REGIOSELECTIVE C-H ACTIVATION AND SEQUENTIAL C-C AND C-O BOND FORMATION REACTIONS OF ARYL KETONES PROMOTED BY AN YTTRIUM CARBENE[1]

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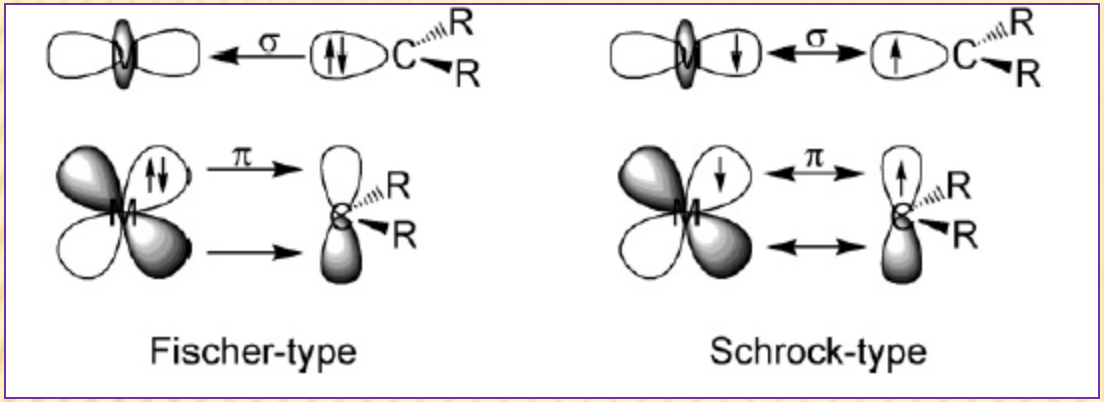
CARBENE OVERVIEW



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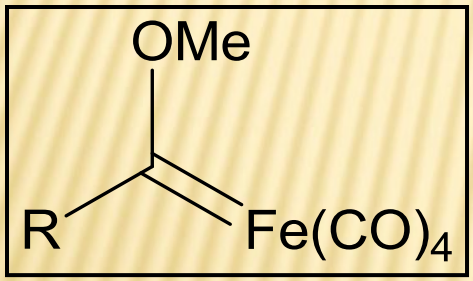
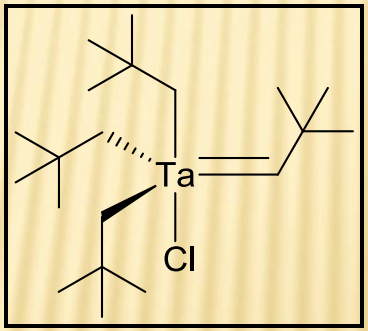
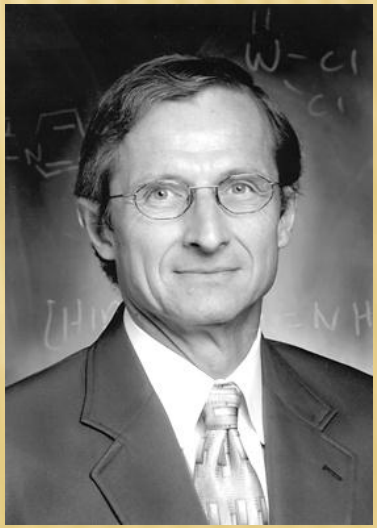
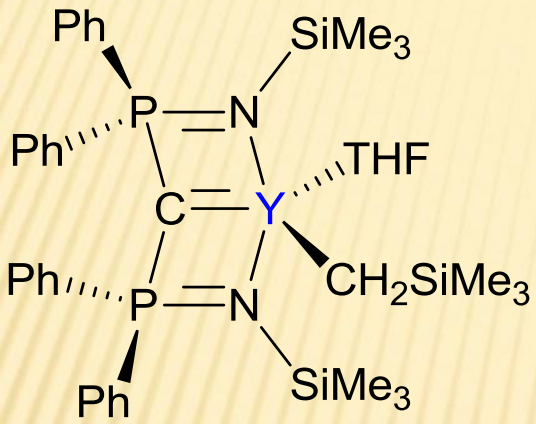


