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Metal Carbonyl Catalysts for the Transformation of Silicon Hydrides to Siloxanes in the Presence of DMF

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It has recently been reported that, upon photochemical irradiation, tertiary silanes (R_3SiH) react with DMF to form disiloxanes ($R_3Si-O-SiR_3$) and Me_3N , using the transition metal alkyl complex ($\eta^5-C_5H_5$)Fe(CO)₂Me as a catalyst. Intermediates of the type $R_3SiOCH_2NMe_2$ were proposed as the important first step via a hydrosilylation reaction but no evidence was obtained for this suggestion. By changing the catalyst to Mo(CO)₆ we have now observed that not only do we form the expected disiloxanes, but for the first time have observed the suggested intermediates. We have synthesized such intermediates via an independent method and demonstrated that they can indeed further react with R_3SiH to form the disiloxane products.