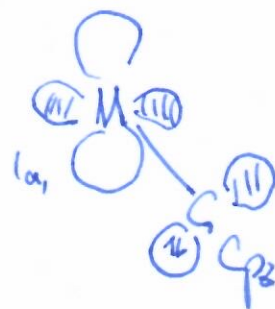
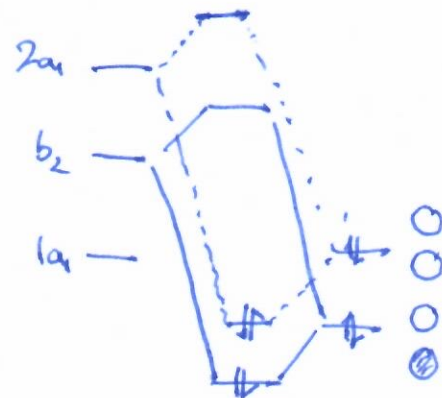
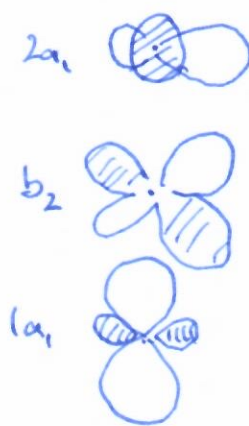
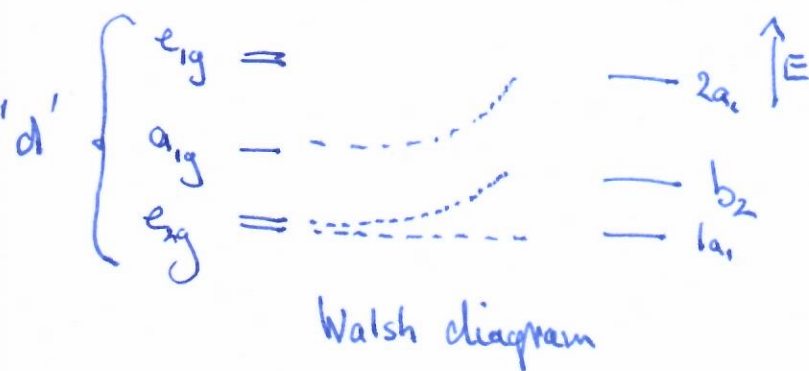
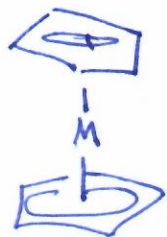
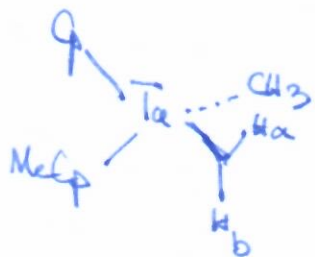


frontier MO's of 'bent metallocene' fragment



dynamic features

not about M-C bond restricted?

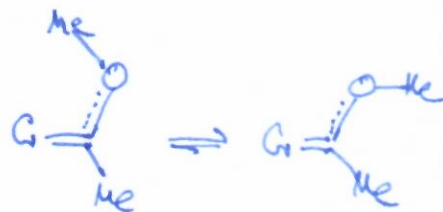


H_a, H_b inequivalent up to 100°C

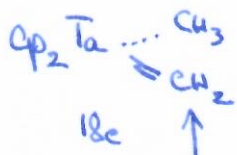
$$\Delta G^\ddagger \geq 25 \text{ kcal/mol}$$



→ 4 Me resonances @ -40°C



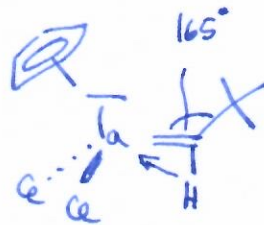
in electronically unsaturated carbones → agostic interactions



$$J_{\text{CH}} = 132 \text{ Hz}$$

(normal sp²-J_{CH} ~ 150 Hz)

but

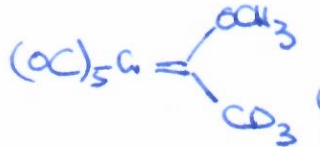
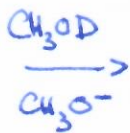
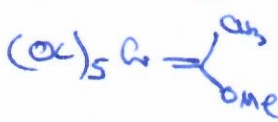
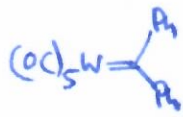
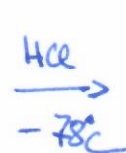
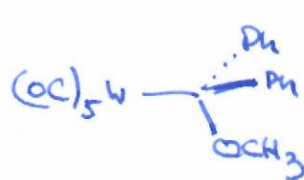
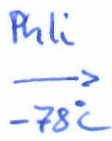
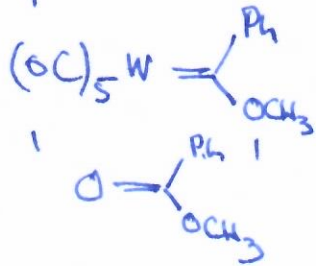


14e

$$J_{\text{CH}} = 84 \text{ Hz}$$

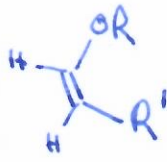
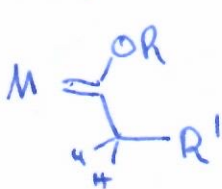
$$\nu_{\text{C-H}} : 2510 \text{ cm}^{-1}$$

Reactivity

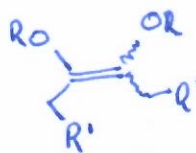


H/D exchange

thermal dec.?