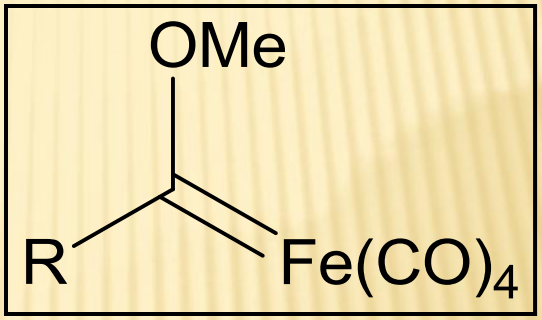


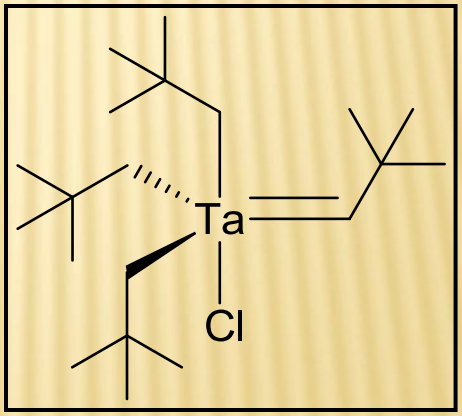
$M{=}C^{+}$ $^{+}M{=}C^{-}$



RARE EARTH CARBENES

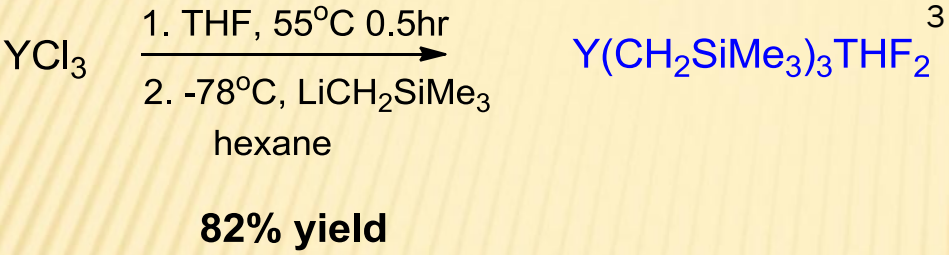




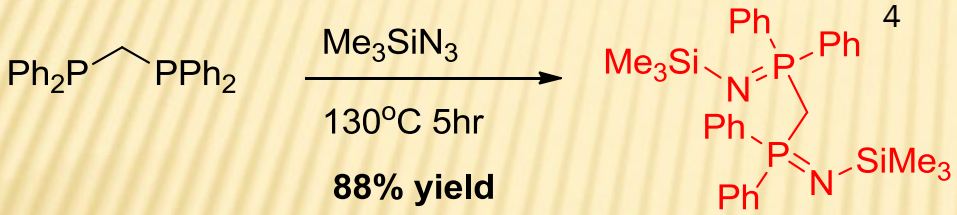


Yttrium Metal

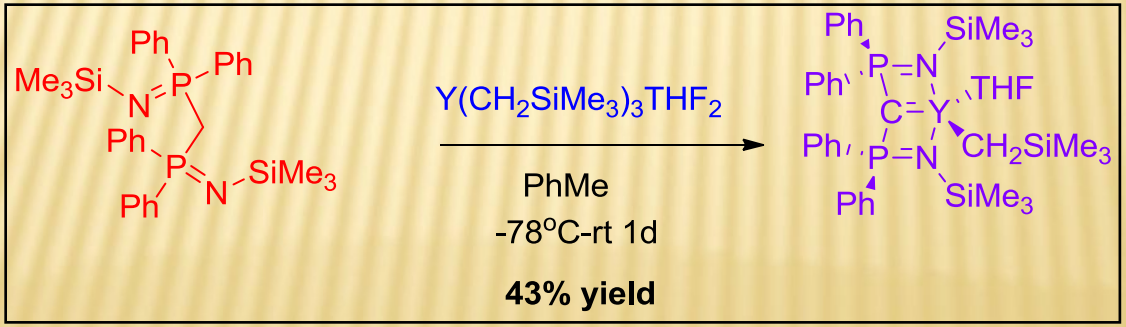
