonding modes of oxo and acetylide groups. Metal clusters containing bridging chalcogen atoms have been known to facilitate C–C bond coupling products, *viz.*, head to head, head to tail, tail to tail coupling of acetylides, when reacted with acetylide complexes in anaerobic conditions. This type of carbon-carbon bond coupling is in contrast to the aerobic reaction of chalcogen bridged metal cluster and metal acetylide complexes, where C–C bond coupling is not observed between the acetylide units. Some coupling products (**46**–**49**) are observed with metal oxo-acetylide complexes not containing chalcogen atoms. Furthermore, various types of bonding modes have been observed for oxo and acetylide units in metal complexes. Oxo ligands can be bonded to metals in terminal as well as bridging mode whereas acetylide units can be linked to metals by σ, π or both types of bonds. Much has been gleaned from the numerous examples of clusters bearing oxo and acetylide ligands; however, interest in the general area of oxo and hydrocarbyl containing complexes remains high. Reactivity studies on such complexes and investigation of physical studies such as non linear activity and cyclic voltammetry will further add to the overall growth of interest in this class of compounds.

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