Controlling Facial Selectivity Towards Carbocations via a Docking Strategy

**Significance:** Reliable facial selectivity in non-chiral carbocations would be a powerful methodology allowing for numerous asymmetric transformations. The formation of a carbocation on a chiral metal complex would allow for subsequent enantioselective attack onto the resulting carbocation. The authors use this strategy and demonstrate a broad scope with moderate to good yields and excellent enantioselectivities.

**Comment:** The analogous reaction on an allylic system led to none of the desired product, suggesting that the extra carbon spacer is necessary to avoid steric congestion. In addition, the authors obtained an X-ray structure of the key allene-iridium complex, which supports the conclusion that the terminal olefin of the allene docks into the iridium complex.

**Selected examples:**

- PinB: 74% yield, 96% ee, \( r/r = 15:1 \) (15 h reaction time)
- OMe: 64% yield, 73% ee, \( r > 20:1 \) (13 h reaction time)
- F: 79% yield, 95% ee, \( r > 50:1 \) (13 h reaction time)
- Ts: 72% yield, 38% ee, \( r > 20:1 \) (21 h reaction time)

**Postulated mechanism:**

The mechanism involves a catalyst-controlled enantiodetermining hydride transfer, followed by Lewis acid activation of the double bond to form the desired product. The diastereomeric complexes are postulated to be controlled by the catalyst, leading to high enantioselectivity.

**SYNFACTS Contributors:** Mark Lautens, Egor M. Larin

**Synfacts 2019, 15(05), 0503 Published online: 15.04.2019 1861-19581861-194X
DOI: 10.1055/s-0037-1611486; Reg-No.: L032195F**