CROSS-COUPLING CATALYSIS

A golden Stille coupling

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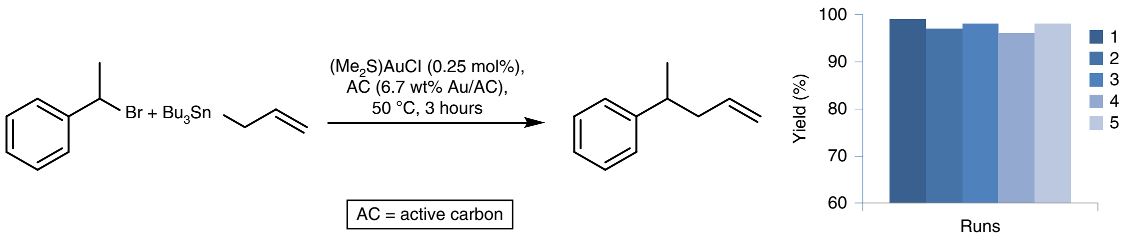

Despite their established use in other areas of catalysis, gold nanoparticles are rarely employed for cross-coupling reactions due to a lower activity compared to other metals. In fact, this important class of synthetic transformations is usually performed with Pd-based catalysts. Now, René Peters and colleagues report the cross-coupling of allylstannanes and activated alkylbromides using in situ formed gold nanoparticles, achieving very high turnover numbers.

While exploring the reactivity of different gold complexes as catalyst for the Stille-type coupling of (1-bromoethyl)benzene and allyltributylstannane, the authors observed that product formation occurred with the simultaneous generation of a dark solid, later identified as gold nanoparticles. A control reaction using commercial gold powder as the catalyst confirmed the heterogeneous character of these cross-couplings, identifying gold complexes as the precatalysts. In order to enable the recovery and reutilization of the nanoparticles formed in situ, the team explored the use of commercial active carbon as an additive, resulting in the quantitative isolation of gold in the form of carbon supported nanoparticles. Incidentally, the addition of active carbon was also capable of accelerating the reaction. Transmission electron microscopy and X-ray diffraction, performed on different samples obtained by varying the amount of active carbon in the reaction mixture, revealed a particle size dependence on the metal-to-active carbon ratio — that is, the metal loading affects the dispersion. The possible formation of Au–Sn alloys — due to the presence of allylstannanes — was excluded at this stage via XPS analysis.

Optimization of the reaction with respect to precatalyst and active carbon loading led to a fully recyclable system along with nearly quantitative yields (pictured). A substrate scope analysis revealed that the method is quite versatile and applicable to benzylic bromides carrying a diverse set of substituents. Besides secondary substrates, primary and tertiary benzyl bromides could also be employed with good results. Aromatic and aliphatic allylic bromides were also reactive in preliminary tests, although in the latter case the partial isomerization of the double bond occurred as a side reaction.

Davide Esposito

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