

CORRIGENDUM

Reference [15] is lacking in the text. It should be placed on Page 1, second column, 10th line from the bottom after high yields.

The following part of the text needs to be replaced:

Mechanistic studies by Friestad and Branchaud^[16] on the Cacchi system suggested that the absence of acid would result in the initial formation of the Mizoroki–Heck product **4 a**, followed by its reduction to **3 a** by accumulated Pd–H species formed from NBU₃. To study this hypothesis in our present catalytic system, we carried out a reaction with deuterated benzylidene acetone ([D₁]-**1 a**) under the optimized reaction conditions (Scheme 2). Either the absence of deuterium or deuterium scrambling at the β-carbon of **3 a**, will support the reaction pathway via Heck reaction followed by reduction. However, the reaction gave reductive Heck product [D₁]-**3 a** in 80% yield with > 97% remaining deuteration at the β-carbon. This rejects the hypothesis of Friestad and Branchaud and supports the pathway in which the Pd-alkyl complex **A** (Scheme 1) is reduced by DIPEA to a palladium hydride species followed by reductive elimination. Alternatively **A** tautomerizes to an O-bound palladium enolate that is subsequently reduced by DIPEA.^[20]

This part should be replaced by the following:

We have performed a deuterium labelling experiment to shed more light on the mechanism of the reaction (Scheme 2). Thus, reaction of 4-D-phenyl-3-buten-2-one ([D₁]-**1 a**) with **2 a** and 5 eq. of DIPEA catalyzed by 1 mol% of Pd(OAc)₂ gave the reductive arylation product [D₁]-**3 a** in 80% yield with 97% retention of deuterium. This conclusively shows a reductive arylation mechanism is active and it excludes the possibility of a Heck reaction followed by a hydrogenation, as in this case all deuterium would be lost. However, the final stages of the mechanism remain obscure. We see two possible mechanisms: protonation of the formed palladium enolate species and reduction of the palladium(II) to palladium(0) with the trialkylamine. The second mechanism: reaction of the palladium alkyl intermediate with the trialkylamine to form the palladium alkylhydride complex seems quite plausible. Reductive elimination of this will lead to the reductive arylation product. A third mechanistic possibility, previously proposed by Friestad and Branchaud, suggested reduction of the palladium enolate by XPd^{II}(Ln)H, Et₃NHX, or other reductants.^[16] However, we have shown in later work that upon use of [D_{1,5}]Et₃N 55% of deuterium is incorporated α to the ketone in the 3-position, providing strong support for the second mechanism.^[20]

In the original paper Reference [20] was still in press. This has now been published.

[15] This strategy of switching between reaction modes was reported more recently also for the oxidative Heck reaction versus conjugate addition, with arylboronic acids, see: S. E. Walker, J. Boehnke, P. E. Glen, S. Levey, L. Patrick, J. A. Jordan-Hore, A.-L. Lee, *Org. Lett.* **2013**, *15*, 1886.

[20] For the detailed mechanistic study on Pd^{II}-NHC catalyzed reductive Heck reaction of aryl iodides to enones using DIPEA as reductant, see; 20 S. Raoufmoghaddam, S. Mannathan, J. G. de Vries, A. J. Minnaard, J. N. H. Reek, *Chem. Eur. J.* **2015**, *21*, 18811–18820.

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