

Rhodium(I)-Catalysed Intramolecular [2+2+2] Cyclotrimerisations of 15-, 20-, and 25-Membered Azamacrocycles: Experimental and Theoretical Mechanistic Studies

Anna Dachs, Anna Torrent, Anna Roglans,* Teodor Parella, Sílvia Osuna, and Miquel Solà*

A new series of 20- and 25-membered polyacetylenic azamacrocycles have been satisfactorily prepared and completely characterised by spectroscopic methods. Various [2+2+2] cyclotrimerisation processes catalysed by Wilkinson's catalyst, $[\text{RhCl}(\text{PPh}_3)_3]$, were tested in the above-mentioned macrocycles. The 25-membered azamacrocycle (like the previously synthesised 15-membered azamacrocycle) led to the expected cyclotrimerised compound in contrast to the 20-membered macrocycle, which is characterised by lack of reactivity.

The difference in reactivity of the 15-, 20- and 25-membered macrocycles has been rationalised through density functional theory calculations.

