

The Chemistry of *o*-Formylphenyl Aryl Phosphines: Intramolecular Oxidative Additions to Iridium(I) and Phosphorus(III)

Edith F. Landvatter

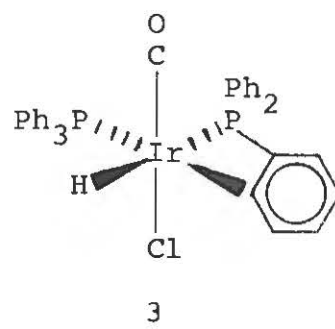
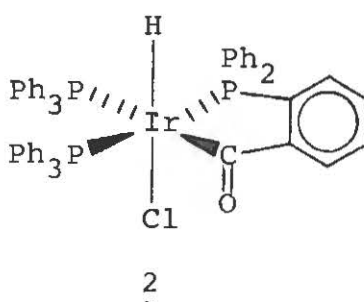
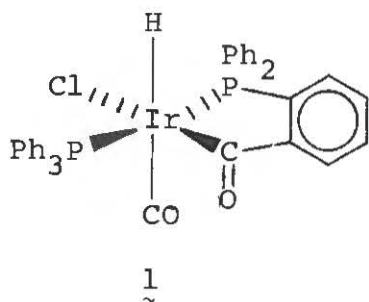
Final Seminar

July 5, 1983

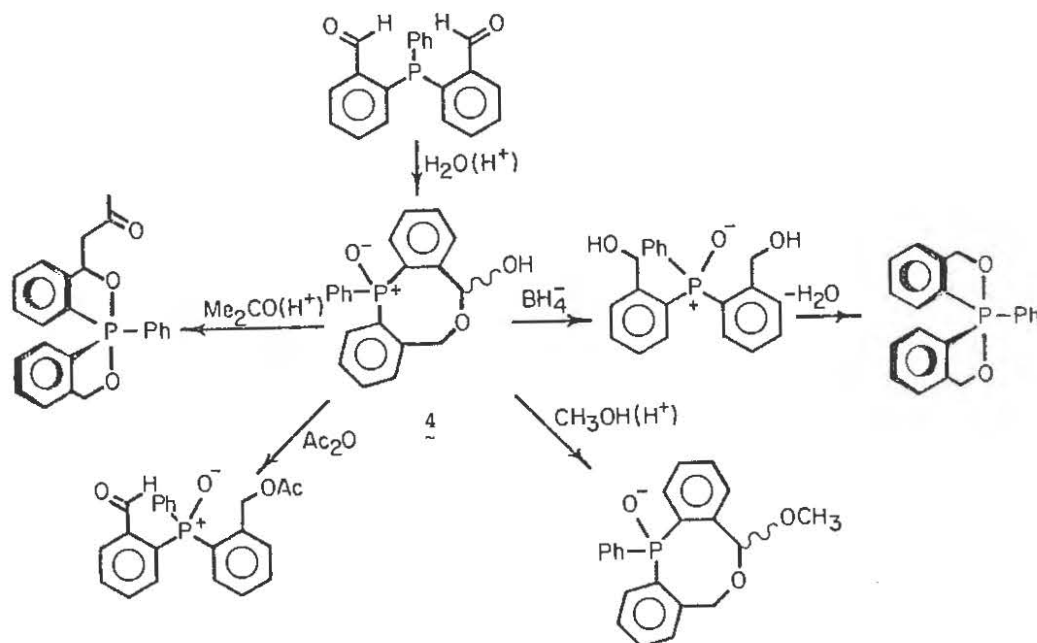
Intramolecular reactions are generally more facile than their intermolecular counterparts. By juxtaposing two functional groups one is often able to accelerate otherwise slow reactions and often trap otherwise unstable intermediates. The present research takes advantage of both of these aspects in probing the interactions of the aldehyde group with low-valent iridium and phosphorus centers. The studies have established new aspects of iridium acyl hydride and organophosphorus chemistry. Additionally, this work revealed some unexpected parallels between the low-valent phosphorus and iridium chemistry.

The interaction of aldehydes with transition metals is important in metal catalyzed aldehyde decarbonylation [1] and hydroformylation [2]. Metal acyl hydrides, intermediates often postulated in mechanisms for these transformations, were first obtained by the addition of chelating aldehydes to $\text{RhCl}(\text{PPh}_3)_3$ [3] and $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ [4].

The addition of $(\text{o-C}_6\text{H}_4\text{CHO})\text{Ph}_2\text{P}$ (PCHO) to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ is a highly efficient process which affords acyl hydride 1 [4]. This complex is stabilized by chelation since the nonchelated acyl hydride $\text{HIr}(\text{PhCO})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ is not obtained either by direct addition of benzaldehyde to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ or by addition of benzoyl chloride to $\text{IrH}_3(\text{CO})(\text{PPh}_3)_2$. The addition of PCHO to $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$ gives an acyl hydride of configuration 2 as the major product. This tris-phosphine iridium(III) acyl hydride is more labile than 1 and decarbonylation of 2 is more facile than for 1. In the decarbonylation of 2, a steady state concentration of a bis-phosphine carbonyl intermediate was detected by IR and ^1H -NMR spectroscopy and is proposed to be the orthometallated complex 3.



In the course of our studies on the reactions of iridium with phosphine aldehydes we had occasion to examine the bis-aldehyde phosphine $(\text{O}-\text{C}_6\text{H}_4\text{CHO})_2\text{PhP}$. We found that this species undergoes unusual chemistry independent of any metal ions. Thus $(\text{O}-\text{C}_6\text{H}_4\text{CHO})_2\text{PhP}$ reacts with water to form the hydrate, **4** [6]. The chemistry of this species was studied and its mechanism of formation was elucidated



References

1. Lau, K. S. Y.; Becker, Y.; Huang, F.; Baenziger, N.; Stille, J. K. J. Am. Chem. Soc. **1977**, *99*, 5665.
2. Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organometallic Chemistry," University Science: Mill Valley, Calif., 1980; pp. 420-33.
3. Suggs, J. W. J. Am. Chem. Soc. **1980**, *102*, 7109.
4. Rauchfuss, T. B. J. Am. Chem. Soc. **1979**, *101*, 1045.
5. Landvatter, E. F.; Rauchfuss, T. B. Organometallics **1982**, *1*, 506.
6. Landvatter, E. F.; Rauchfuss, T. B. J. Chem. Soc., Chem. Commun. **1982**, 1170.