[2+2+2] Cycloaddition reactions involving allenes catalysed by rhodium

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The transition metal-catalysed [2+2+2] cycloaddition reaction of three unsaturated partners constitutes one of the most attractive methodologies for the construction of six-membered rings.[1] The reaction, which was initially developed for three alkynes delivering benzenes, has evolved to involve many other unsaturations. Allenes, characterized by their two perpendicular π bonds, have been recognized as versatile substrates or intermediates in modern organic synthesis and, due to the high density of unsaturation, have shown particular promise in the development of cycloaddition and cycloisomerization reactions.[2]

We report the development of the rhodium-catalysed [2+2+2] cycloaddition reaction of polyunsaturated scaffolds containing allene moieties. First of all, allene-ene/yne-allenes substrates have been reacted to diastereoselectively afford structures with a cyclohexenic or cyclohexadienic ring core. The cycloadducts obtained feature an exocyclic diene which could be further upgraded to pentacyclic scaffolds by a Diels-Alder reaction.[3] One of the main advantages of using allenes in the place of alkynes as substrates in cycloaddition reactions is the stereochemical complexity that they generate. We have followed the study of the [2+2+2] cycloaddition reaction of allene-ene/yne-allenes for the synthesis of enantiopure tricyclic compounds with up to 6 stereogenic centres by the chiral pool strategy. Finally, the reactivity of a cyano-yne-allene scaffold has been studied under rhodium catalysis to afford, after a dehydrogenative [2+2+2] cycloaddition, 1,2-dihydro-2,6-naphthyridine scaffolds that can easily be converted to 2,6-naphthyridine containing molecules.

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[1] For a monograph, see: Tanaka, K. (Ed.), Transition-Metal-Mediated Aromatic Ring Construction, Wiley, **2013**.

[2] For selected reviews, see: a) Aubert, C.; Fensterbak, L.; Garcia, P.; Malacria, M.; Simonneau, A. *Chem. Rev.* **2011**, *111*, 1954; b) Ma, S. *Chem. Rev.* **2005**, *105*, 2829.

[3] Haraburda, E.; Torres, O.; Parella, T.; Solà, M.; Pla-Quintana, A. *Chem. Eur. J.* **2014**, *20*, 5034.