Palladium-catalyzed bisfunctionalization of active alkenes by β-acetonitrile-α-allyl addition: application to the synthesis of unsymmetric 1,4-di(organo)fullerene derivatives

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ABSTRACT

A new, efficient palladium-catalyzed bisfunctionalization of ethylidene malononitriles by addition of acetonitrile and allyl groups is developed for the construction of all-carbon quarternary and tertiary centers simultaneously. This methodology is successfully applied to the synthesis of unsymmetric 1,4-disubstituted C_{60}.

Palladium-catalyzed β-nucleophilic-α-allyl addition of active olefins through π-allyl-palladium intermediates has emerged as a mild and efficient multiple bond-forming method for the simultaneous construction of all-carbon quaternary and tertiary centers,[1,2] which are important structural units in a wide range of bioactive substances and natural products.[3] Over the past decade, we and other groups have been interested in developing new palladium-catalyzed β-nucleophilic-α-allyl addition reactions toward active alkenes through various π-allyl palladium intermediates, including heteroatom- and carbon-nucleophile addition/allylation,[2e–k] bis-allylation,[2a–d] acetonation/allylation,[2l,m] amidoallylation,[2n] and iminoallylation (Fig. 1).[2o] The palladium-catalyzed decarboxylative reaction for the formation of π-allyl palladium species is an environmentally friendly and economical process[1c,4,5]; the reaction proceeds under essentially neutral conditions with high atom economy. Based on this concept, we envisioned that the bis-π-allylpalladium[2a] analogue acetonitrile-(π-allyl)palladium complex should be formed by the reaction of cyanoacetic acid allyl ester with a palladium catalyst, which will undergo acetonitrile/allyl addition to the active alkenes (Fig. 1). Furthermore, in continuation

of our interest in transition metal catalyzed functionalization of [60]fullerene (C_{60}),[6] we reasoned that if successful, this methodology would be applicable to the selective bisfunctionalization of C_{60} because of its electrophilic nature and specialized alkene component. Transition metal catalyzed functionalization of C_{60} has emerged as a promising method for preparing functionalized C_{60} derivatives with high selectivity and high functional group compatibility under mild reaction conditions.[7] However, investigations on the synthesis of unsymmetric 1,4-di(organo)fullerenes have been seldom studied,[8] in particular, a one-step catalytic method has not been reported.

Herein, we report a new Pd-catalyzed bisfunctionalization of various malononitriles 1 with cyanoacetic acid allyl ester (2), that affords the β-acetonitrile-α-allyl addition products 3 in good to high yields (Eq. 1). Moreover, we have successfully applied this method to the synthesis of unsymmetric 1-acetonitrile-4-allyl-[60]fullerene 4a in good yield in one step.

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