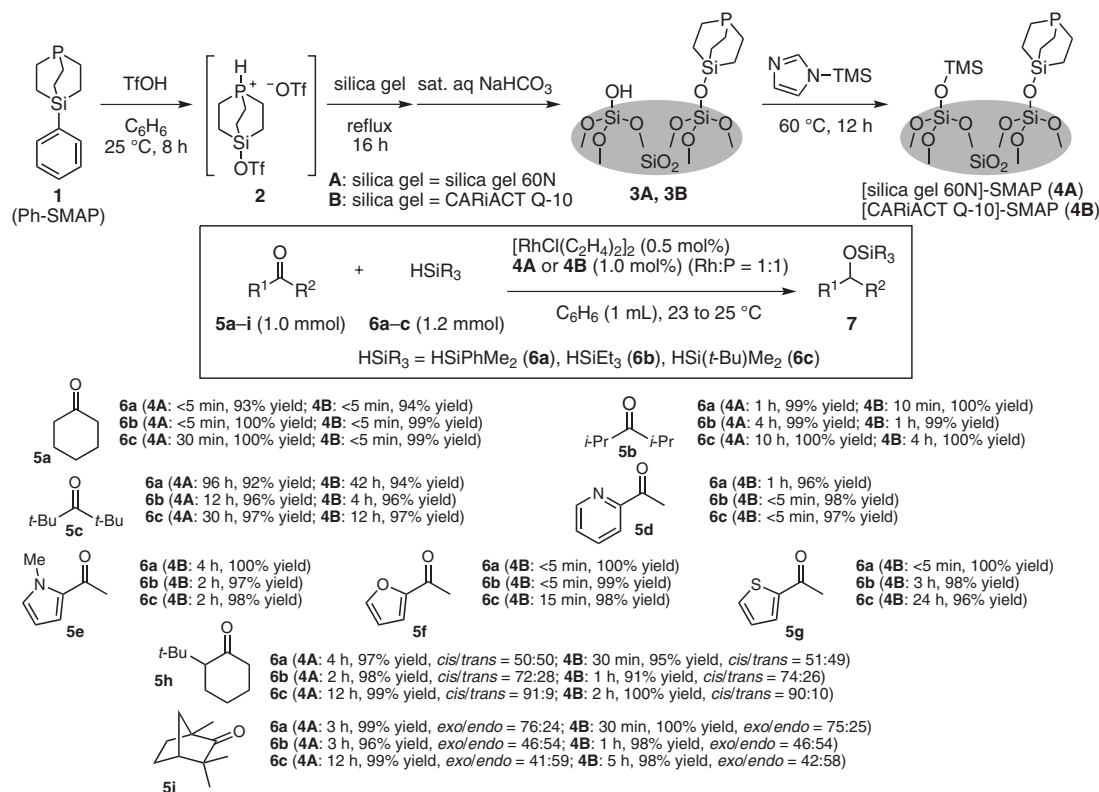


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 Synthesis of Silica-Supported Compact Phosphines and Their Application to Rhodium-Catalyzed Hydrosilylation of Hindered Ketones with Triorganosilanes
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[Silica]-SMAP-Rh System for the Hydrosilylation of Hindered Ketones



Significance: Silica gel-supported SMAPs, [silica gel 60N]-SMAP (4A) and [CARIACT Q-10]-SMAP (4B), consisting of a compact trialkylphosphine (SMAP) were prepared. Thus, the reaction of Ph-SMAP (1) with TfOH afforded silyl triflate 2. Surface treatment of silica gel 60N and CARIACT Q-10 with 2 gave phosphine-functionalized silica gels 3A and 3B. The surface silanols were end-capped with Me₃Si group to afford 4A and 4B. Hydrosilylation of ketones 5a-i with triorganosilanes 6a-c was carried out in the presence of [RhCl(C₂H₄)₂]₂ and 4A or 4B to give the silyl ethers 7 (27 examples, 91–100% yield).

Comment: Catalysts 4A and 4B were recovered by filtration and reused six and five times without any loss of catalytic activity, respectively. The leaching of Rh was checked by ICP-AES analysis, and determined to be <0.1%. The complexation reactions of 4A and 4B with [RhCl(cod)]₂ afforded [silica gel 60N]-[(SMAP)-RhCl(cod)] and [CARIACT Q-10]-[(SMAP)-RhCl(cod)], respectively. These structures were confirmed by ¹³C, ³¹P CP/MAS NMR spectra and XAFS. The data demonstrate the formation of mono(phosphine)-Rh(I) complexes. The authors believe that such species facilitate the reaction of hindered ketones.

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