

Effect of Phosphine Ligand Substitution on the Structures, Reactivities, and Ligand Rearrangements in Organotriosmium Compounds

David Hughes Hamilton

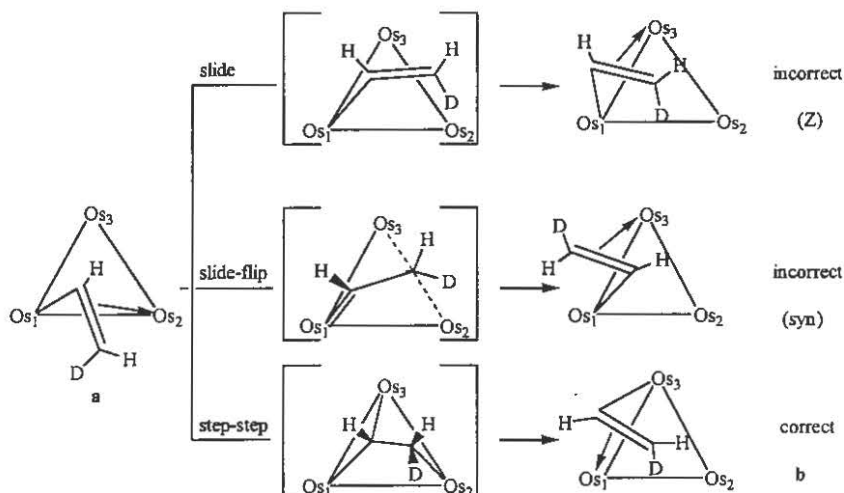
Final Seminar

May 13, 1999

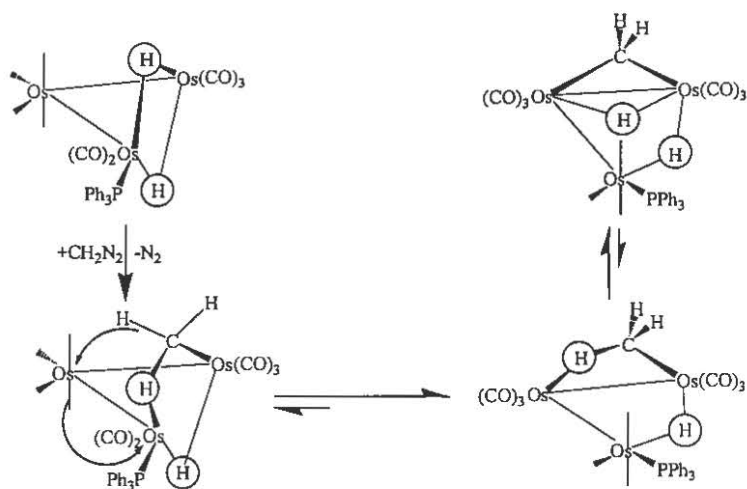
The Fischer-Tropsch reaction involves the hydrogenation of carbon monoxide to form long chain alkanes or oxygenates. Much effort has been directed at the elucidation of the mechanism of the Fischer-Tropsch reaction since Fischer and Tropsch first reported their reaction and proposed a mechanism in 1926.^{1,2} These efforts have led to a few insights upon which there is general agreement. There is general agreement that the reaction involves the stepwise polymerization of methylene species.³⁻⁶ The two most highly regarded mechanisms for the chain propagation step in the Fischer-Tropsch reaction are discussed below. An alkyl mechanism was first proposed by Pettit et al. in 1980.^{7,8} They proposed a mechanism where an alkyl group and a methylene group couple to form a longer chain. Maitlis and co-workers have recently proposed an alternative mechanism in which alkenyl species are key intermediates for chain propagation.⁹ Vinyl and alkyl triosmium compounds have been known for years. We have undertaken a careful study of both since these compounds could provide important insight into their role in the Fischer-Tropsch reaction.

The hydridovinyl triosmium cluster compound $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\text{PPh}_3)(\mu, \eta^2\text{-CH=CH}_2)$ exists as two well-defined structural isomers. In solution the individual isomers slowly equilibrate. In order to probe the possible effects of phosphine ligand substitution, studies of the related compounds $(\mu\text{-H})\text{Os}_3(\text{CO})_9(\text{L})(\mu, \eta^2\text{-CH=CH}_2)$, for $\text{L} = \text{PEt}_3$, $\text{P}(p\text{-MeOPh})_3$, $\text{P}(p\text{-Tol})_3$, and PCy_3 , have been conducted. The equilibrium constants determined are: 0.20 for $\text{L} = \text{PEt}_3$; 0.45 for $\text{L} = \text{P}(p\text{-MeOPh})_3$, $\text{P}(p\text{-Tol})_3$, and PPh_3 ; and 2.20 for $\text{L} = \text{PCy}_3$. These values demonstrate increasing preference for positioning the vinyl group remote from rather than adjacent to the phosphine ligand as the size of the ligand increases. The half-life for approaching equilibrium from a pure sample of the adjacent isomer also varies in the same order: PEt_3 (48 min), PPh_3 (83 min), and PCy_3 (570 min). Analysis of the selectively deuterated vinyl compound, $(\mu\text{-D})\text{Os}_3(\text{CO})_9\text{PPh}_3(\mu, \eta^2\text{-CH=CHD})$ shows that the C-D bond of the vinyl group is *cis* to the Os-C bond in the adjacent isomer but *trans* in the remote isomer. This result allows mechanistic discrimination between possible rearrangement pathways. Removal of a carbonyl ligand from $(\mu\text{-H})\text{Os}_3(\text{CO})_9\text{PPh}_3(\mu, \eta^2\text{-CH=CH}_2)$ by trimethylamine oxide occurs selectively from the adjacent isomer to produce the vinylidene compound, $(\mu\text{-H})_2\text{Os}_3(\text{CO})_8\text{PPh}_3(\mu_3\text{-}\eta^2\text{-C=CH}_2)$.

