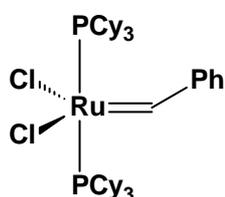


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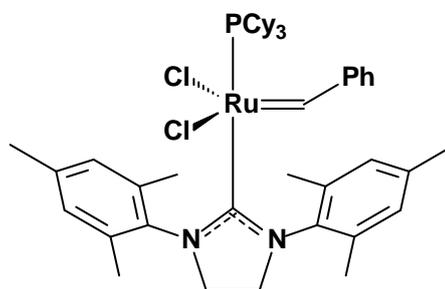
Summary

Synthesis of selected cage alkenes and their attempted ring-opening metathesis polymerisation with well-defined ruthenium catalysts

In this study a number of cage alkenes were synthesised and tested for activity towards ring-opening metathesis polymerisation (ROMP) with the commercially available catalysts **55** (Grubbs-I) and **56** (Grubbs-II).



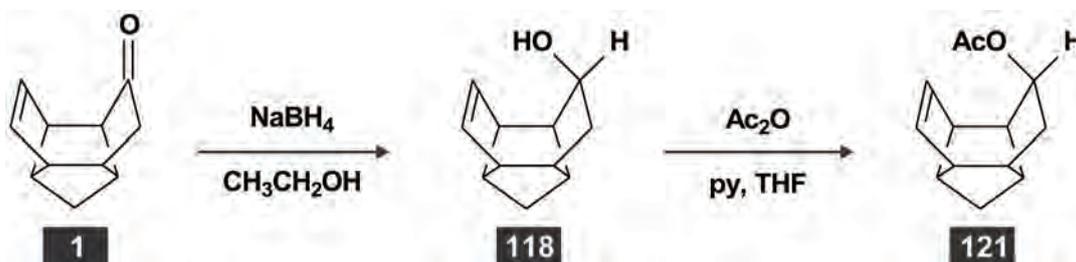
55 (Grubbs-I)



56 (Grubbs-II)

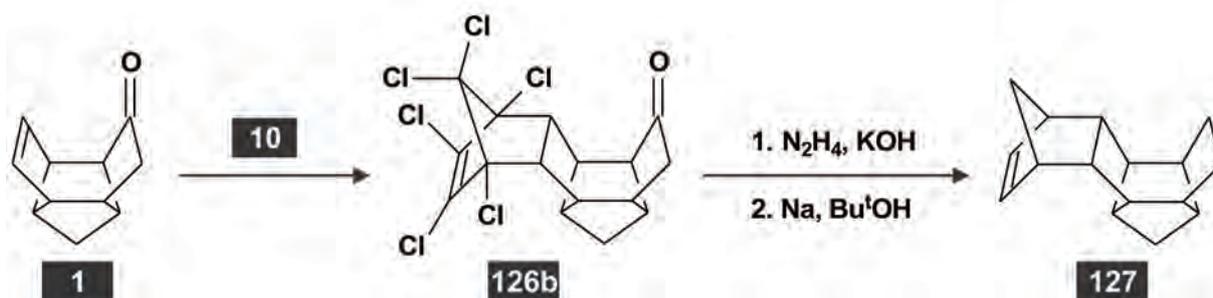
Synthesis of cage monomers

The first group of monomers are derivatives of tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undec-2-en-6-one (**1**). The synthesis of these cage alkenes are summarised in **Scheme 7.1**.



