

Model Chemistry on Metal Surfaces: Synthesis, Structure
and Reactivity Studies of Tungsten-Osmium Mixed-Metal Clusters

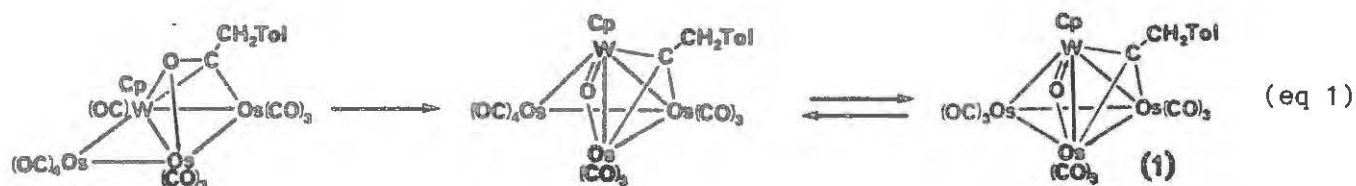
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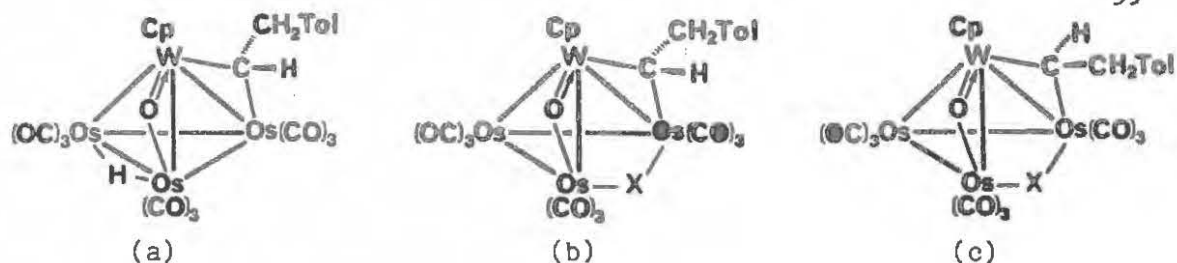
Recent interest in the chemistry of cluster compounds results from the belief that clusters may serve as models for metal surfaces.¹ Cluster bound alkylidyne, vinylidene, alkylidene, alkyne, alkene and hydride groups are of particular importance due to their implicated role in catalytic processes of metal surfaces.² Currently mixed-metal clusters are also under intense scrutiny, because of the advantages of enhanced reactivity and selectivity over their homonuclear counterparts.³

$\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$, **1**, a complex with triply bridging alkylidyne and doubly bridging oxo ligands has been prepared from pyrolysis of $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]^4$ by loss of two equivalents of CO.⁵ Compound **1** undergoes monocarbonylation to give $\text{CpWOs}_3(\text{CO})_{10}(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$, which is an intermediate in the acyl C-O bond scission process (eq 1). Reaction of **1** with phosphorus donors generates both addition and substitution products:

