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,1,4 Negishi,1 Songashira1 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.

References and Notes

SYNLETT
Spotlight 30
trans-Di(µ-acetato)-bis[o-(di-o-tolylphosphino)benzyl]dipalladium(II)
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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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