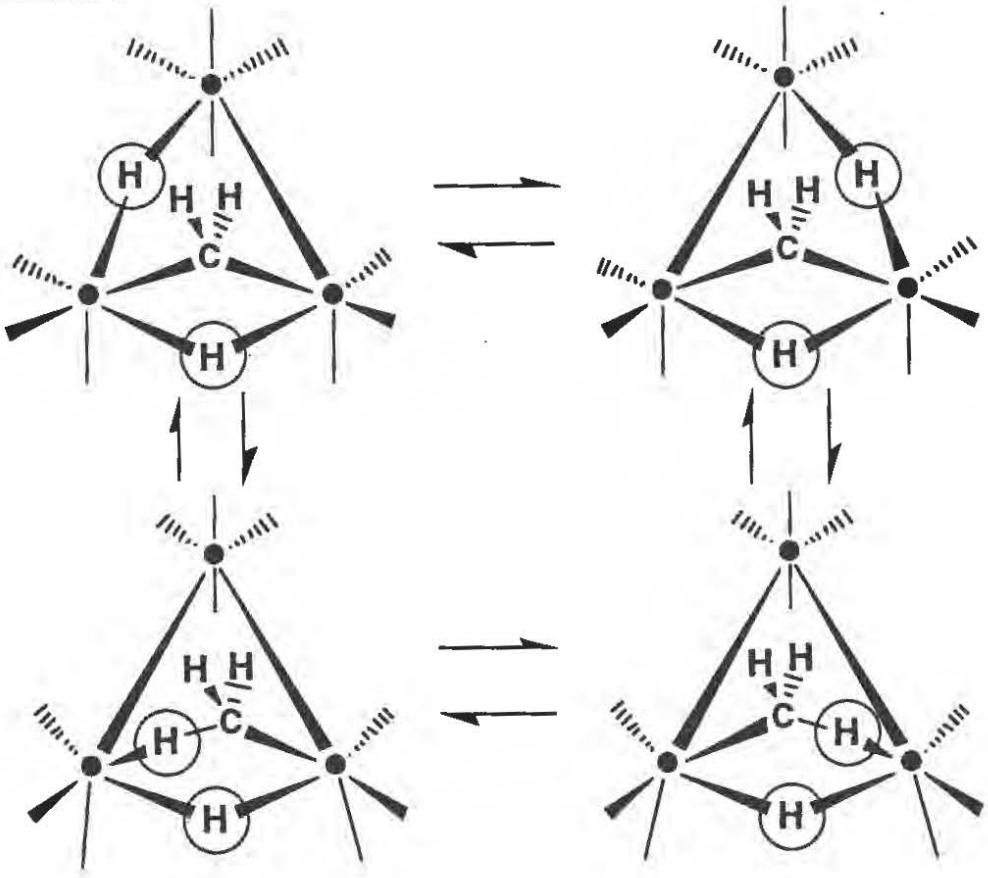
Multi-nuclear NMR Studies on Solution Structures and Dynamics of Triosmium Hydrido Carbonyl Phosphine Cluster Compounds

Makoto Koike Final Seminar July 9, 1991

The methyl compound, $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-}CH_3)$, is part of a tautomeric pair derived from the interaction of $H_2Os_3(CO)_{10}$ with diazomethane [1]. However, only the methylene tautomer crystallized from solution and its structure was determined by X-ray and neutron diffraction studies [2]. Though the methyl protons were found to be spectroscopically equivalent, deuterium labelling studies showed that the methyl moiety has an agostic interaction [3]. Two solution structures, which differ in the position of the bridging methyl moiety relative to the bridging hydride ligand, have been proposed for the methyl tautomer [3,4].

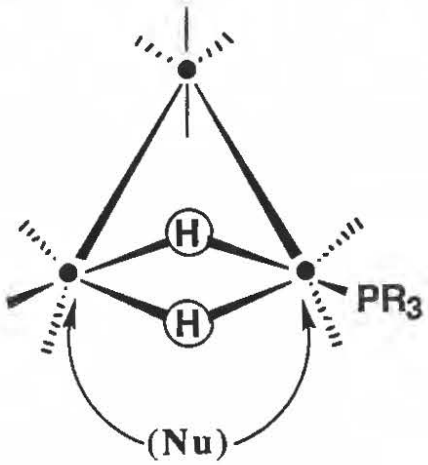
Though the two models cannot be distinguished by ^1H NMR studies, couplings of carbonyl carbons to hydride ligand nuclei and the symmetry of the methyl tautomer shown by ^{13}C NMR spectra strongly support the structure originally proposed [3]. All of the carbonyl resonances of the tautomers have been assigned by the combination of $^{13}C\{^1H\}$ COSY and ^1H selectively decoupled ^{13}C NMR experiments. Finally, ^{13}C spin saturation transfer experiments on the pair have established the overall solution dynamics of these compounds (See Scheme I).

