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Exploring novel reactivities of a tripodal triamidoamine-supported zirconium catalyst

Tripodal ligand-supported metal catalysts have demonstrated intriguing reactivity in bond forming reactions. A zirconium triamidoamine catalyst, $(N_3N)Zr$ $[\kappa^5\text{-}(Me_3SiNCH_2CH_2)_2NCH_2CH_2NSiMe_2CH_2]Zr$ (**1**) has been effective in catalyzing the formation of phosphorus, germane and arsenic bonds. It has been advantageous to expand this chemistry to organosilanes, as silane polymers have applications in electronics, materials, organic chemistry, and ceramics. In the course of pursuing silane substrates, it was found that $(N_3N)ZrNMe_2$ (**2**) has been effective for the dehydrocoupling of silanes, affording a mixture of aminosilanes and dehydrocoupled products. Complex **1** fails to react with organosilanes to afford the zirconium silyl derivative and is not catalytically active in dehydrocoupling. This and other observations suggest that the reaction is proceeding via α–silylene elimination process by which a low valent silicon fragment is extruded from the unobserved zirconium silyl intermediate, rather than a "traditional" σ-bond metathesis reaction observed for other dehydrocoupled reactions catalyzed by **1**. Attempts to trap the silylene and to fully understand the mechanism by which aminosilanes are formed are ongoing.