Development of Silylsilanolates as New Silylating Reagents

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Arylsilanes are gathering significant attention in the areas of material, agrochemical, and pharmaceutical sciences. One of the most reliable methods for the synthesis of arylsilanes is the alkali metal-halogen exchange of aryl halides followed by trapping with silicon electrophiles. This method suffers from low functional group tolerance because of the high reactivity of arylmetal intermediates. Thus, the silylation of aryl halides using transition metal catalysts and silylating reagents has been employed in recent years. Although these transition metal-catalyzed silylation reactions proceed under relatively mild conditions, conventional silylating reagents leave much room for improvement in terms of stability, reactivity for transmetalation, and handling.

We have developed silylsilanolates as new silylating reagents. Most of these reagents are stable solids with easy preparation and handling. Application of silylsilanolates to palladium-catalyzed silylation of aryl halides afforded silylated products under very mild conditions. A variety of silylsilanotes could be prepared, which enabled the introduction of various silyl groups. This silylation reaction could be applied to a broad scope of aryl iodide, bromide, chloride, and pseudohalides such as triflate. Silylation is amenable to even complex molecules which were previously considered difficult to silylate. Our ^{31}P and ^{19}F NMR experiments disclosed that the Pd(II) complex bearing silylsilanolate substituent is the key precursor of the silylpalladium intermediate. The reaction mechanism of this palladium-catalyzed silylation was also studied by using DFT calculation to reveal how the silyl groups on silylsilanolates migrate to the palladium atom.