Comparative Study on the Reactivity of H_2, $PhCH{=}CH_2$, and $PhC{\equiv}CMe$ with $[Cp^*Ru(H_2O)(NBD)]^+$

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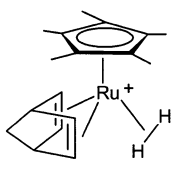
Summary: $[Cp^*Ru(H_2O)(NBD)]BF_4$ reacted with H_2 in benzene to give $[Cp^*Ru(\eta^6\text{-}C_6H_6)]BF_4$ and nortricyclene. Like the reaction of $[Cp^*Ru(H_2O)(NBD)]BF_4$ with H_2, a formal [2 + 2 + 2] homo-Diels−Alder cycloaddition of $MeC{\equiv}CPh$ to NBD occurred when $[Cp^*Ru(H_2O)(NBD)]BF_4$ was treated with $MeC{\equiv}CPh$. In contrast, an unusual coupling product, which is formed by a formal addition of a C−H bond of styrene across one of the double bonds of NBD, was produced when $[Cp^*Ru(H_2O)(NBD)]BF_4$ was treated with $CH_2{=}CHPh$.

Dihydrogen, alkenes, and alkynes are important ligands in organometallic chemistry.[1] These ligands are similar in terms of their bonding interactions with transition-metal centers.[2] Dihydrogen[3] forms metal−ligand σ bonds by donating its σ-bonding electron pair to an empty orbital of the metal and metal−ligand π-bonds by back-donation of metal dπ electrons to the σ^* orbital. Alkenes and alkynes form metal−ligand σ bonds by donating their π-bonding electron pairs to empty orbitals of the metal and metal−ligand π-bonds by back-donation of metal dπ electrons to the π^* orbitals. In this regard, it would be interesting to see if these ligands could also undergo mechanistically related organometallic reactions. Comparative study on the reactivity of dihydrogen, alkenes, and alkynes may help to develop the chemistry of σ complexes, since the well-developed chemistry of metal alkyne and olefin complexes could be applied. This communication describes the reactions of hydrogen, $PhCH{=}CH_2$, and $PhC{\equiv}CMe$ with $[Cp^*Ru(H_2O)(NBD)]^+$. It is expected that these reactions will lead to products via the intermediates **A**−**C**, respectively. Through the study, we also hope to provide further insight into the hydrogenation process via dihydrogen−olefin complexes and carbon−carbon coupling reactions through olefin and alkyne complexes. To our knowledge, this is the first example of studying the reactions of H_2, olefin, and alkyne with the same metal fragment.



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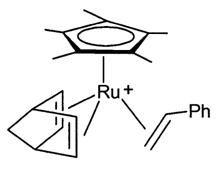

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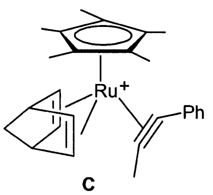
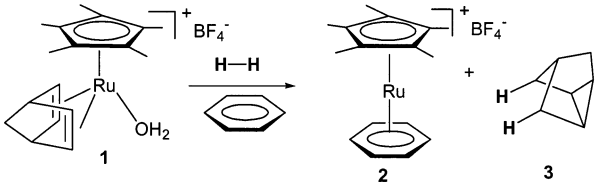


C

Exposure of a benzene solution of $[Cp^*Ru(H_2O)(NBD)]BF_4$ (**1**)[4] to H_2 for 3 h produced $[Cp^*Ru(\eta^6\text{-}C_6H_6)]BF_4$ (**2**)[5] and nortricyclene (**3**) (eq 1). Thus, a formally [2 + 2 + 2] homo-Diels−Alder cycloaddition of H_2 to NBD occurred in the reaction. Benzene was used as the solvent in order to trap the $[Cp^*Ru]^+$ fragment. As complex $[Cp^*Ru(H_2)(COD)]^+$ is known to contain a dihydrogen ligand,[6] it is reasonable to assume that reaction of $[Cp^*Ru(H_2O)(NBD)]^+$ with H_2 initially gave the dihydrogen complex $[Cp^*Ru(H_2)(NBD)]^+$ (**A**) (rather than the dihydride $[Cp^*RuH_2(NBD)]^+$), which undergoes a hydrogen transfer reaction to give **3** and the $[Cp^*Ru]^+$ fragment. Further reaction of the $[Cp^*Ru]^+$ fragment with benzene would produce complex **2**. It is noted that nortricyclene **3** is also formed in the protonation of $[Cp^*RuH(NBD)]$.[6] The closely related dihydrogen complexes *fac*-$[M(H_2)(\eta^4\text{-}NBD)(CO)_3]$ (M = Cr, Mo, W) have been characterized by IR spectroscopy and were proposed as the intermediates in photocatalytic hydrogenation of norbornadiene to nortricyclene.[7]



