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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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