SYNTHESIS OF YTTRIUM CARBENE



82% yield



88% yield

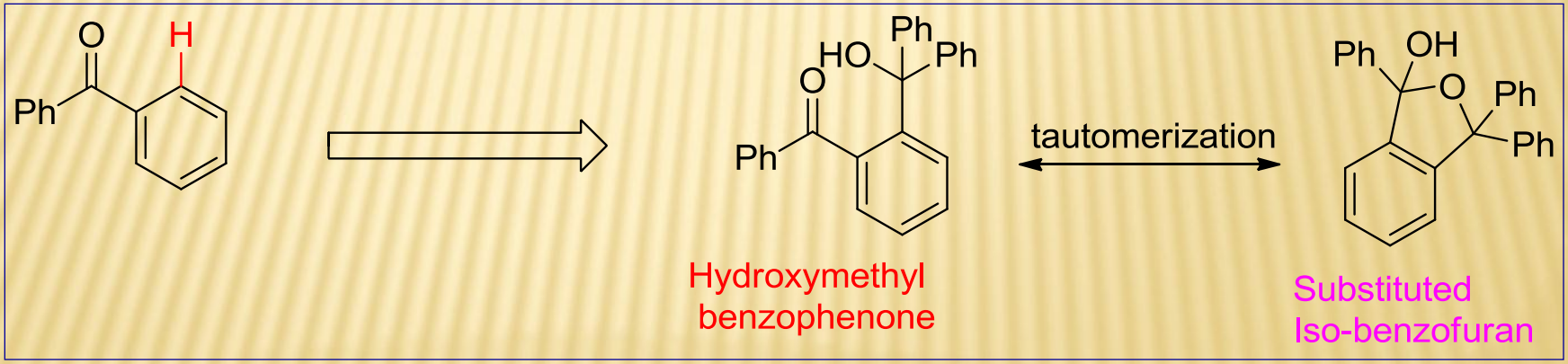


43% yield

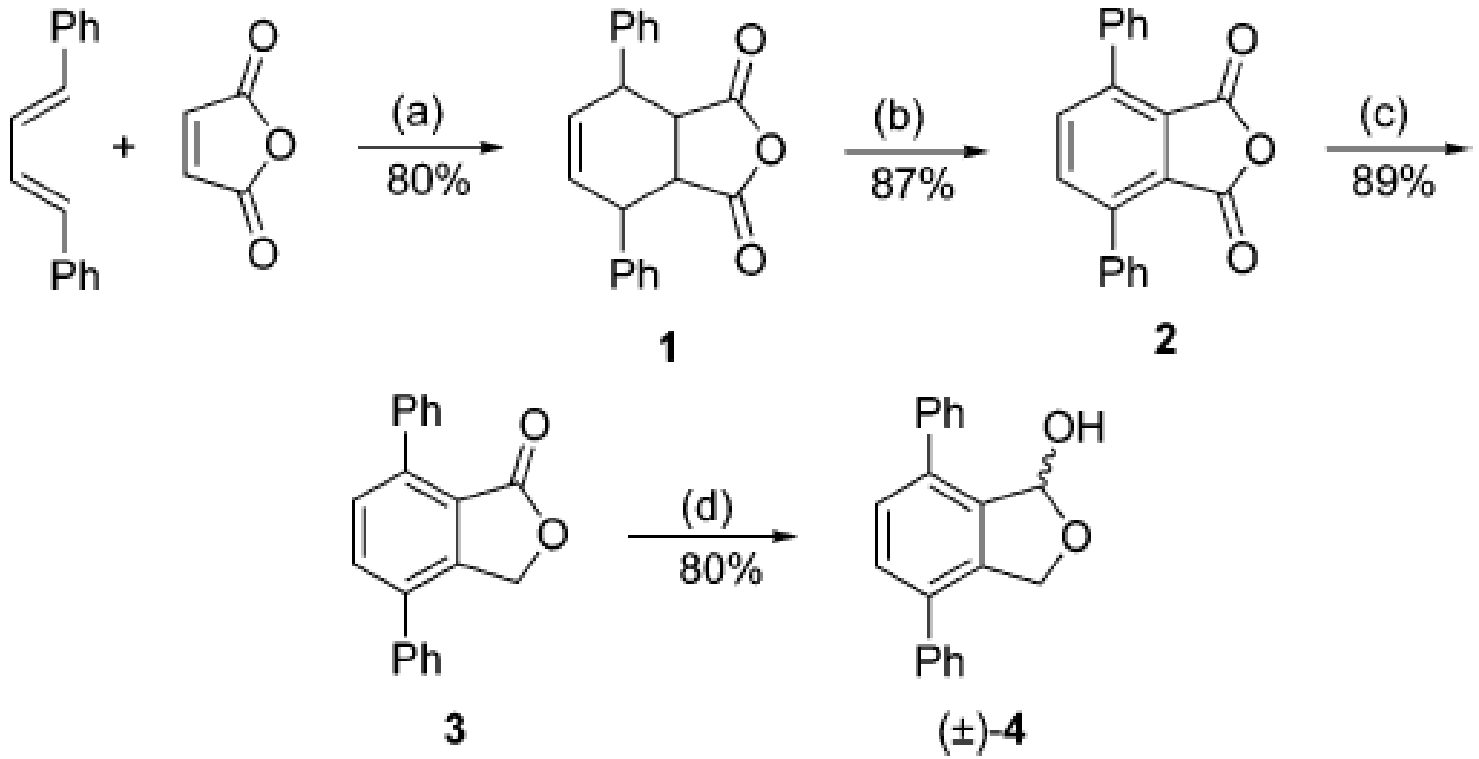
REACTIVITY

- Wittig type reactivity to give alkenes
- Some reactivity with carbonyl compounds

Until now.....