The methyl/methylene tautomeric pair of phosphine-substituted triosmium clusters, $(\mu\text{-H})\text{Os}_3(\text{CO})_9\text{L}(\mu\text{-CH}_3) / (\mu\text{-H})_2\text{Os}_3(\text{CO})_9\text{L}(\mu\text{-CH}_2)$ ($\text{L} = \text{PEt}_3$, PEt_2Ph , PPh_3 , and $\text{PPh}_2i\text{-Pr}$) have been synthesized from the reaction of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\text{L}$ and ethereal diazomethane, while the analogous reaction with $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\text{PCy}_3$ yields only the methylene compound. The structure of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9(\text{PPh}_3)(\mu\text{-CH}_2)$, has been determined by single-crystal X-ray crystallography and by detailed analysis of the ^1H and ^{13}C NMR spectra. The methylene tautomer consists of a triangular array of osmium atoms with the methylene moiety bridging one of the Os-Os edges.



The triphenyl-phosphine ligand is bound to the osmium atom opposite the methylene-bridged edge in an "in-plane" position. The location of the two hydrogen atoms on the methylene ligand were also determined from the crystal structure and were shown to be orthogonal to the Os-Os edge bridged by the methylene moiety. While the structure of the methyl tautomer cannot be determined directly, it has been inferred by a combination of spectroscopy, labeling, and reactivity studies. These studies support a structure with the methyl group bridging an Os-Os edge adjacent to the phosphine ligand in contrast to the location of the hydrocarbon moiety in the methylene tautomer. The two tautomers are in equilibrium with each other, implying an unexpected migration of the hydrocarbonyl ligand along the metal framework with concomitant migration of a carbonyl ligand. In addition, protonation occurs exclusively at the Os-C bond of the methylene ligand to produce a cationic methyl compound; the methyl group bridges the same edge that the parent methylene ligand bridges. The temperature at which this compound undergoes reductive elimination of methane is lower when more strongly coordinating anions are utilized.



The compounds $(\mu\text{-H})_2\text{Os}_3(\text{CO})_9\text{L}$ ($\text{L} = \text{CO}$, PEt_3 , PPh_3 , $\text{P}(p\text{-Tol})_3$, $\text{P}(p\text{-MeOPh})_3$, PCy_3) catalyze the polymerization of diazomethane. The nature of L has a strong effect on the rate of the polymerization. The rate constants for the compounds are as follows: $\text{L} = \text{CO}$ 1.3 (2) min^{-1} , PPh_3 0.81 (12) min^{-1} , $\text{P}(p\text{-MeOPh})_3$ 58 (5) min^{-1} , $\text{P}(p\text{-Tol})_3$ 70 (6) min^{-1} , PEt_3 0.23 (4) min^{-1} , and PCy_3 0.24 (4) min^{-1} . The more donating ligands have slower rates of polymerization as illustrated by the fact that $\text{L} = \text{PEt}_3$ and PCy_3 have essentially the same rate constant and similar pK_a 's (8.69 vs. 9.70) but quite different cone angles (132° vs. 162°). The triaryl derivatives also show that the rate depends primarily upon the electronic nature of the phosphine ligand, since the cone angles are identical but the pK_a 's are quite different.

References

1. Fischer, F.; Tropsch, H., *Brennstoff-Chem.* **1926**, 7, 97.
2. Fischer, F.; Tropsch, H., *Chem. Ber.* **1926**, 59, 830.
3. Biloen, P. J. R., *Neth. Chem. Soc.* **1980**, 99, 33.
4. Biloen, P.; Sachtler, W. M. H., *Adv. Catal.* **1981**, 30, 165.
5. Brady III, R. C.; Pettit, R., *J. Am. Chem. Soc.* **1980**, 102, 6181.
6. Brady III, R. C.; Pettit, R., *J. Am. Chem. Soc.* **1981**, 103, 1287.
7. Maitlis, P. M.; Long, H. C.; Quyoum, R.; Turner, M. L.; Wang, Z.-Q., *Chem. Commun.* **1996**, 1.