Triamidoamine-supported zirconium catalyzed dehydrocoupling of phosphines

Dehydrocoupling of primary phosphines was applied to make phosphorus-phosphorus bonds using a Zr catalyst. A catalytic dehydrocoupling reaction was carried out to form known dimers $[(C_2H_4)_2(PH)]_2$ from 1,2-diphosphinoethane and $[(C_6H_4)PH_2(\mu\text{-}PH)]_2$ from *o*-bisphosphinobenzene. Further understanding of the mechanism of dehydrocoupling primary phosphines to form phosphorus-phosphorus bonds was gained by study of the thermal decomposition the phosphido complexes. This investigation showed formation of $[(C_6H_4)PH_2(\mu\text{-}PH)]_2$ as an intermediate toward the final product dimers. A new diphosphine $[(C_6H_4)PH]_2$, was observed in the reaction but could not be isolated. Catalytic hetrodehydrocoupling reactions of other primary and secondary phosphines were also explored. The relationship of steric and electronic properties of phosphorus to the dehydrocoupling will also be presented.