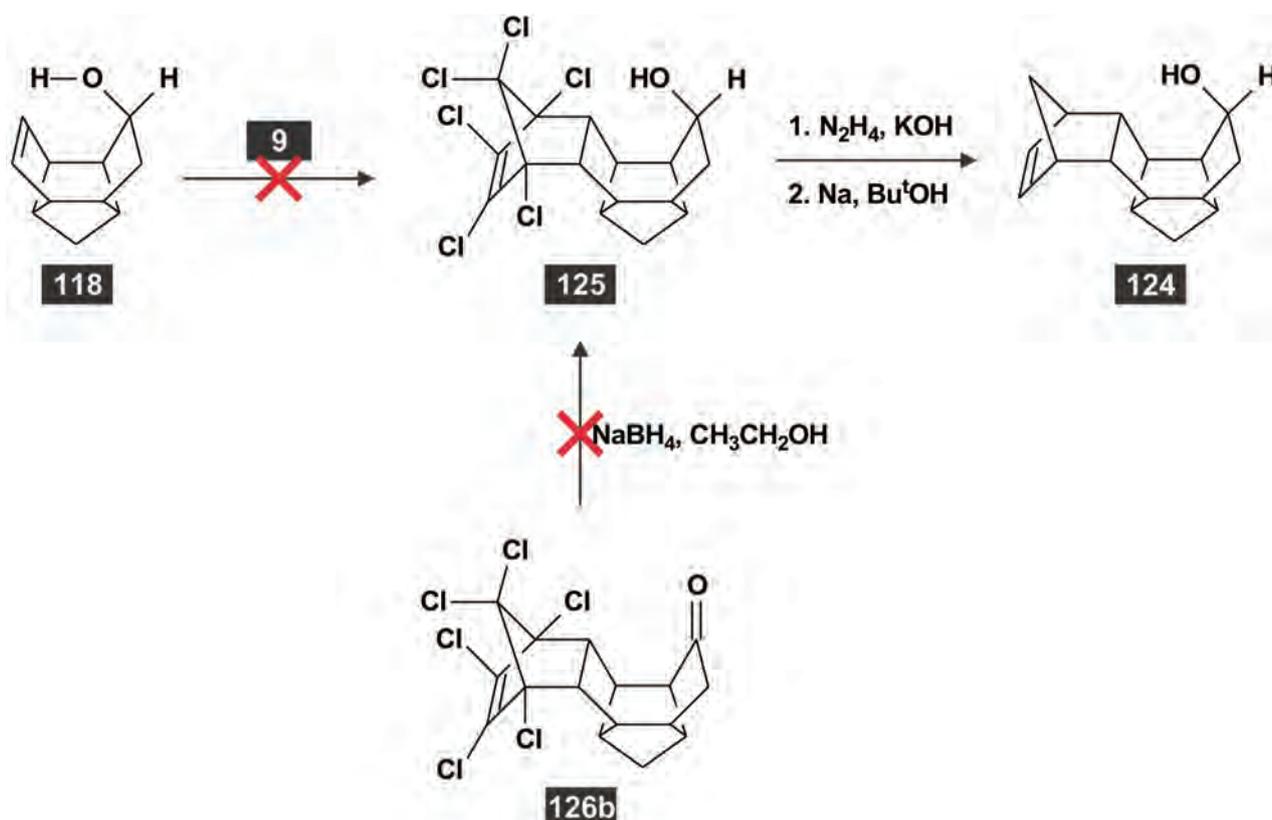
Scheme 7.1: Synthesis of derivatives of **1**.

The cage alkene **126b** was synthesised by a Diels-Alder reaction between **1** and hexachlorocyclopentadiene (**9**, **Scheme 7.2**). The geometry of **126b** was determined from XRD data. Knowledge of the geometry of **126b** also established the geometry of **127** since conformational changes during the conversion from **126b** to **127** are unlikely.