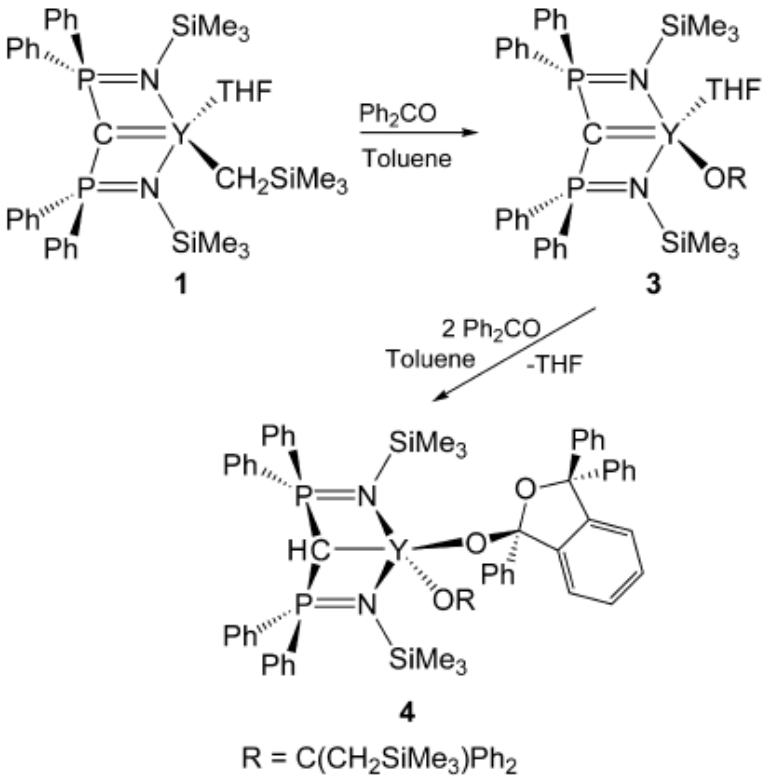


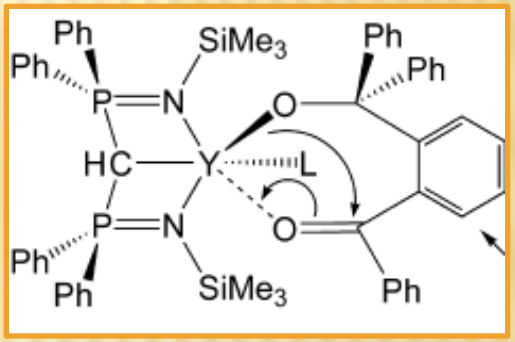
ALTERNATE METHOD TO SUBSTITUTED *ISO*-BENZOFURANS[6]



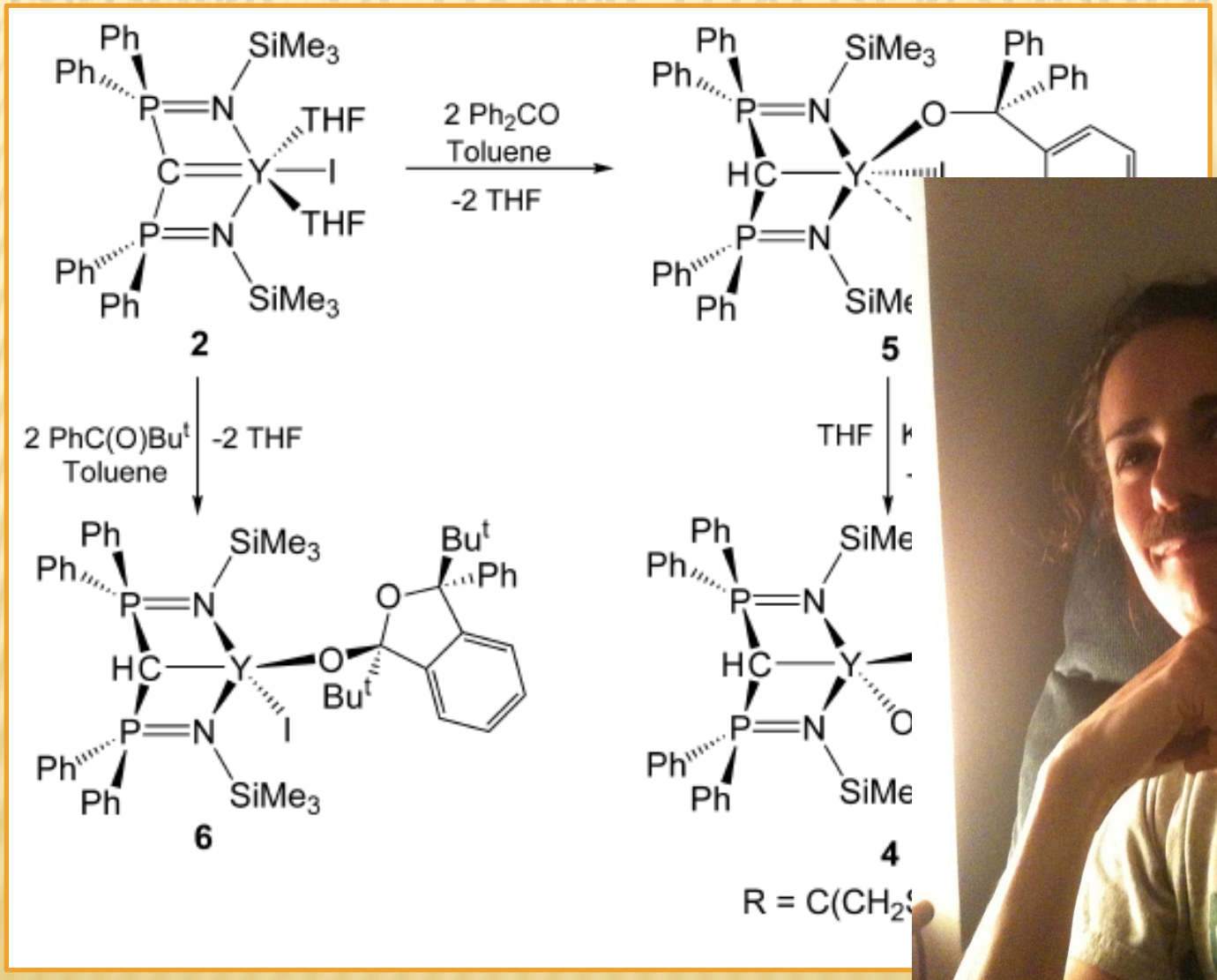
[a] Reagents and conditions: (a) xylenes, 140 °C, 15 h; (b) DDQ, toluene, 111 °C, 18 h; (c) Zn, HOAc, 100 °C, 17 h; (d) DIBAL-H, dichloromethane, −60 °C, 70 min.

