

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

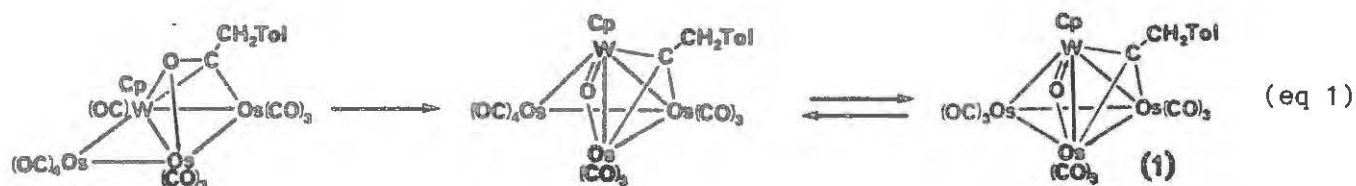
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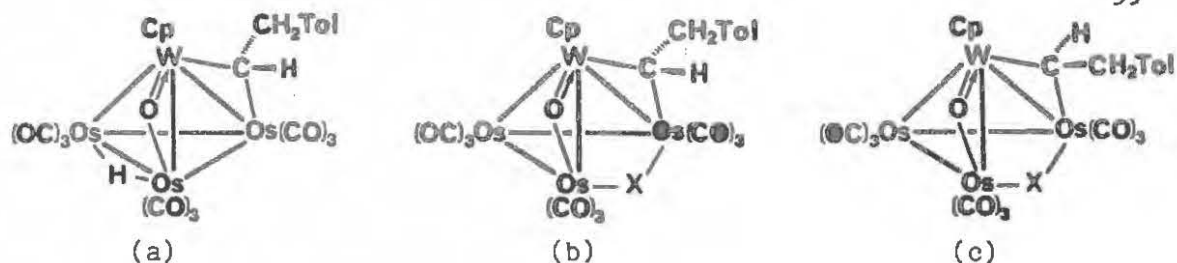
Recent interest in the chemistry of cluster compounds results from the belief that clusters may serve as models for metal surfaces.<sup>1</sup> Cluster bound alkylidyne, vinylidene, alkylidene, alkyne, alkene and hydride groups are of particular importance due to their implicated role in catalytic processes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

$\text{CpWOs}_3(\text{CO})_9(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})$ , **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.<sup>5</sup> 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:

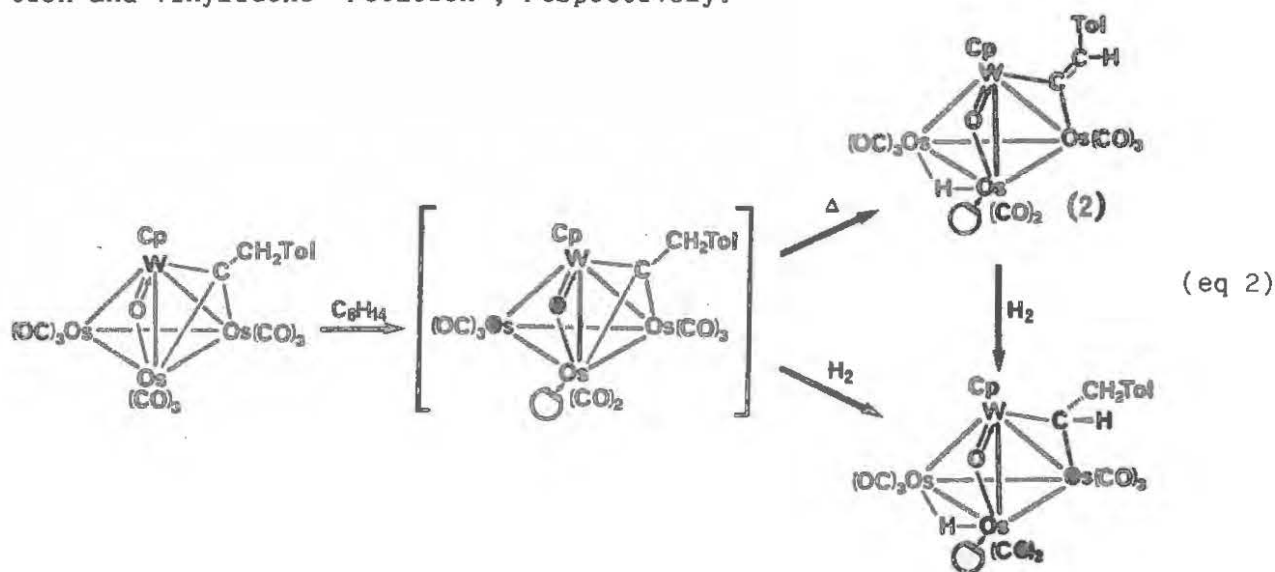


Treatment of **1** with diphenylacetylene provides a butterfly cluster  $\text{CpWOs}_3(\text{CO})_8(\mu\text{-O})(\mu_3\text{-CCH}_2\text{Tol})(\text{C}_2\text{Ph}_2)$  with retention of the alkylidyne functional group and addition of alkyne ligand. This complex undergoes reaction under an  $\text{H}_2$  atmosphere, or decarbonylation to give  $\text{CpWOs}_3(\text{CO})_7(\mu\text{-H})_2(\mu\text{-O})(\mu_4\text{-}\eta^2\text{-CCHTol})$  (CPh=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  $\text{H}_2$  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, X = H, Cl, Br and  $\text{SC}_6\text{H}_5$ , 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,<sup>6</sup> the interconversion of isomers a and b and c, involving H-migration and alkylidene isomerization, respectively. For the other alkylidene complexes, X  $\neq$  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  $\text{BCl}_3$  generates  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-OBCl}_3)(\mu\text{-CHCH}_2\text{Tol})$  in which  $\text{BCl}_3$  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  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-H})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$ ,<sup>7</sup>  $\text{CpWOs}_3(\text{CO})_9(\mu\text{-Cl})(\mu\text{-O})(\mu\text{-CHCH}_2\text{Tol})$ , 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  $\text{N}_2$  or  $\text{H}_2$  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  $\text{C}_8\text{H}_{14}$  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  $\text{C}_2\text{H}_4$  group is coordinated to an Os atom associated with the bridging hydride. The reversible  $\text{C}_2\text{H}_4$  insertion into Os-H-Os bond and its reverse,  $\beta$ -hydride elimination,<sup>8</sup> 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  $\text{C}_8\text{H}_{14}$  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  $\text{C}_8\text{H}_{14}$  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.<sup>9</sup>

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  $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_7(\mu_3\text{-}\eta^2\text{-C}_2\text{Tol}_2)$ .<sup>11</sup> This effort resulted in the isolation of a fourth  $\text{WOs}_3$  cluster  $[\text{CpW}(\text{CO})_3](\mu\text{-H})_2\text{Os}_3\text{-}(\text{CO})_9(\mu_3\text{-CTol})$ <sup>12</sup>, 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  $\text{Cp}_2\text{W}_2\text{Os}(\text{CO})_5(\mu\text{-CTol})(\mu_3\text{-CTol})$ .<sup>13</sup>

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