Redox-Neutral Manganese-Catalyzed Silylation of Alkenes

Significance: Xie and co-workers report a manganese-catalyzed dehydrosilylation and hydrosilylation of alkenes. They have shown that the reaction is easily scalable and affords the silylated product in good yields. The reaction proceeds equally well with both aliphatic and aromatic alkene starting materials.

Comment: Notably, the reaction is highly selective for the linear silylated product, stemming from the anti-Markovnikov addition of the silyl radical to the alkene. Additionally, under the specific conditions, either the dehydrosilylation or hydrosilylation product can be accessed with excellent selectivity.

Proposed mechanism:

Selected examples:

Mn$_2$(CO)$_{10}$ (5 mol%) ligand A (10 mol%)

PhCF$_3$, 140 °C, air, 24 h

>50 examples up to 89% yield
up to 100 mmol scale

Mn$_2$(CO)$_{10}$ (3 mol%) ligand B (6 mol%)

PhCF$_3$, 120 °C, air, 24 h

13 examples up to 89% yield
H:Dehy up to >99:1