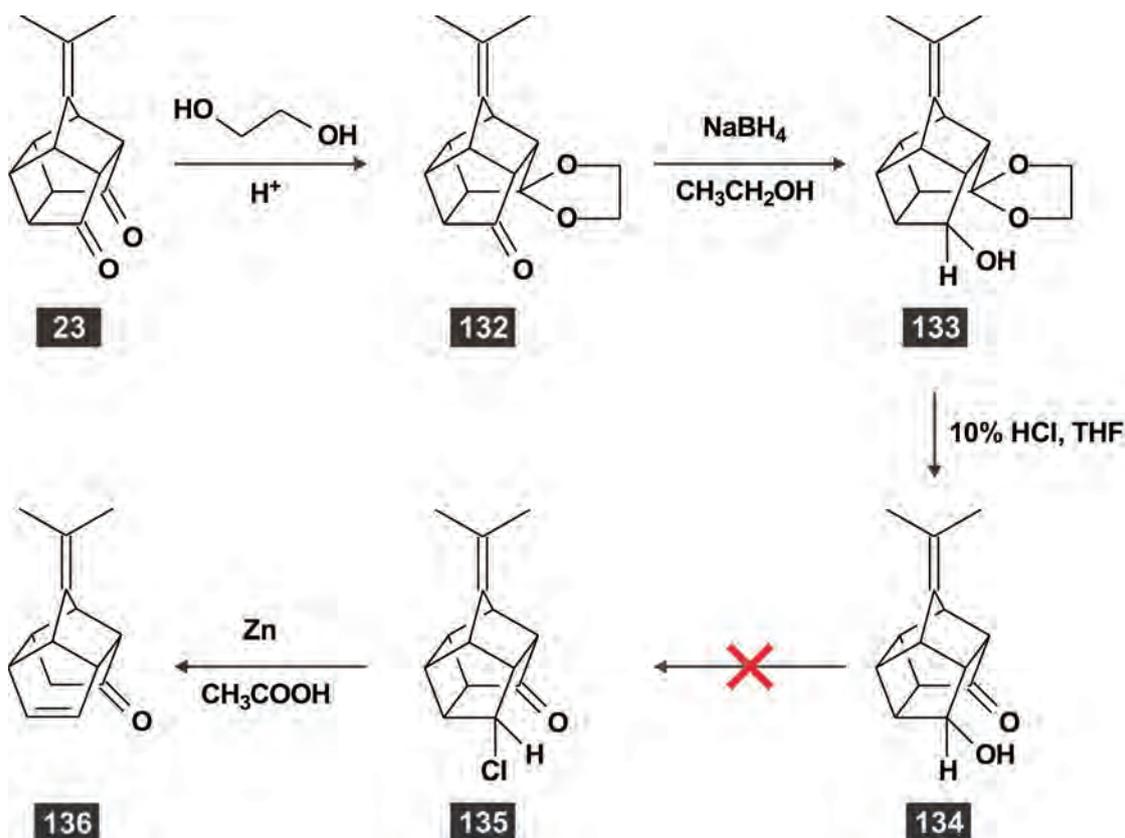
Scheme 7.2: Synthesis of hexacyclo[7.6.1.0^{3,8}.0^{2,13}.0^{10,14}]hexadec-5-ene (**127**).

Synthesis of the cage alkene **125** by the cycloaddition of **9** to **118** failed. The cage alkene *exo*-11-hydroxy-4,5,6,7,16,16-hexachlorohexacyclo[7.6.1.0^{3,8}.0^{2,13}.0^{10,14}]hexadec-5-ene (**124**, **Scheme 7.3**) could therefore not be prepared. Synthesis of **125** by reduction of **126b** with various reduction systems was not successful. Theoretical aspects of these reactions were investigated with molecular modelling. A possible explanation for the unreactive nature of **126b** towards reduction is presented, but the lack of reactivity of **118** towards **9** eluded clear explanations.



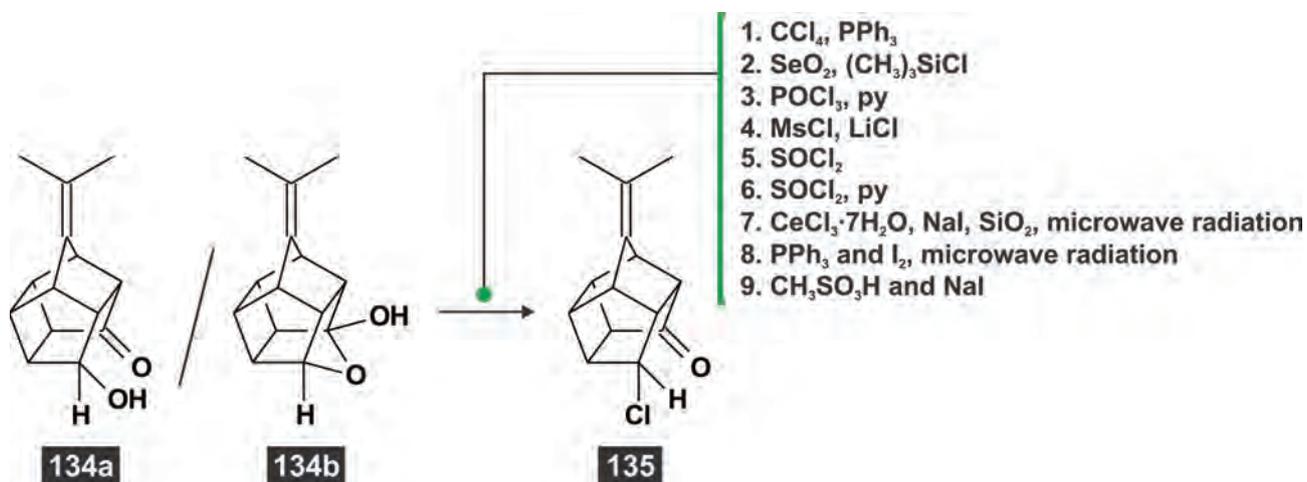
Scheme 7.3: Attempted synthesis of **125** and **124**.