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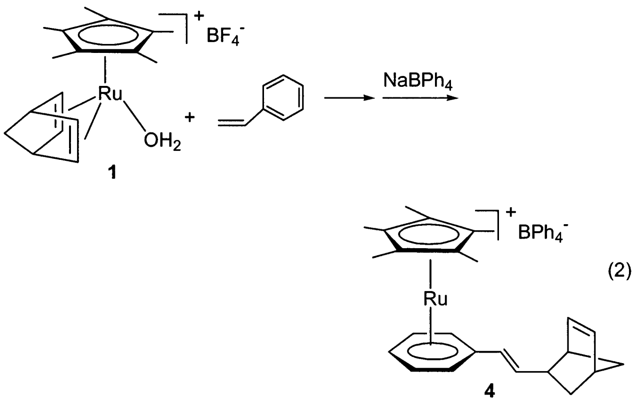
To compare the reactivity of H_2 with olefins and alkynes, the reactions of $CH_2{=}CHPh$ and $MeC{\equiv}CPh$ with $[Cp^*Ru(H_2O)(NBD)]BF_4$ (**1**) were carried out. No appreciable reactions were observed when a mixture of **1** and styrene in dichloromethane was stored at room temperature for 3 h. When the reaction mixture was stored at room temperature for 2 days, a mixture of species were produced, from which complex **4** (eq 2) was

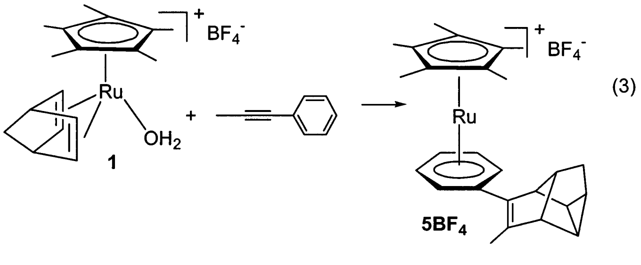


(2)

isolated after treatment of the crude product with $NaBPh_4$. Unlike the reaction of H_2, the product due to [2 + 2 + 2] homo-Diels−Alder cycloaddition of styrene to NBD was not detected in the styrene reaction.

The structure of **4** has also been confirmed by X-ray diffraction, and the molecular structure of the complex ion is shown in Figure 1. The X-ray diffraction reveals that a styrene molecule is incorporated into NBD and the aromatic ring is η^6-bonded to ruthenium. The solid-state structure is fully supported by the solution $^{13}C\{^1H\}$ and ^1H NMR and analytical data. Complex **4** can be thought as being formally formed by addition of a C−H bond of styrene across one of the double bonds of NBD. The formation of **4** is unusual, because cycloaddition products are usually obtained in metal-promoted coupling reactions of norbornadiene with olefins.[8]

Alkynes are more reactive toward **1** than styrene. In dichloromethane, **1** readily reacted with $MeC{\equiv}CPh$ to give **5BF$_4$** (eq 3). The compound has been fully charac-



(3)

terized by NMR spectroscopy and elemental analysis. The BF_4^- counteranion of **5BF$_4$** can be replaced with BPh_4^- to give **5BPh$_4$**, the structure of which has also been confirmed by X-ray diffraction. As indicated in Figure 2, a $MeC{\equiv}CPh$ molecule has added to the NBD ligand and the aryl group is η^6-coordinated to ruthenium.

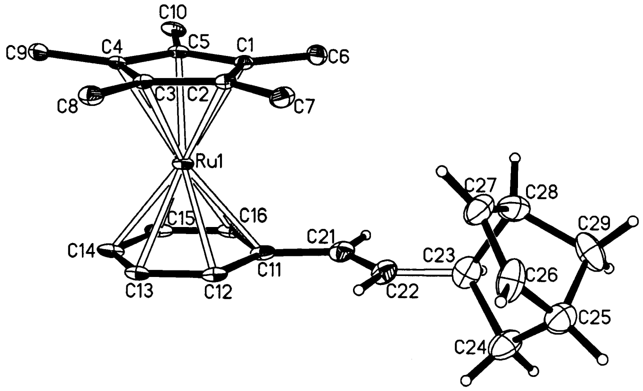


Figure 1. Molecular structure of **4**. The hydrogen atoms and counteranion are omitted for clarity.

