

ISOTOPIC LABELLING AND HYDRIDE ATTACK
ON ORGANOTRIOSMIUM CLUSTER COMPOUNDS

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Final Seminar

October 20, 1981

The relatively new techniques of reflectance infrared-spectroscopy and high-resolution electron energy-loss spectroscopy (EELS) have provided an abundance of data pertaining to species adsorbed on metal surfaces. In several cases, however, identification of the species observed has been hindered for lack of appropriate models with which to correlate vibrational data. Metal clusters have been proposed as suitable models [1], although the transferability of vibrational data from clusters to surface species has been questioned [2].

Surface-adsorbed formate has been implicated in the surface decompositions of formic acid, as well as in the water-gas shift reaction. In order to provide chemists with a "benchmark" for identifying formate species, a full normal-coordinate analysis of the formate ligand in $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CH})$ [3] has been performed. The complexes $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CH})$, $\text{HOs}_3(\text{CO})_{10}(\text{O}_2\text{CD})$, and $\text{HOs}_3(\text{CO})_{10}(\text{O}_2^{13}\text{CH})$ were synthesized by reaction of the appropriately-labelled formic acid with the "lightly-stabilized" complex $\text{Os}_3(\text{CO})_{10}(\text{C}_8\text{H}_{14})_2$ [4]. The good computer fit of the observed frequencies in the approximation of a free formate ligand indicates that metal involvement in the normal coordinates is negligible. The abnormally high C-H stretching force constant and $^1J_{\text{CH}}$ values for the complex have been attributed to significant covalency in the metal-ligand bonding. Comparison with the observed frequencies for formate adsorbed on Cu(100) [5a] and Ag(110) [5b] supports the applicability of the complex as a reference for surface formate.

The nature of the species occurring from adsorption of C_2H_2 and C_2H_4 on Pt(111) [6] has been hotly debated by Ibach, Demuth, and Somorjai [7]. In an attempt to clarify the matter, vibrational studies have been undertaken on the complexes $\text{HOs}_3(\text{CO})_{10}(\text{CHCH}_2)$ and $\text{H}_2\text{Os}_3(\text{CO})_9(\text{CCH}_2)$ [8]. The vinyl complexes were prepared by insertion of C_2H_2 or C_2D_2 into $\text{H}_2\text{Os}_3(\text{CO})_{10}$ or $\text{D}_2\text{Os}_3(\text{CO})_{10}$. The insertions gave rigorously cis-labelled vinyl ligands. Trans-labelled species were made by base-catalyzed isomerization. The vinylidene complexes were synthesized by pyrolysis of the vinyl complexes. A poor computer fit to the observed frequencies in both types of complex has been interpreted as implying significant metal involvement in "ligand" normal coordinates. A study of the more complete model Os_3CCH_2 is underway. Comparison of the observed infrared frequencies of the clusters with EELS data from adsorbed C_2H_2 and C_2H_4 on Pt(111) [6] strongly implicates vinylidene species as the predominant form of annealed $\text{C}_2\text{H}_2/\text{Pt}(111)$ and implicates the absence of vinyl species in $\text{C}_2\text{H}_4/\text{Pt}(111)$.

The observed base-catalyzed isomerization of the labelled vinyl complexes, together with the previous report of a phosphine adduct of $\text{HOs}_3(\text{CO})_{10}(\text{CHCH}_2)$ [9], prompted the reaction of LiHBET_3

with $\text{HOs}_3(\text{CO})_{10}(\text{CHCH}_2)$ to give the ethylidene complex $\text{HOs}_3(\text{CO})_{10}(\text{CHCH}_3)^-$, isolated as tetraalkylammonium salts. Hydride attack at the β -carbon of $\text{H}_2\text{Os}_3(\text{CO})_9(\text{CCH}_2)$ gives the ethylidyne complex $\text{H}_2\text{Os}_3(\text{CO})_9(\text{CCH}_3)^-$, similarly isolated. Hydride also attacks the α -carbon of the μ_2 -carbyne complex $\text{HOs}_3(\text{CO})_{10}(\text{COCH}_3)$ to give the methoxycarbene complex $\text{HOs}_3(\text{CO})_{10}(\text{CHOCH}_3)^-$. It was hoped that protonation of this complex would give the methyne complex $\text{HOs}_3(\text{CO})_{10}(\text{CH})$. The reactivity of the product, however, indicates that CO insertion has occurred to give the ketenyl complex $\text{HOs}_3(\text{CO})_9(\text{CHCO})$.

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