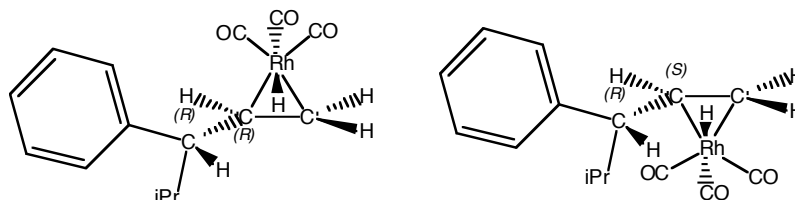


Do alkyl-rhodium reactant complex stabilities on each diastereoface account for hydroformylation stereoselectivity?

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A theoretical investigation on the stability of alkyl-rhodium reactant complexes and transition states (TS) in the hydroformylation reaction of 3-phenyl-4-methyl-1-pentene with an unmodified rhodium catalyst ($\text{H-Rh}(\text{CO})_3$) has been carried at the B3P86/6-31G* level, employing effective core potentials for Rh in the LANL2DZ valence basis set, to evaluate both regio- and diastereoselectivity. The structural features of all possible reactant and TS complexes, with a second chiral center at the inner olefin carbon upon complexation (see Scheme 1), have been considered with the aim of correlating stability and steric hindrance.



Scheme 1. Attack on the Si and Re faces.

Significant differences in relative stabilities of low energy reactant adducts are obtained depending on the mutual arrangement of the bulky groups (especially phenyl ring and metal catalyst) as compared to the TS. The extent of the attack on either one of the olefin double bond faces sharply favors the Si face (Si:Re = 90:10 from reactant populations). The diastereomeric π -olefin complexes then evolve to produce either linear (ℓ) or branched (b) species depending on in which sense the catalyst rotates. Using the TS populations, the ratio between the diastereofaces becomes 77:23. Seemingly the product composition does not reflect the position of the equilibrium between the diastereomeric reactant complexes as it was suggested to verify [1].

The regioselectivity of the substrate diastereofaces is different as well, because at this level $b:\ell$ and $b':\ell'$ are 41:59 and 58:42, respectively. Those values correspond to a total regioselectivity ($b+b':\ell+\ell' = B:L$) of 45/55, in a quantitative agreement with the experimental results ($B:L = 45/55$). A very close result ($B:L = 43/57$) is obtained using the TS values separately for the two faces coupled to the Si:Re ratio above, determined on the reactant adducts. Conversely, the diastereoselectivity is predicted only qualitatively, because the theoretical and experimental values for $b:b'$ turn out to be 71:29 and 85:15, respectively, although the same populations at the TS (that satisfactorily produce B) have been used. The $\ell\ell'$ ratio, computationally available only, is 83/17. Subsequent reaction steps have been considered to evaluate the possible occurrence of barriers even higher than the rhodium-alkyl TS. The comparison of this system with related substrates of different steric hindrance shows intriguing results.

[1] A. Stefani, D. Tatone and P. Pino, *Helvet. Chim. Acta*, **62**, 1098 (1979).