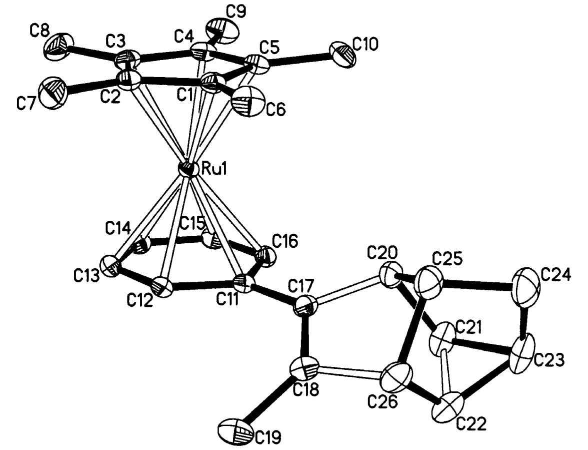


Figure 2. Molecular structure of **5BPh$_4$**. The hydrogen atoms and counteranion are omitted for clarity.

Overall, the reaction between $MeC{\equiv}CPh$ and **1** is similar to that between hydrogen and **1** in that a formal [2 + 2 + 2] homo-Diels−Alder cycloaddition of $MeC{\equiv}CPh$ to NBD also occurred. Undoubtedly, complex **5** is formed through intermediate **C**. Catalytic [2 + 2 + 2] homo-Diels−Alder cycloadditions of $RC{\equiv}CR'$ to NBD have been achieved with complexes such as $[Ni(COD)_2]/PR_3$ and $[Co(acac)_3]/PR_3/Et_2AlCl$.[8] Homo-Diels−Alder cycloadditions of $RC{\equiv}CR'$ to COD could also be effected by ruthenium complexes such as $[(\eta^5\text{-}C_9H_7)RuCl(COD)]$ and $[CpRuCl(COD)]$.[9] Interestingly, $[Cp^*RuCl(COD)]$ catalyzed [2 + 2] cycloadditions of alkynes to NBD.[10]

It is noted that both H_2 and $MeC{\equiv}CPh$ readily undergo formally [2 + 2 + 2] cycloaddition reactions with the NBD ligand of **1**. However, styrene is much less reactive toward **1** and does not react in a similar manner. To have a better understanding of the reactions, a B3LYP computational study was carried out.

Preliminary quantum-chemical calculations show that the reactions of H_2 and alkynes with NBD in the model complexes $[CpRu(H_2)(NBD)]^+$ and $[CpRu(HC{\equiv}CH)(NBD)]^+$, respectively, proceed through a stepwise mechanism. For comparison, the corresponding reaction of olefin has also been calculated for the $[CpRu(H_2C{=}CH_2)(NBD)]^+$ model complex (see Figure 3). In Figure 3, **PC** stands for the precursor model complex and **PR** is the structure that can lead to the product after a reductive elimination step.