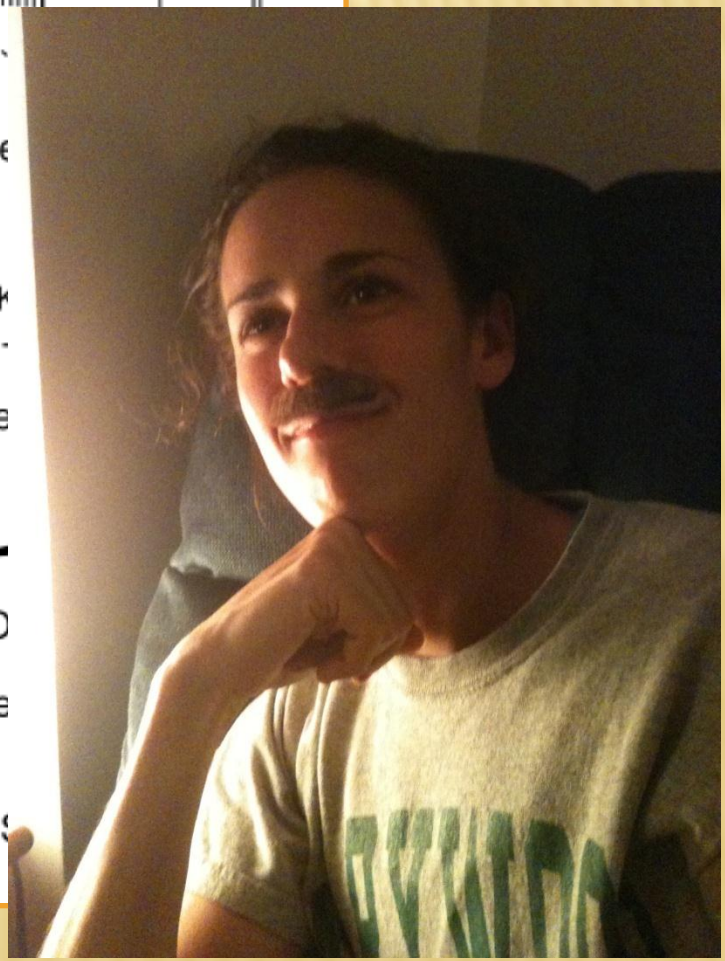
SCHEME 1: SYNTHESIS OF 3 & 4



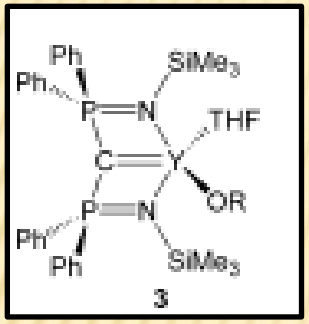


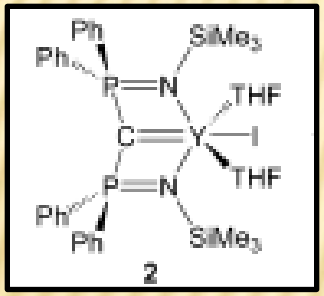
TRAPPING OF OXYMETHYLBENZOPHENONE





SOLVENT EFFECTS





+ Ph_2CO

Toluene

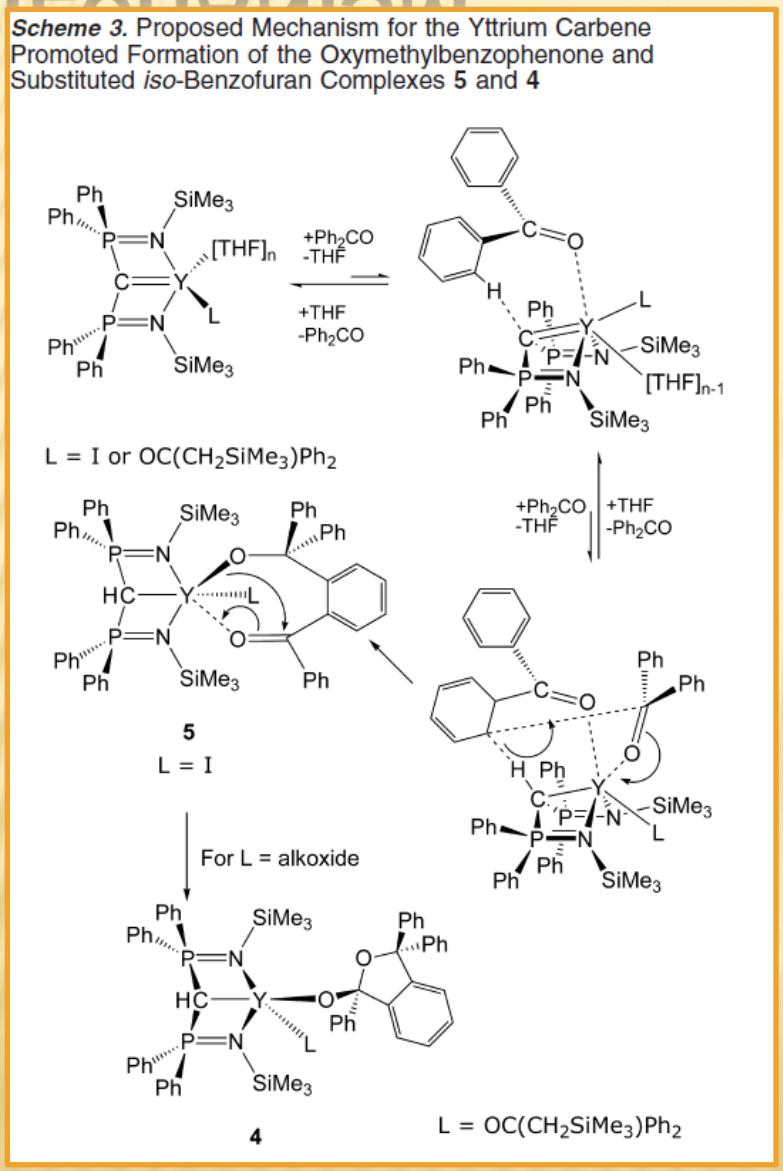
Results in red color due to charge transfer

