

P01

THE AGOSTIC INTERACTION IN THE BRANCHED INTERMEDIATE EXPLAINS THE β -REGIOSELECTIVITY IN THE RH-CATALYZED HYDROFORMYLATION OF 1,1-DIPHENYLETHENE

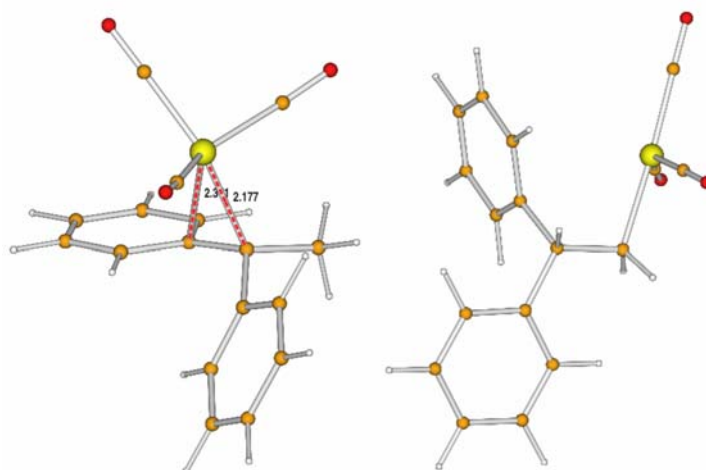
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Theoretical calculations on the hydroformylation of 1,1-diphenylethene, carried out at the B3P86/6-31G*/LANL2DZ level on the approaching path of the fourth CO group, show an unexpected and remarkably high free energy activation barrier for the tertiary alkyl-Rh(CO)₃ intermediate, whereas the reaction pathway is much more favorable for the linear one, once the linear alkyl-Rh(CO)₃⋯CO adduct has been formed. For this substrate, the high barrier for the branched intermediate (at left hand side in the figure) can be ascribed to the agostic interaction with the π density of one of the aromatic rings. The hindered formation of the alkyl-Rh(CO)₄ branched species, overlooked thus far because of

its thermodynamic stability, instead of the insertion of an alkyl group onto one of the coordinated CO groups (as previously hypothesized in the literature [1]) or subsequent steps, that is the H₂ oxidative addition and the aldehyde reductive elimination, is actually responsible for the absence of the quaternary aldehyde. This is a novel



finding. Nonetheless, the barrier for the CO addition to the branched intermediate is not a peculiarity of this system: other vinylidene substrates show a similar behavior.

The valuable contribution of theoretical methods in exploring experimentally inaccessible species and in interpreting mechanistic aspects comes out from this study as well as the importance of the organic part structure in organometallic complexes.

[1] R. Lazzaroni, R. Settambolo, G. Uccello-Barretta, A. Caiazzo, S. Scamuzzi, *J. Mol. Cat. A: Chemical* **1999**, *143*, 123