The synthesis of cage alkenes from 4-isopropylidene-pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-undecane-8,11-dione (**23**) did not meet with much success (**Scheme 7.4**).



Scheme 7.4: Synthesis of 10-isopropylidene-tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undec-2-en-6-one.

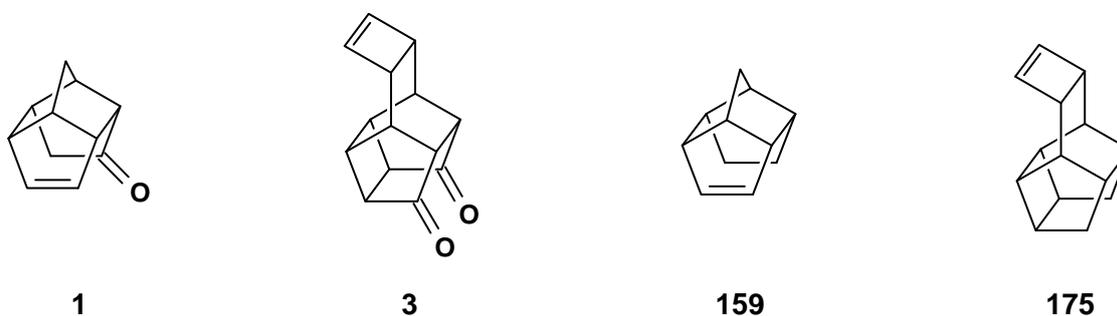
Numerous synthetic methods were investigated to affect the transformation from **134a/134b** to **135** (**Scheme 7.5**). These attempts evolved into theoretical investigations to uncover the reasons for the observed reactivity. Possible explanations were established by considering the differences and similarities between the geometries and electronic structures of reactive and unreactive cage alcohols.



Scheme 7.5: Methods used for halogenation of **134b/134a**.

ROMP of cage monomers

ROMP of cage monomers based on **1** were mostly unsuccessful. Only the cage monomer **127** showed some reactivity. Endocyclic cage monomers with a tetracycloundecane (TCU) framework showed no reactivity. The results from NMR experiments verified the experimental results. Hexacyclo[8.4.0.0^{2,9}.0^{3,13}.0^{4,7}.0^{4,12}]tetradec-5-en-11,14-dione (**3**) exhibited notable ROMP reactivity. Examination of the orbitals of the cage alkenes used in this study suggested that the reactivity of **1** and **3** could possibly be enhanced by removal of the carbonyl groups. Decarbonylation of **1** and **3** yielded the cage hydrocarbons **159** and **175**, respectively. ROMP tests revealed that **175** is an excellent monomer, but **159** was unreactive.



The results obtained for the ROMP reactions in this study was rationalised by considering aspects such as ring strain, energy profiles, steric constraints, and frontier orbital theory. The concept of ring strain is less useful when describing the reactivity of cage alkenes towards ROMP and therefore the concepts of fractional ring strain and fractional ring strain energy (RSE^f) were developed. A possible link between RSE^f and the ROMP reactivity of cage alkenes was also established. The following criteria were put forth to predict the reactivity or explain the lack of reactivity of cage alkenes towards ROMP reactions with Grubbs-I and Grubbs-II.

The criteria for ROMP of cage monomers

1. Sufficient fractional ring strain energy (RSE^f).
2. A reasonable energy profile when compared to a reference compound such as cyclopentene.
3. Ability to form a metallacyclobutane intermediate with reasonable distances between different parts of the cage fragment.
4. Sufficient ability of the polymer fragment to take on a conformation that exposes the catalytic site.
5. Sufficient size, shape, orientation and energy of HOMO and/or NHOMO at the alkene functionality of the cage monomer and of the LUMO at the catalytic site.

Keywords: Cage alkenes, cage compounds, Ring-opening metathesis polymerisation, ROMP, Ruthenium carbene catalysts, Grubbs-I, Grubbs-II