Pd-CATALYZED HYDROFORMYLATION USING FORMALDEHYDE AS SYNGAS SURROGATES

Benedetta Palucci,^a Carmen Claver, ^{a,b} Cyril Godard,^b Jorge Sánchez Quesada,^c and Sergio Castillón ^b

^a Centre Tecnològic de la Química, 43007 Tarragona, Spain ^b Departament de Química Física i Inorgánica, Universitat Rovira i Virgili, 43007 Tarragona, Spain

The hydroformylation of alkenes is an iconic industrial applications of homogeneous catalysis due to the added-value of the resulting aldehydes. [1] Although this process has undergone continuous growth since its invention, it still mainly relies on the use of expensive transition-metal catalysts such as those based on rhodium and ruthenium and the dangerous use of syngas. In contrast, palladium has not been appropriately exploited in the area of hydroformylation since catalysts based on this metal originally targeted the formation of alternating polyketones from olefins with carbon monoxide, or esters/carboxylic acids in the presence of methanol or water as nucleophiles. [2] Although some studies have focused in the use of palladium in hydrofromylation, only recently it has been reported a Pd-catalytic system which delivers exclusively the linear aldehyde, compared to other methods in which the branched regioisomer is observed.^[3] Here we present a new approach to catalyse the hydroformylation of alkenes by palladium employing formaldehyde as syngas surrogates.^[4] A mechanism, supported by ¹H-NMR and GC studies, explaining the exclusive formation of the linear aldehydes is also proposed. This strategy is attractive as it utilizes highly available chemicals, a cheap and abundant metal for making added value molecules, avoiding the use of more dangerous syngas.

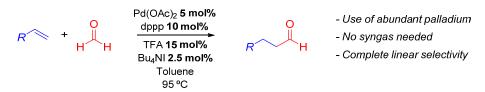


Figure 1. Pd-catalysed hydroformylation using formaldehyde as syngas surrogate.

^c International Flavors & Fragrances Inc., Avda Felipe Klein, 2, 12580 Benicarló, Spain

^[1] a) A. F. R. Börner, *Hydroformylation: Fundamentals, Processes and Applications in Organic Synthesis*, **2016**; b) M. Taddei, Mann, A., *Hydroformylation for Organic Synthesis*, **2013**; c) F. Ungvári, *Coord. Chem. Rev.* **2007**, 251, 2072-2086; d) P. W. N. M. K. van Leeuwen, P. C. J.; Claver, C.; Pàmies, O.; Diéguez, M., *Chem. Rev.* **2011**, 111, 2077-2118.

^[2] a) J. Pospech, Fleischer, I., Franke, R., Buchholz, S., and Beller, M., *Angew. Chem.* **2013**, 52, 2852-2872; b) B. H. M. Drent E., *Chem. Rev.* **1996**, 96, 663-681; c) I. del Río, C. Claver, P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem.* **2001**, 2719-2738.

^[3] W. C. Ren, W.; Dai, J.; Shi, Y.; Li, J.; Shi, Y., J. Am. Chem. Soc. 2016, 14864-14867.

^[4] B. Palucci, , C. Claver, C. Godard, J. S. Quesada, S. Castillón. Manuscript in preparation.