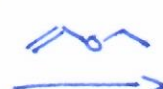
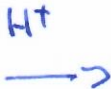
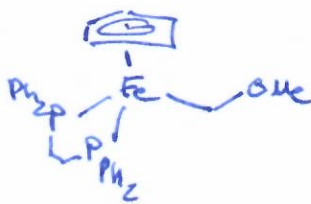
and/or



and/or

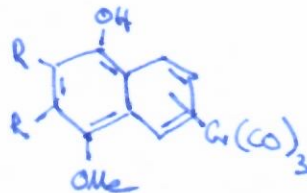
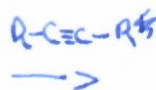
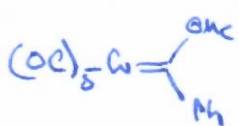


carbene transfer:



q Fischer carbene no more?

Dötz Reaction:

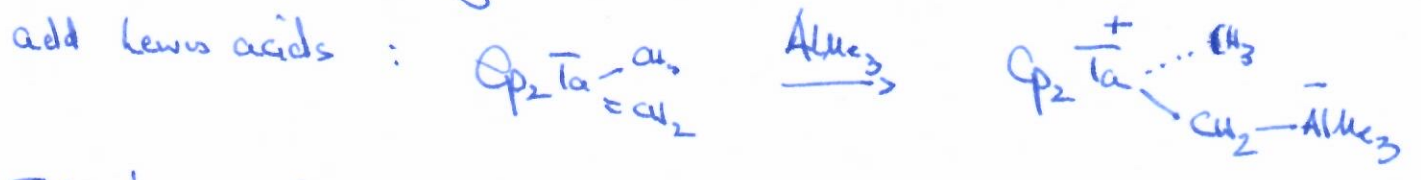


Angew. Chem. 1984, 23, 97

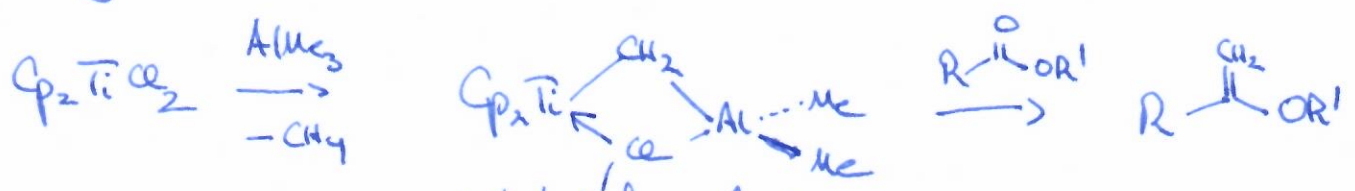
Schwack carbenes - nucleophilic C



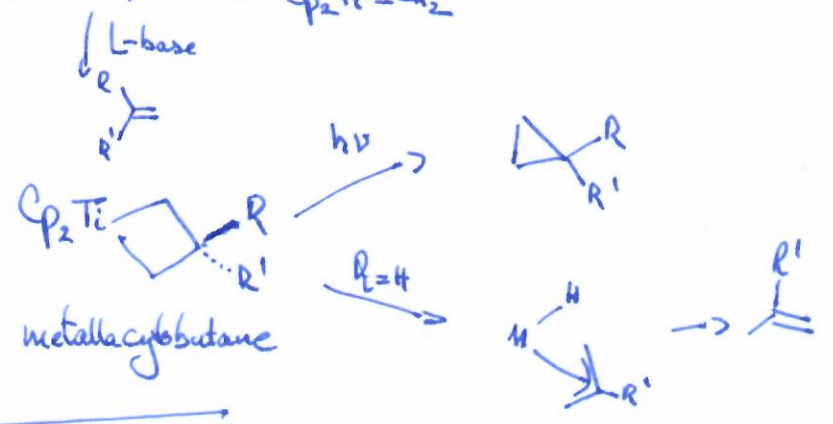
'Wittig' like



Tebbe's reagent

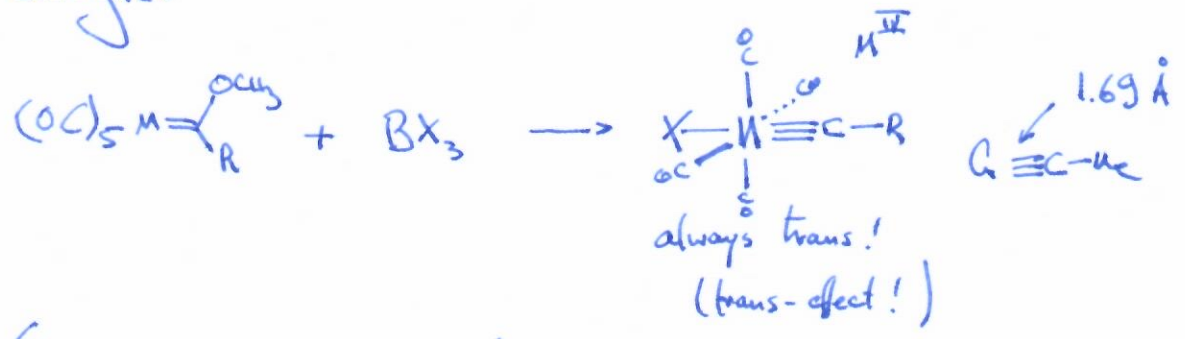


protected form of $Cp_2Ti=CH_2$



formation of carbynes

Fischer



Schwack:

