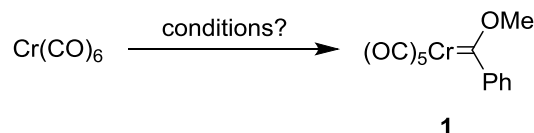
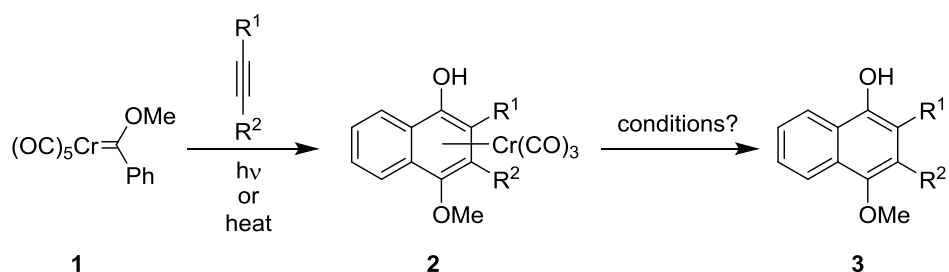


Stoichiometric, Metal-Mediated Reactions

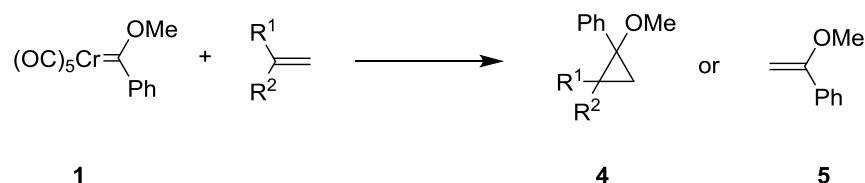
- Outline the differences between Fischer- and Schrock-type metal carbene complexes (i.e. metal alkylidenes).
- Suggest a method for the synthesis of metal carbene complex **1** from chromium hexacarbonyl:



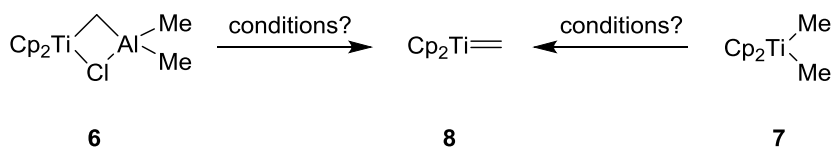
- Consider the reaction of carbene **1** with an alkyne (the Wulff-Dötz reaction; shown below). Give a mechanism for this reaction, and suggest conditions for the liberation of **3** from arylmetal species **2**. For the regioselectivity shown, would you expect R<sup>1</sup> or R<sup>2</sup> to be the largest group?



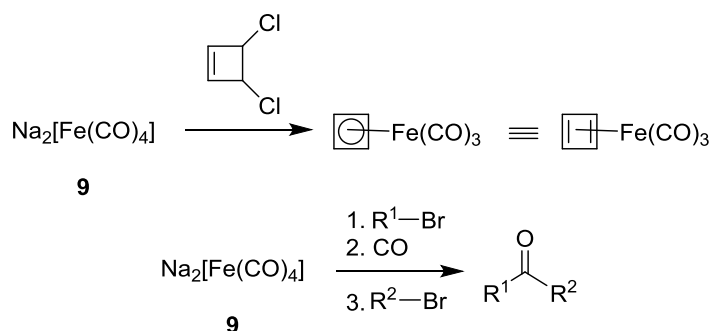
- Consider the reaction of carbene **1** with an alkene. Suggest mechanisms for the formation of products **4** and **5**.



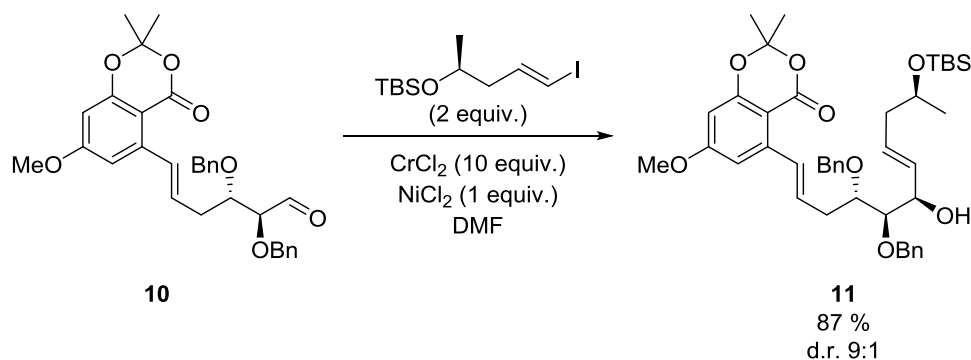
- The Tebbe and Petasis reagents, **6** and **7** respectively, must both be activated before use as methylenating agents. Suggest conditions for the conversion of each reagent to the active species **8**.



- Collman's reagent, **9**, is useful for a number of reactions involving umpolung reactivity at electrophilic carbon centres. Given this, suggest mechanisms for the following reactions:

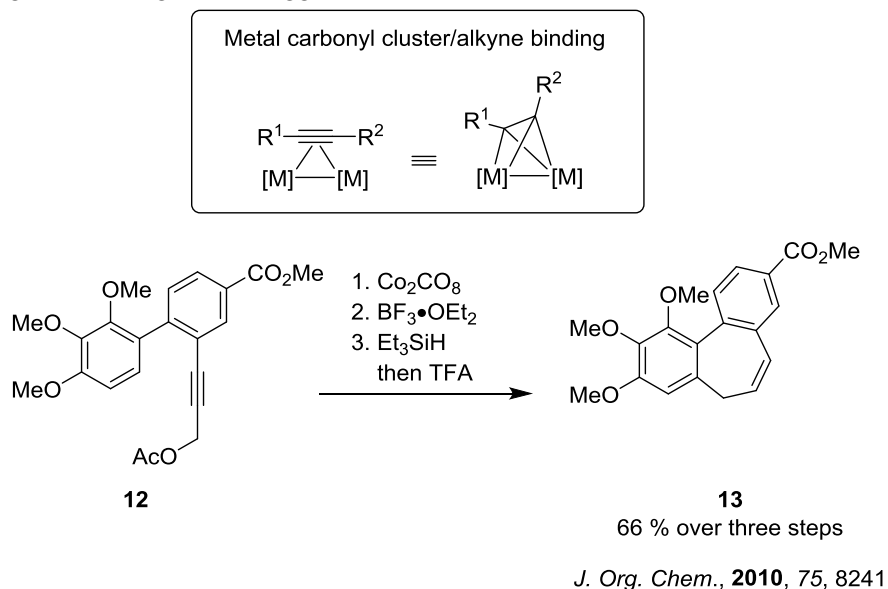


7. Consider the following Nozaki-Hiyama-Kishi reaction. Which model for nucleophilic addition to aldehydes best fits the observed stereoselectivity (e.g. Felkin-Anh, Cram-Chelation, Cornforth)? If the same transformation had been carried out using a Grignard reagent, how would the chemo- and diastereoselectivity compare?



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8. Below is shown a characteristic mode for the binding of alkynes to metal carbonyl clusters. Considering this binding mode, suggest mechanisms for the conversion of **12** to **13**.



9. Give a mechanism for the samarium (II) iodide-mediated conversion of **14** to **15**.