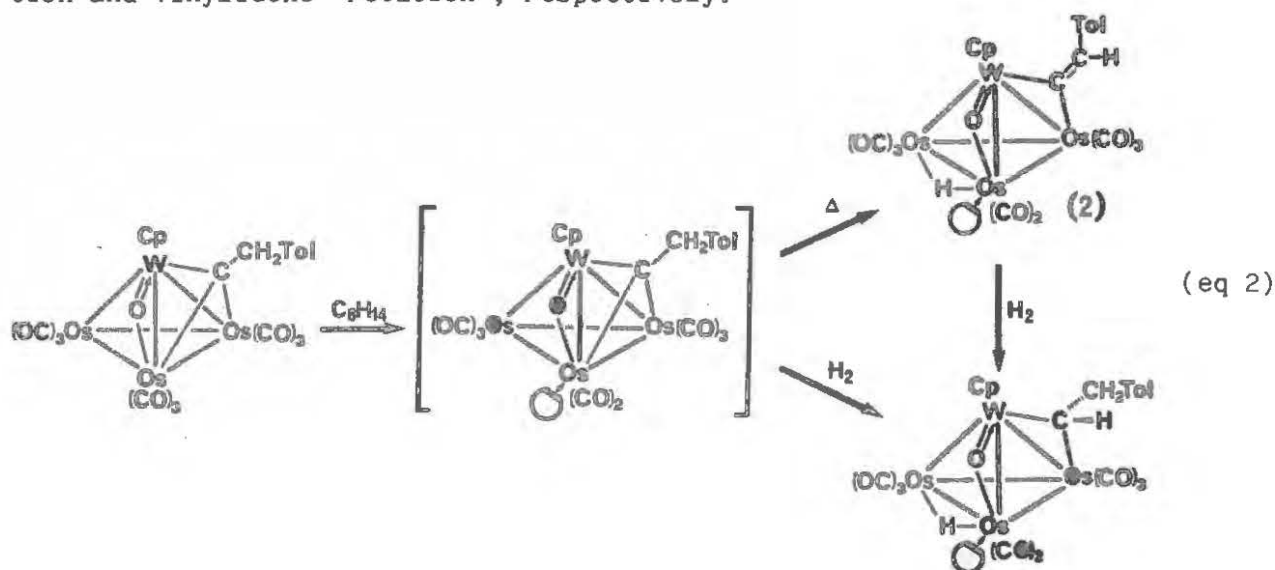


Treatment of **1** with diphenylacetylene provides a butterfly cluster $\text{CpWOs}_3(\text{CO})_8(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})(\text{C}_2\text{Ph}_2)$ with retention of the alkylidyne functional group and addition of alkyne ligand. This complex undergoes reaction under an H_2 atmosphere, or decarbonylation to give $\text{CpWOs}_3(\text{CO})_7(\mu\text{-H})_2(\mu\text{-O})(\mu_4\text{-}\eta^2\text{-CCHTol})$ ($\text{CPh}=\text{CHPh}$) or $\text{CpWOs}_3(\text{CO})_7(\mu\text{-O})(\mu\text{-}\eta^2\text{-CHCHTol})(\text{C}_2\text{Ph}_2)$, respectively. The former represents the only example of alkylidyne to vinylidene transformation under an H_2 atmosphere; the latter reacts with CO inducing coupling between coordinated alkyne, and alkenyl moieties (which arises from alkylidyne by means of a 1,2-hydrogen migration) to form two butadienyl complexes $\text{CpWOs}_3(\text{CO})_8(\mu\text{-O})[\text{C(Ph)=C(Ph)CH=CHTol}]$ (which exists as isomers).

Reaction of **1** with various HX reagents, $\text{X} = \text{H, Cl, Br}$ and SC_6H_5 , provides three alkylidene complexes with the formulation of $\text{CpWOs}_3(\text{CO})_9(\mu\text{-X})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$ (isomers a, b and c). In the case of the hydrido-alkylidene all three isomers have been observed,⁶ the interconversion of isomers a and b and c, involving H-migration and alkylidene isomerization, respectively. For the other alkylidene complexes, $\text{X} \neq \text{H}$, only b isomers and c isomers are isolated, of which isomer c is the thermodynamically more stable form. Treatment of $\text{CpWOs}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$ (isomers b and c) with gaseous BCl_3 generates $\text{CpWOs}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-OBCl}_3)(\mu\text{-CHCH}_2\text{Tol})$ in which BCl_3 has been found to coordinate the bridging oxo-ligand, thereby activating the reverse alkylidene isomerization from isomers-c to b. The structures of a, b and c are confirmed by the structural studies on $\text{CpWOs}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$,⁷ $\text{CpWOs}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$, and $\text{CpWOs}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-OBCl}_3)(\mu\text{-CHCH}_2\text{Tol})$, respectively.