+ Ph_2CO

THF

Colorless, NO REACTION

MECHANISM

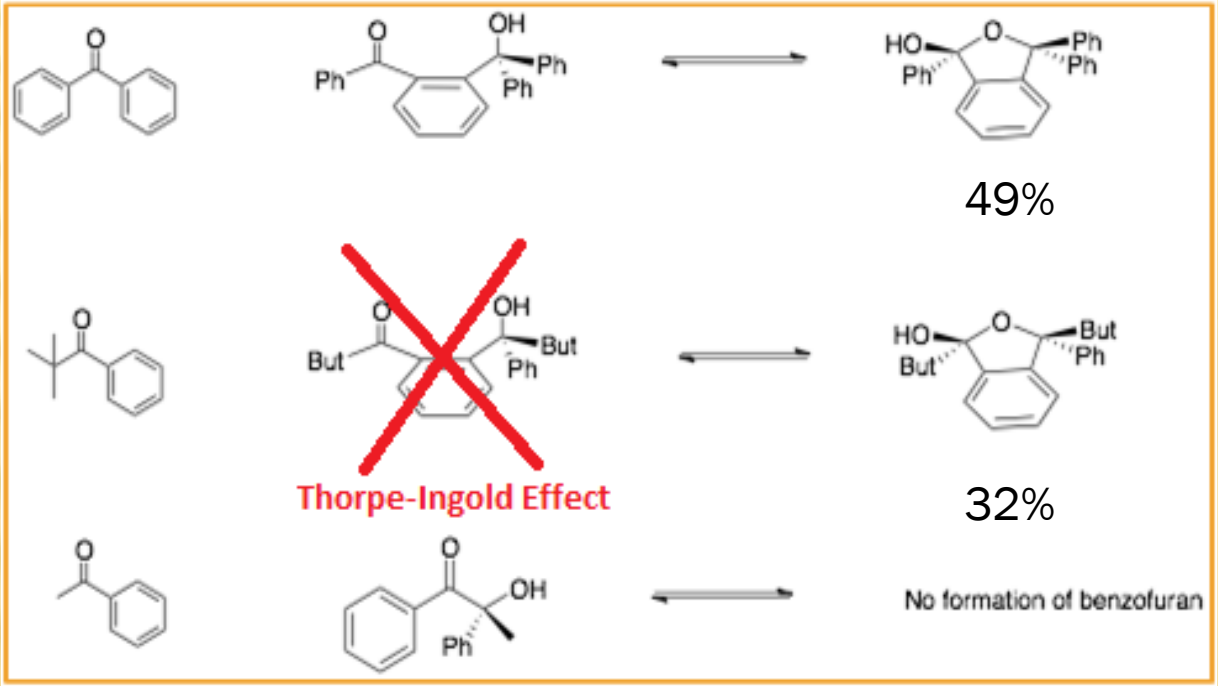


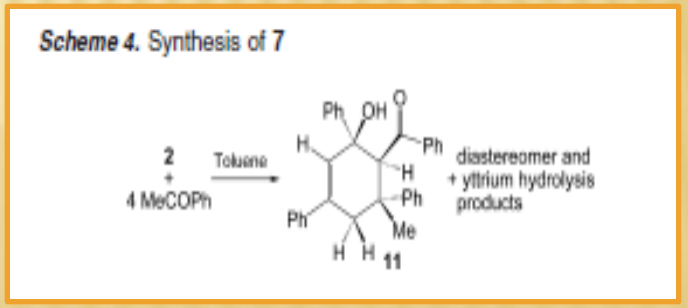
Reaction Notes

-C-H activation is rate limiting
-C-C bond formation is rapid
-Tautomerization of oxymethylbenzophenone to iso benzofuran
