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Synthesis of [Ru(II)(Tp)(Cl)(PPh_3)(CH_3CN)] and its reactions with selected terminal alkynes: Experimental and computational studies

Tsang-Hsiu Wang [a], Wen-Lin Huang [a], Li-Yu Huang [a], Ming-Che Li [a], Pei-I Hsiao [a], Yu-Wen Yang [a], Wei-Chen Sun [a], Yih-Hsing Lo [a,*], Chia-Her Lin [b], Hsin-Pei Chen [c]

[a] *Department of Natural Science, Taipei Municipal University of Education, Taipei, 100, Taiwan, ROC*
[b] *Instrumentation Center, College of Science, National Taiwan Normal University, Taipei, 106, Taiwan, ROC*
[c] *Department of Chemical Engineering, Tatung University, Taipei, 104, Taiwan, ROC*

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ABSTRACT

The ruthenium complex [Ru(II)(Tp)(Cl)(PPh_3)(CH_3CN)] (**3**) [Tp = hydrotris(pyrazolyl)borate] contains substitutional ligands, acetonitrile and chloride, and serves as a starting material for the synthesis of new ruthenium complexes. We found that water was also involved in reactions and formed the alkenyl ketone compound [Ru(Tp)(PPh_3)(C(CH_2Ph) = CHC(O)Ph)] (**4**) and the acyl complex [Ru(Tp)(PPh_3)(C(O)CH_2(C_6H_5)F)] (**5**). We suggest that water could be an impurity in the solvent, methanol. Methanol cannot be purified before a synthesis procedure, and water is more reactive than methanol. In order to have a better understanding on those new ruthenium complexes, the density functional theory (DFT) has been carried out at the PBE/DZVP level on the proposed mechanisms of the selected reactions. For the reactions of compound **3** with methyl propiolate or ethyl propiolate in the presence of methanol, the solvent can be the nucleophile, and a similar observation can be seen if methanol is replaced by ethanol.

Ruthenium vinylidene complexes have attracted a great deal of attention due to developing new types of organometallic intermediates [1]. Those organometallic intermediates could have various unusual reactivities [2]. In the past decades, people are interested in the chemistry of the ruthenium complexes which contain Cp ligands. We used Tp ligand instead of Cp ligand owing to its strong σ-bonding and more steric effect [3]. Herein we report the synthesis procedure of the [Ru(II)(Tp)(Cl)(PPh_3)(CH_3CN)] (**3**) and new ruthenium complexes. The proposed mechanisms for reactions of **3** with selected terminal alkynes under mild conditions are discussed. In addition, the computational method has been used to investigate the proposed mechanisms of two intermediates with methanol and water.

According to a literature procedure [4] and our own synthesis procedure, the compound **3** could be obtained. Treatment of **3** with phenylacetylene afforded the complex alkenyl ketone compound [Ru(Tp)(PPh_3)(C(CH_2Ph) = CHC(O)Ph)] (**4**) (Scheme 1). A reliable mechanism is proposed in Scheme 2. Initially, the compound **3** reacts with phenylacetylene and forms ruthenium vinylidene complex. The acetonitrile is eliminated, and another phenylacetylene coordinates to the ruthenium vinylidene complex. The phenylacetylene migrates to C_α in the ruthenium vinylidene complex. The C≡C bond reacts with C_α and forms C=C owing to electrophile of vinylidene group, and then H_2O reacts with the complex and forms an intermediate which contains a hydroxyl group. A pair of electrons on the hydroxyl group migrates to C_γ and forms a C=O bond, and H migrates insertion to C_β and forms a C–H bond. Finally, oxygen coordinates to ruthenium and forms the compound **4**.

In addition, the density functional theory [5–6] (DFT) has been used to explore the proposed mechanism. In order to reduce computational cost, Ph ligands on phosphorus were replaced by H. The calculations were done with the functional of Perdew, Burke and Ernzerhof [7–8] (PBE). The DZVP basis set [9–10] was used for all atoms. All calculations were performed by employing Gaussian 03 program [11]. The calculated potential energy surfaces of the reaction of the intermediate ([Ru](CCHPh)(CCPh)) with water and methanol are shown in Fig. 1. The intermediate reacts with H_2O and form a stable complex, and it is exothermic of 3.8 kcal/mol at 298 K. Complex formation is followed by hydrogen transfer from water to a carbon, leading to a C–H bond formation. The reaction barrier is predicted to be 41.5 kcal/mol, and the overall reaction is slightly exothermic. Thus the reaction will proceed to a reasonable extent at processing temperature. Similar observation can be seen on the intermediate reacting with methanol. From our calculation results, we suggest that water is slightly easier to react with the intermediate than methanol due to forming stable complex and more exothermic reaction energy.

Reaction of **3** with 1-ethynyl-4-flourobenzene gave the acyl complex [Ru(Tp)(PPh_3)(CH_3CN)(C(O)CH_2(C_6H_5)F)] (**5**). The proposed mechanism is shown in Scheme 3. The compound **3** reacts with 1-ethynyl-4-flourobenzene in the presence of methanol and forms

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* Corresponding author.
E-mail address: yhlo@tmue.edu.tw (Y.-H. Lo).

