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. 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. Currently mixed-metal clusters are also under intense scrutiny, because of the advantages of enhanced reactivity and selectivity over their homonuclear counterparts.

CpWOs₃(CO)₉(µ-O)(µ₃-CCH₂Tol), 1, a complex with triply bridging alkylidyne and doubly bridging oxo ligands has been prepared from pyrolysis of CpWOs₃(CO)₁₁[µ₃-n²-C(O)CH₂Tol]⁴ by loss of two equivalents of CO.⁵ Compound 1 undergoes monocarbonylation to give CpWOs₃(CO)₁₀(µ-O)(µ₃-CCH₂Tol), 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 CpWOs₃(CO)₈(µ-O)(µ₃-CCH₂Tol)(C₂Ph₂) with retention of the alkylidyne functional group and addition of alkyne ligand. This complex undergoes reaction under an H₂ atmosphere, or decarbonylation to give CpWOs₃(CO)₇(µ-H)(µ-O)(µ₄-n²-CCH₂Tol)(C₂Ph₂) or CpWOs₃(CO)₇(µ-O)(µ₄-n²-CCH₂Tol)(C₂Ph₂), respectively. The former represents the only example of alkylidyne to vinylidene transformation under an H₂ atmosphere; the latter reacts with CO inducing coupling between coordinated alkynyl moieties (which arises from alkylidyne to vinylidene transformation) to form two butadienyl complexes CpWOs₃(CO)₈(µ-O)[C(Ph)=C(Ph)CH=CH₂Tol](which exists as isomers).

Reaction of 1 with various HX reagents, X = H, Cl, Br and SC₆H₅, provides three alkylidene complexes with the formulation of CpWOs₃(CO)₉(µ-H)(µ-O)(µ-CCH₂Tol),(isomers a, b and c). In the case of the hydrido-alkylidyne all three isomers have been observed, the interconversion of isomers a and b and c, involving H-migration and alkylidyne isomerization, respectively. For the other alkylidene complexes, X = H, only b isomers and c isomers are isolated, of which isomer c is the thermodynamically more stable form. Treatment of CpWOs₃(CO)₉(µ-Cl)(µ-O)(µ-CCH₂Tol)(isomers b and c) with gaseous BCl₃ generates CpWOs₃(CO)₉(µ-Cl)(µ-Cl)(µ-OBCl₃)(µ-CCH₂Tol) in which BCl₃ has been found to coordinate the bridging oxo-bridging oxo functionality, thereby activating the reverse alkylidyne isomerization from isomers-c to b. The structures of a, b and c are confirmed by the structural studies on CpWOs₃(CO)₉(µ-H)(µ-O)(µ-CCH₂Tol), CpWOs₃(CO)₉(µ-Cl)(µ-O)(µ-CCH₂Tol), and CpWOs₃(CO)₉(µ-Cl)(µ-OBCl₃)(µ-CCH₂Tol), respectively.
Reaction of 1 with cyclooctene under N₂ or H₂ atmosphere affords CpWO₃⁻(CO)₈(C₈H₁₄)(µ-H)(µ-O)(µ-CCH₂Tol), 2, or CpWO₃(CO)₈(C₈H₁₄)(µ-H)(µ-O)(µ-CCH₂Tol), respectively. The reaction presumably proceeds by cyclooctene substation to give an alkylidyne intermediate CpWO₃(CO)₈(C₈H₁₄)(µ-H)(µ-O)(µ-CCH₂Tol); the interconversion between the alkylidene, vinylidene and alkylidyne species are discussed (eq 2). Furthermore, each C₈H₁₄ 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 CpWO₂(CO)₈(C₂H₄)(µ-H)(µ-O)(µ-CCH₂Tol), for which an X-ray diffraction study reveals an unusual feature in that the C₂H₄ group is coordinated to an Os atom associated with the bridging hydride. The reversible C₂H₄ insertion into Os-H-Os bond and its reverse, β-hydride elimination, has been established by dynamic NMR techniques. Exchange with either cis or trans-C₆H₂(CO₂CH₂)₂ gives another extreme of such olefin insertion reaction, an alkyl complex Cp₃WO₃(CO)₈(µ-O)(µ-CCH₂Tol)[CH-(CO₂CH₃)₂CH₂(CO₂CH₃)] 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 C₈H₁₄ with diphenylacetylene to give CpWO₃(CO)₈(µ₃-O)-(µ₃-n²-CCH₂Tol)(µ-n-CPh=CHPh), which has been structurally characterized. Subsequent reaction with C₈H₁₄ regenerates 2, suggesting that the insertion of the alkyne is reversible. Reaction with Cp₂W₉O₃(CO)₉(µ₃-O)(µ₃-n²-CCH₂Tol). 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 M₃(µ₃-n²-C=CH₂) systems.
Finally, an attempt was made to optimize conditions for the synthesis of CpWOs₃(CO)₁₁[µ₃-n²-C(0)CH₂Tol] from the reaction of H₂Os₃(CO)₁₀ with CpW(CO)₂-(CTol), in which three mixed-metal compounds are formed, i.e., CpWOs₃(CO)₁₁[µ₃-n²-C(0)CH₂Tol], CpW₃Os₃(CO)₁₀(µ₃-CTol)₂H¹⁰ and Cp₂W₂Os(CO)₇(µ₃-n²-C₂Tol)₂.¹¹ This effort resulted in the isolation of a fourth WOs₃ cluster [Cp₂W(CO)₅(µ-H)₂Os-(CO)₉(µ₃-cTol)], which has been identified as an intermediate in the formation of CpW₃Os₃(CO)₁₀(µ₃-CTol)₁₂H. Reaction of D₂Os₃(CO)₁₀ with Cp(CO)₂(CTol) reveals a remarkable isotope effect which is manifested in the increased yield of deuterated CpW₃Os₃(CO)₁₁[µ₃-n²-C(0)CD₂Tol], from 26% to 49%. Pyrolysis of Cp₂W₂Os(CO)₇(µ₃-n²-C₂Tol)₂ initiates a reversible alkyne C-C bond scission to give Cp₂W₂Os(CO)₅(µ-CTol)(µ₃-CTol).¹³

References

6. See: Park, J. T. Ph.D. Thesis, University of Illinois at Urbana-Champaign, 1983, Chapter 4; although the structural assignment for isomers b and c is incorrect.