Scheme I

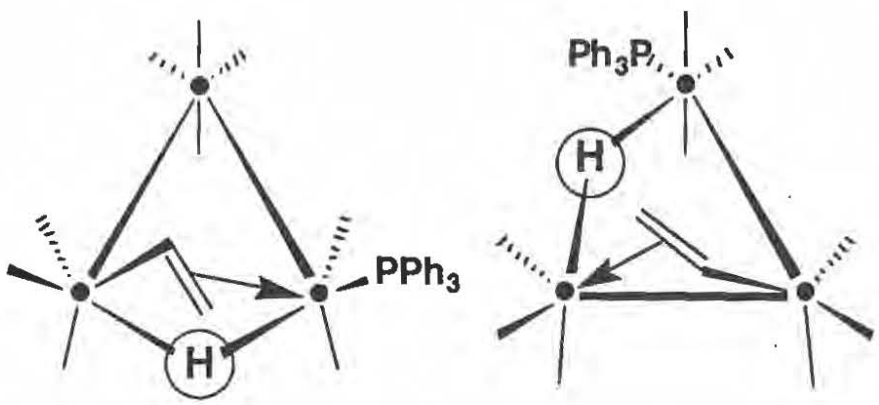


Although the reactivity of the unsaturated triosmium carbonyl cluster, $H_2Os_3(CO)_{10}$, with numerous unsaturated hydrocarbons and Lewis bases has been extensively investigated

[4,5], the reactivity of phosphine-substituted analogs has received considerably less attention [6]. Phosphine substitution may alter the reactivity of clusters. Moreover, for the specific case of $(\mu\text{-H})_2Os_3(CO)_9(PR_3)$, substitution creates two distinct sites, namely $Os(CO)_3$ and $Os(CO)_2(PR_3)$ centers, which may exhibit different reactivity toward nucleophile (Nu).



The reaction of $(\mu\text{-H})_2Os_3(CO)_9(PPh_3)$ with acetylene at room temperature provides two isomers of a hydridovinyl cluster, $(\mu\text{-H})Os_3(CO)_9(PPh_3)(\mu, \eta^2\text{-CHCH}_2)$. The solid-state structure of each isomer has been determined by single-crystal X-ray crystallography. The solution structures and dynamics have been studied by extensive ^{13}C NMR studies, including $^{13}C\{^1H\}$ COSY and ^{13}C spin saturation transfer experiments. Both isomers undergo dynamic interchange of the σ and π bonds of the vinyl moiety.



CO and Bu^{t}NC were employed for the purpose of investigating the site selectivity in $(\mu\text{-H})_2Os_3(CO)_9(PMe_2Ph)$ with the incoming molecule. The ^{13}CO labelling experiments in the reaction of $(\mu\text{-H})_2Os_3(CO)_9(PMe_2Ph)$ with CO to give $(\mu\text{-H})(H)Os_3(CO)_{10}(PMe_2Ph)$ show random scrambling of labelled carbonyl ligands. The reaction of $(\mu\text{-H})_2Os_3(CO)_9(PMe_2Ph)$ with Bu^{t}NC at -78 °C produces a pair of two isomers of an isonitrile cluster, $(\mu\text{-H})(H)Os_3(CO)_9(PMe_2Ph)(Bu^tNC)$. In contrast, the same reaction at room temperature gives two pairs of two isomers of the isonitrile cluster. The solution structures of the isomers have been deduced by extensive NMR studies. Though two isomers in the same pair are interchangeable by the intramolecular exchange of the terminal and the bridging hydride ligands, one isomer in a pair does not convert to an isomer in the other pair. The origin of each pair of isomers is proposed to be the initial site of isocyanide coordination to the starting complex.

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