    -modulated by electrophilicity of yttrium (coligands)

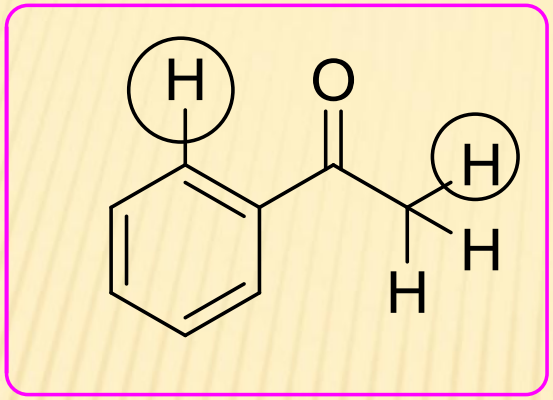
EFFECTS OF KETONE VARIATION

Ketone	Tautomeric Products



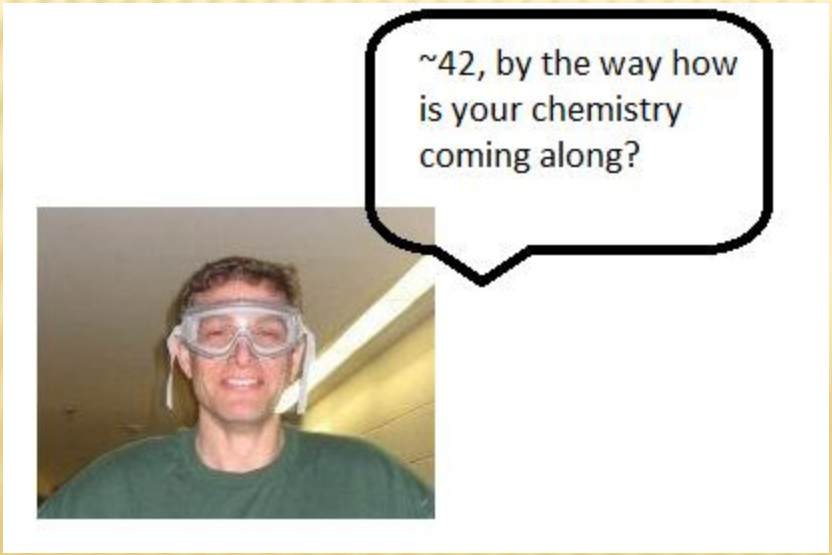


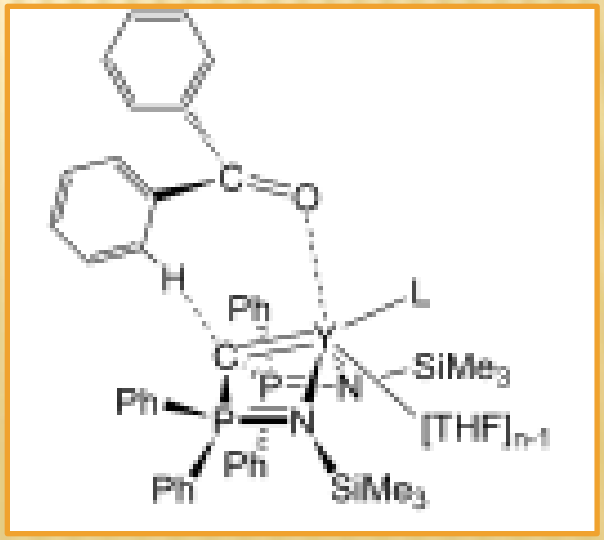
REGIOSELECTIVE ACETOPHENONE C-H ACTIVATION



