PB&J: Phosphorus and Boron at the Junction of Two \( \pi \)-Systems

Significance: The 1,1-alkenyloboration of alkynes is an unique route to large conjugated \( \pi \)-systems. Erker and co-workers demonstrate that the 1,1-alkenyloboration of diarylphosphino-enynes proceeds similarly to give hexatrienes \( 1 \). Upon thermolysis, two concurrent transformations occur: 6\( \pi \)-electrocyclic ring closure of the hexatriene moiety and nucleophilic aromatic substitution (SNAr) of a pentafluorophenyl group by the phosphine nucleophile to yield heterotricyclic products \( 2 \).

Comment: These reactions are a convenient synthetic route to new molecules containing vicinal P/B Lewis pairs. Thermolysis products are only reported for \( 1a \) and \( 1b \). Would the thermolysis of \( 1c \) and \( 1d \), which contain bulky (Mes)\( _2 \)P nucleophiles, result in electrocyclic ring closure without concurrent SNAr?