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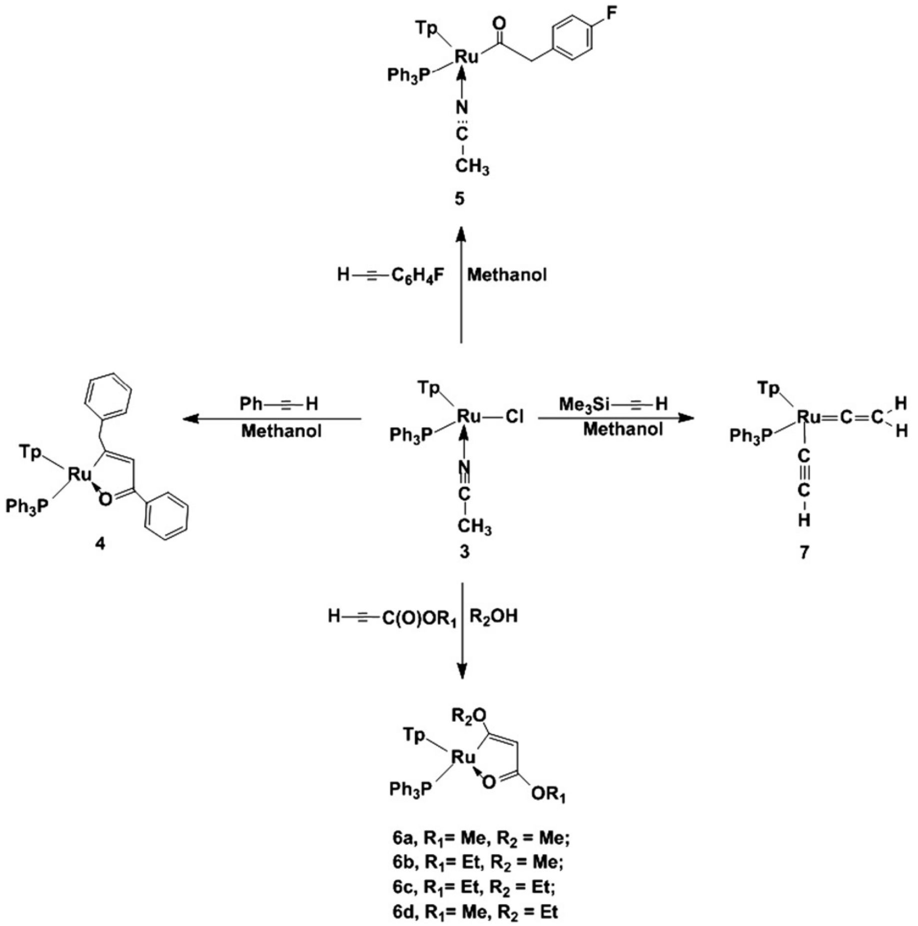
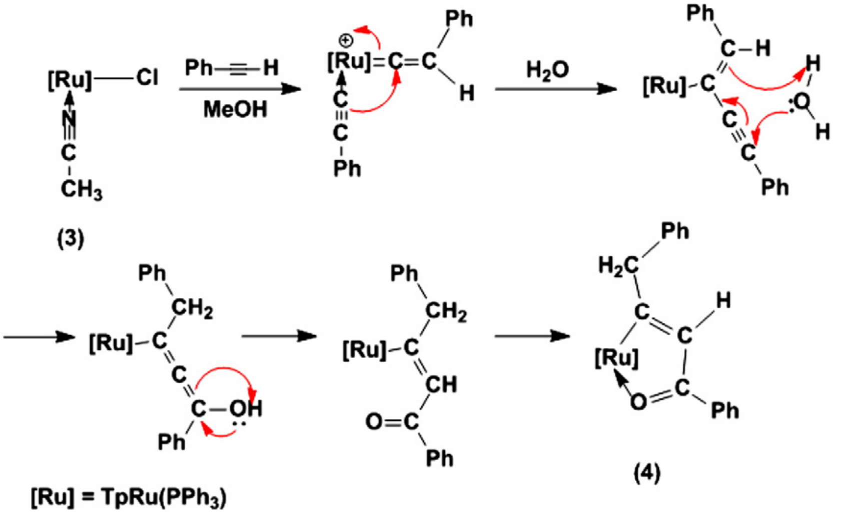


Scheme 1.

ruthenium vinylidene complex. Lone pair on H_2O reacts with C_α and forms an intermediate with a hydroxyl group. HCl is eliminated from the intermediate, and the compound **5** is formed. The calculated potential energy surfaces of the reaction of the intermediate $[Ru(Tp)(PPh_3)(CH_3CN)(=C=CH(C_6H_5)F)]Cl$ with water and methanol are shown in Fig. 2. The intermediate reacts with H_2O and forms a stable complex, and this step is exothermic by 8.0 kcal/mol at 298 K. Complex formation is followed by hydrogen transfer from water to a carbon, leading to a C–H bond formation. The reaction barrier for the H transfer from the complex is 41.0 kcal/mol. The overall reaction is exothermic of 35 kcal/mol. Similar observation can be seen on the reaction of the intermediate with methanol. Initially, the intermediate reacts with methanol and forms a stable complex. This step is exothermic by 7.6 kcal/mol at 298 K and is slightly less than the reaction of the intermediate with water by 0.4 kcal/mol. The reaction barrier for the H transfer from the complex is 37.6 kcal/mol and is slightly lower than the reaction of the intermediate with water by 3.4 kcal/mol. The overall reaction is exothermic by 30.7 kcal/mol



Scheme 2.