Recently, many efforts have been directed towards palladium catalysts with superior profiles to the often thermally unstable Pd(0) catalysts usually prepared in situ. During this research, Herrmann and Beller developed palladacycle 1 as a thermally stable and versatile catalyst. 1-2 1 was shown to give significantly higher turn over numbers (TON) than many in situ prepared systems in Heck-type reactions, 1-3 and it was also used successfully for palladium-catalyzed Suzuki, 1 Stille, 1 Negishi, 1 Songashira coupling reactions as well as for aromatic aminations. 1

Preparation: 2 Palladacycle 1 can be easily obtained by gently heating equimolar amounts of tris(o-tolyl)phosphine and palladium acetate in toluene. After removal of the solvent, the crude catalyst is precipitated with hexane and can be re-crystallized from toluene/hexane. The yellow crystals thus obtained are moisture and oxygen stable and can be stored at room temperature for months without decomposition.

Abstracts

(A) Due to the thermal stability of 1, even aryl chlorides are feasible substrates for the Heck reaction. However, additives like n-Bu4NBr or Ph4PCl are necessary in at least stoichiometric quantities to obtain good yields. The more reactive aryl bromides usually do not require additives and give yields > 90%. 1-3

(B) In Tietze’s elegant total synthesis of cephalotaxine, palladacycle 1 catalyzed an intramolecular Heck cyclization of 2 to give 3 in high yield. 5 Other catalyst systems failed to give the reaction. Analogues of cephalotaxine were prepared in a similar fashion. 6

(C) While other catalysts gave inconsistent or unsatisfactory results, 1 catalyzes the Stille reaction of polymer bound 4 with various aryl bromides. After cleavage, biaryls 5 are obtained in good yields. Catalyst loads can be lowered to 0.1 mol%, but longer reaction times are needed. The reaction can also be carried out using solution chemistry, although the yields are not as high. 4

(D) Palladium-catalyzed Ullmann-type homocoupling reactions have also been performed using 1. Hydroquinone is necessary to reduce Pd(II)/Pd(IV) to Pd(0). The reaction can also be performed using the in situ generation of 1 with comparable yields. 7

References and Notes


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