

UAF Chemistry & Biochemistry Dept.
American Chemical Society
Seminar

Date: 9/15/08 Monday
Time: 7:00 PM
Place: 201 Reichardt Building

PHOSPHORUS-BRIDGING CARBONYL GROUPS: ANALOGUES OF ALDEHYDES AND KETONES

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The use of a metal carbonyl “matrix” allows the stabilization of phosphorus-bridging carbonyl groups in air-stable readily synthesized iron carbonyl derivatives of the general type $(R_2NP)_2COFe_2(CO)_6$ ($R_2N =$ *bulky* dialkylamino group particularly iPr_2N). Such compounds undergo the following types of reactions: (1) Attack of nucleophiles such as organolithium compounds, alkylidenephosphoranes, etc., on the phosphorus-bridging carbonyl group under mild reaction conditions to give alcohols $[(R_2NP)_2C(R)OH]-Fe_2(CO)_6$ or rearrangement products thereof; (2) Extrusion of the phosphorus-bridging carbonyl group at $\sim 100^\circ C$ to give a $(R_2NP)_2Fe_2(CO)_6$ unit with reactive sites on the phosphorus atoms which can be trapped by a variety of reagents. For example, alcohols trap $(R_2NP)_2Fe_2(CO)_6$ as $(R_2NPH)(R'OPNR_2)Fe_2(CO)_6$ whereas the $(R_2NP)_2Fe_2(CO)_6$ unit can also add to the $C\equiv N$ of acetonitrile or benzonitrile; the $C=O$ of aldehydes, ketones, or even maleic anhydride; and the $C=C$ of acrylonitrile. The nature of the $(R_2NP)_2Fe_2(CO)_6$ intermediate in such reactions has been studied experimentally by matrix isolation studies at low temperatures and by density functional theory.

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