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An Anionic Dinuclear Ruthenium Dihydrogen Complex of Relevance for Alkyne *gem*-Hydrogenation

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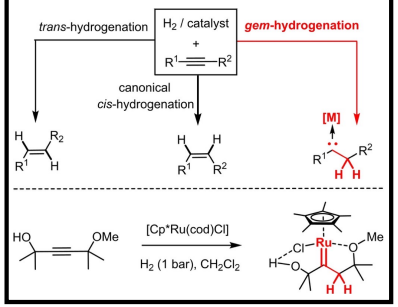
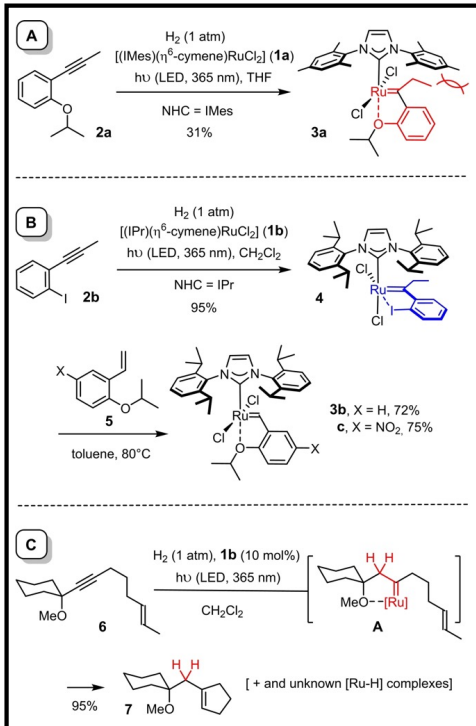
1. INTRODUCTION

Common:
cis- or *trans*-hydrogenation
Here:
gem-hydrogenation



2. THIS WORK (*gem*-hydrogenation for 2nd generation Grubbs-type cat.)



A: steric hindrance of IMes-NHC led to low yield of 2nd generation Grubbs-type **3a**

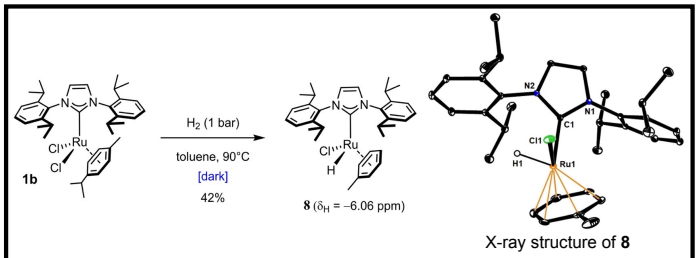
B: Indirect route using less hindered IPr-NHC for 2nd generation Grubbs-type **3b, 3c** via the metathesis with olefin **5**

C: Hydrogenative metathesis of enyne **6** to **7** catalyzed by **1b** led to unknown ruthenium hydride complexes ***worth investigating***

3. CONTROL EXPERIMENTS

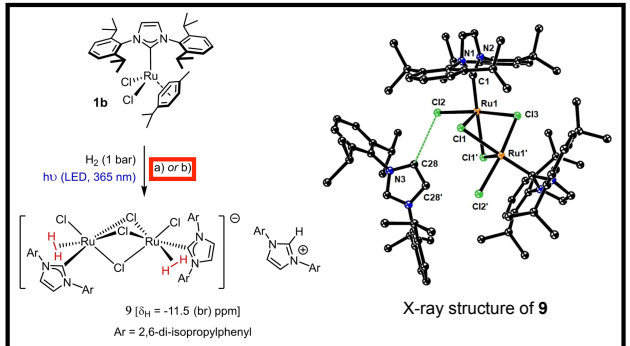
Under darkness:
generation of complex **8**

Under irradiation:
generation of bimetalic complex **9**

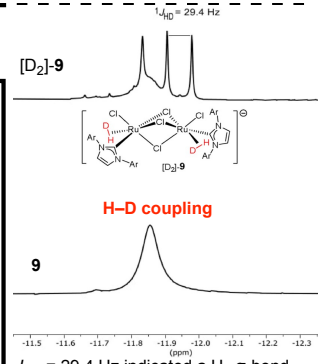


Using **8** instead of **1b** failed to transform **6** to **7** (**THIS WORK C**)

a) H_2 (1 bar), UV (365 nm, LED), toluene, RT, 22%;
b) [IPr-H]Cl (1 equiv), H_2 (1 bar), UV (365 nm, LED), toluene, RT, 73%



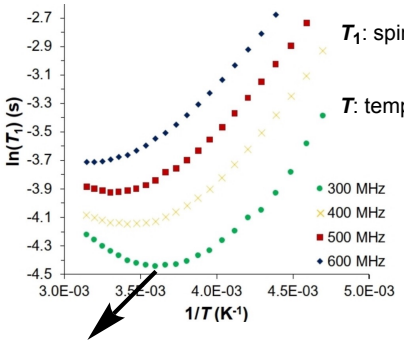
Ru: **octahetral** (H_2 coordination couldn't be confirmed by XRD)



J_{HD} = 29.4 Hz indicated a H_2 σ-bond due to Morris and Heinekey's works,[1,2] who conclude that the coupling constant is correlated with the H–H length.

4. FURTHER STUDIES (proving a H–H σ-bond in complex)

Investigation of temperature dependence of mininum spin-lattice relaxation time



T_1: spin-lattice relaxation time (ms)

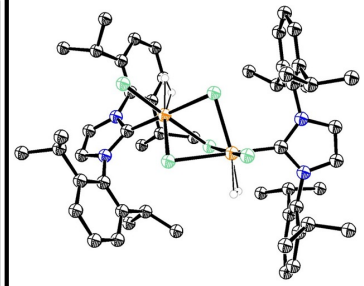
T: temperature (K)

T_1(min) = 11.8 ms (300 MHz)

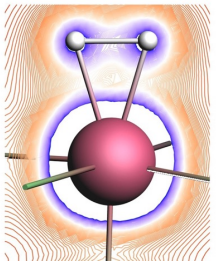
Hamilton and Crabtree's study: $d_{H-H} = 58.15 \times \sqrt[6]{\frac{T_{1,H-H}(\min)}{\nu}}$

calculation → d_{H-H} = 0.96 Å (commonly observed in H–H σ-bond)

Computational study



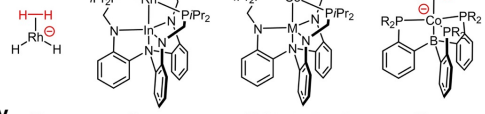
DFT calculated model perfectly matched the geometry of the solid-state of **9**



calculated electron density map also indicated a **σ-bond** of H_2, where the electron density observed in **H–H bond** rather than **Ru–H bond**

Cationic σ-complex: common
(low **e⁻ density** prevents oxidative insertion of H_2)

Anionic σ-complex: very rare examples
10: extremly unstable, observed only; **11~13**: require Lewis-acidic metalloid ligand to decrease the **e⁻ density**



This work (complex **9**) a NEW TYPE homobimetallic anionic σ-ruthenium complex

Well confrimed by various methods of σ-bond