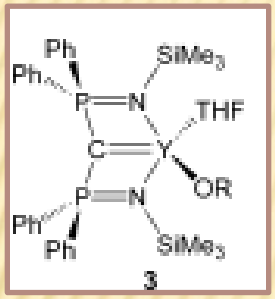
3 Factors

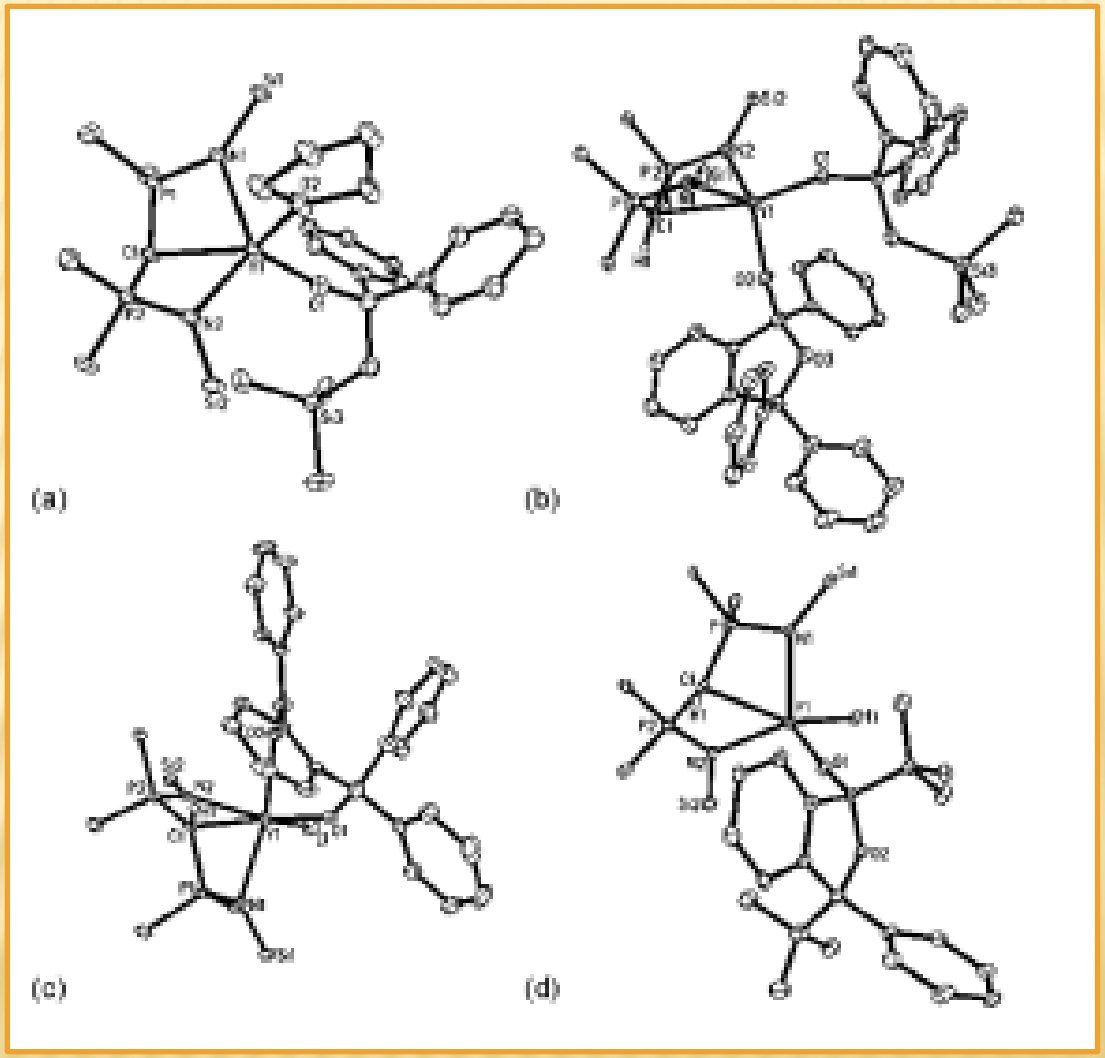
- Sterics
- Electronics
- ?

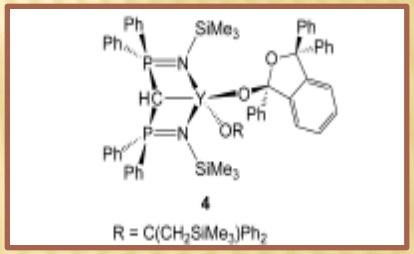


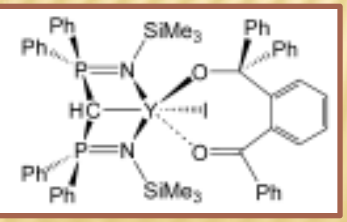


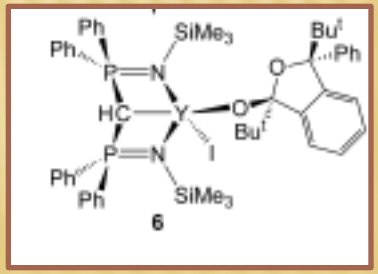
CRYSTAL STRUCTURES











CONCLUSION

- New modes of reactivity for rare earth carbenes were discovered
- This reaction is regioselective
- One pot reaction
- Strategies to make this catalytic and broaden scope of yttrium reactivity are underway

REFERENCES

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- 2. Wikipedia http://en.wikipedia.org/wiki/Yttrium
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- 4. Alberto, R et al. *Z. Anorg. Allg. Chem.* **2004,** *630,* p2709-16
- 5. Liddle, Stephen et al. *Chem. Comm.* **2008**, p1747-9.