### 1 Motivation – OH-Effects in Metathesis

In the course of a synthesis of pseudomonic acid antibiotics[1] and non-natural analogues[2] from C2-symmetric diene 3[3,4] we discovered two interesting effects of unprotected OH-groups in olefin metathesis reactions: a directing and an activating effect.[4,5] This activating effect was recently shown in Enyne-metathesis.[6,7] Here we present a very strong activating and directing effect in enyne-metathesis. There is also strong evidence for metathesis starting at the alkene instead of starting at the alkyne in combination with wide tolerance of functional groups.[8]

### 2 The Goal & the Problem (The beauty & the beast)

- Dihydropyran 1: very useful building block for ent-Pseudomonic acid A, available via RCEYM from 2?
- Ru can attack at four different positions (a-d)
- 6 different pathways
- 4 different products

#### RCEYM – OH or OPG

- 2a, free OH-group, reacts smoothly (~80% conversion)
- Ethylene atmosphere is not required (see Imahori et al.[6,7]).
- 2b shows nearly no conversion — No clean product isolated or identified.
- Adding of PhOH to 2a (extra intramolecular activation)[9]: full conversion

### 3 Towards Generalization – internal alkynes

- Isolated yield in RCEYM: 30-60%
- Spectroscopy of crude material: 80-100% clean conversion

- Formation of 6b can be controlled by choosing high dilution

### 5 The Mechanism – an assumption

- RCEYM leads to structure 1
- Strong preference for only two out of four pathways (b, d).

#### Ru can coordinate at the allylic or the propargylic OH-group

- Start of metathesis possible at the alkene or at the alkyne

#### Two unprotected OH-groups: dihydropyran 6c formed selectively

- Protection of the primary OH-group
- Full conversion after 2h reflux

#### Protection of allylic OH-group

- Uncomplete (near to zero) conversion of the starting material 8
- No product isolated or identified.

#### Free allylic OH-group (comparison 2 → 4, 8 → 9) is necessary!

- Propargylic OH-group not required
- b is the only possible way to dihydropyran-formation!

### 6 Reactions with Dihydropyrans

#### OH-directing effect: selective formation of dihydropyrans

- Broad tolerance of functional groups
- Strong preference for allylic instead of propargylic OH-groups
- OH-activating effect:
  - No use of ethylene-atmosphere required (see [6,7])
  - Ring closing proceeds most likely first-ene, then-yne mechanism

### 7 Conclusions

#### References