Reaction of 1 with cyclooctene under N_2 or H_2 atmosphere affords $\text{CpW(CO)}_3(\text{CO})_8(\text{C}_8\text{H}_{14})(\mu\text{-H})(\mu\text{-O})(\mu\text{-CCH}_2\text{Tol})$, 2, or $\text{CpW(CO)}_3(\text{CO})_8(\text{C}_8\text{H}_{14})(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$, respectively. The reaction presumably proceeds by cyclooctene substitution to give an alkylidene intermediate $\text{CpW(CO)}_3(\text{CO})_8(\text{C}_8\text{H}_{14})(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$; the interconversion between the alkylidene, vinylidene and alkylidyne species are discussed (eq 2). Furthermore, each C_8H_{14} substituted alkylidene and vinylidene complex exists as two isomers in solution resulting from H-migration and vinylidene "rotation", respectively.



Compound 2 undergoes olefin exchange with ethylene to provide $\text{CpW(CO)}_3(\text{CO})_8(\text{C}_2\text{H}_4)(\mu\text{-H})(\mu\text{-O})(\mu\text{-CCH}_2\text{Tol})$, for which an X-ray diffraction study reveals an unusual feature in that the C_2H_4 group is coordinated to an Os atom associated with the bridging hydride. The reversible C_2H_4 insertion into Os-H-Os bond and its reverse, β -hydride elimination,⁸ has been established by dynamic NMR techniques. Exchange with either cis or trans- $\text{C}_2\text{H}_2(\text{CO}_2\text{CH}_3)_2$ gives another extreme of such olefin insertion reaction, an alkyl complex $\text{CpW(CO)}_3(\text{CO})_8(\mu\text{-O})(\mu\text{-CCH}_2\text{Tol})[\text{CH}(\text{CO}_2\text{CH}_3)\text{CH}_2(\text{CO}_2\text{CH}_3)]$ being isolated, as demonstrated by an X-ray diffraction study.

The related insertion of an alkyne into the Os-H-Os bond has also been discovered by exchange of C_8H_{14} with diphenylacetylene to give $\text{CpW(CO)}_3(\text{CO})_8(\mu_3\text{-O})(\mu_3\text{-}\eta^2\text{-CCH}_2\text{Tol})(\mu\text{-}\eta\text{-CPh=CHPh})$, which has been structurally characterized. Subsequent reaction with C_8H_{14} regenerates 2, suggesting that the insertion of the alkyne is reversible. Reaction with $\text{CpW(CO)}_2(\text{CTol})$, equivalent to be an alkyne by the isolobal analogy, provides a TBP pentanuclear cluster $\text{Cp}_2\text{W}_2\text{Os}_3(\text{CO})_9(\mu_3\text{-O})(\mu_3\text{-}\eta^2\text{-CCH}_2\text{Tol})$. Variable temperature NMR studies show that the vinylidene ligand undergoes a one-third cycle of circumambulation, as indicated in the theoretical calculation by Hoffmann on $\text{M}_3(\mu_3\text{-}\eta^2\text{-C=CH}_2)$ systems.⁹

Finally, an attempt was made to optimize conditions for the synthesis of $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]$ from the reaction of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with $\text{CpW}(\text{CO})_2\text{-}(\text{CTol})$, in which three mixed-metal compounds are formed, i.e., $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}]$, $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-CTol})_2\text{H}^{10}$ and $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}_2\text{Tol}_2)$.¹¹ This effort resulted in the isolation of a fourth WOs_3 cluster $[\text{CpW}(\text{CO})_3](\mu\text{-H})_2\text{Os}_3\text{-}(\text{CO})_9(\mu_3\text{-CTol})$ ¹², which has been identified as an intermediate in the formation of $\text{CpWOs}_3(\text{CO})_{10}(\mu_3\text{-CTol})_2\text{H}$. Reaction of $\text{D}_2\text{Os}_3(\text{CO})_{10}$ with $\text{CpW}(\text{CO})_2(\text{CTol})$ reveals a remarkable isotope effect which is manifested in the increased yield of deuterated $\text{CpWOs}_3(\text{CO})_{11}[\mu_3\text{-}\eta^2\text{-C(O)CD}_2\text{Tol}]$, from 26% to 49%. Pyrolysis of $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}_2\text{Tol}_2)$ initiates a reversible alkyne C-C bond scission to give $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_5(\mu\text{-CTol})(\mu_3\text{-CTol})$.¹³

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