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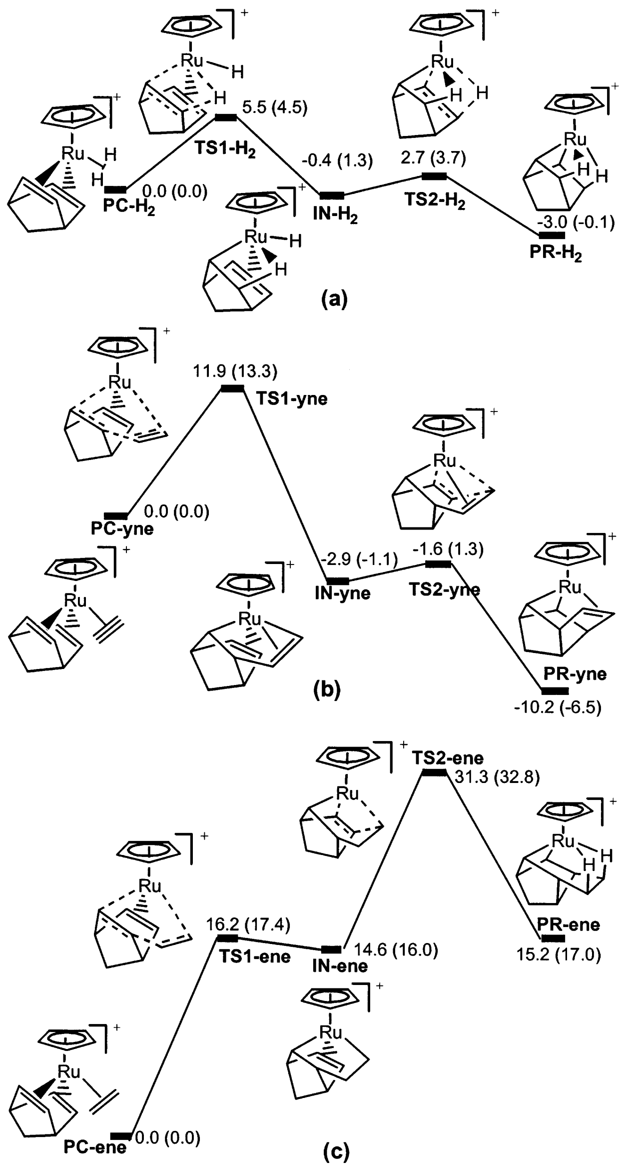

Figure 3. Schematic illustration of the stepwise reaction pathways for $[CpRu(H_2)(NBD)]^+$ (a), $[CpRu(C_2H_2)(NBD)]^+$ (b), and $[CpRu(C_2H_4)(NBD)]^+$ (c) together with calculated relative energies (kcal/mol) and free energies (kcal/mol, in parentheses) for species involved in the reactions.

The energy profiles of Figure 3 show that the reactions of H_2 and HC≡CH with NBD are energetically very favorable and that the corresponding reaction of $H_2C{=}CH_2$ has substantially high reaction barriers. These results explain the experimental observation that a [2 + 2 + 2] cycloaddition occurs easily for the reactions of H_2 and MeC≡CPh with NBD in complex **1** while styrene reacts slowly with NBD and the reaction does not give a similar [2 + 2 + 2] cycloaddition product.

In the reaction of H_2, the first hydrogen transfer leads to the formation of a hydride intermediate (**IN-H$_2$**) containing an agostic interaction. In the reaction of HC≡CH, the intermediate formed after the first C−C bond formation corresponds to an η^2-alkenyl structure (**IN-yne**) which is more stable than the parent model complex. However, the corresponding intermediate (**IN-ene**) formed from the reaction of $H_2C{=}CH_2$ is found to be significantly unstable. The stabilities of **IN-H$_2$** and **IN-yne** are apparently related to the additional agostic bond and metal−π interaction in the Ru−η^2-alkenyl unit, respectively. In **IN-ene**, no agostic interaction is possible because of the five-membered-ring structural arrangement. In addition, **IN-ene** shows greater H- - -H repulsions because two hydrogens originally from $H_2C{=}CH_2$ are oriented in a way that creates significant repulsion with the hydrogens on the Cp ring.

The low barriers for **TS1-H$_2$** and **TS1-yne** can be related to the spherical property of hydrogen's 1s orbital and the extra $\pi_\perp$ bonding orbital of alkyne. The spherical property of hydrogen's 1s orbital increases the tendency of its orbital overlap with the receiving carbon.[11] The extra $\pi_\perp$ bonding orbital of alkyne is oriented in such a way that it is ready to interact with the orbitals from the receiving carbon. When **TS2** species are considered, very small barriers are calculated for the reactions of the H_2 and HC≡CH cases. For the H_2 case, the easy C−H bond formation is again due to hydrogen's spherical s-type orbital. The calculated structure of **IN-yne** shows that the α-carbon of the η^2-alkenyl unit has a pyramidal geometry. The orientation of the hydrogen associated with the α-carbon indicates that the Ru−C σ bond bends toward the adjacent olefinic carbon. Apparently, the bending of the Ru−C σ bond facilitates orbital overlap between the α-carbon and the adjacent olefinic carbon and thus favors the C−C formation and lowers the reaction barrier from **IN-yne** to **PR-yne**. **IN-ene** does not have the extra $\pi_\perp$ orbital, and therefore the corresponding pathway has much higher barriers. **PR-yne** is also relatively quite stable when compared to **PR-ene**. The metal−π interaction in **PR-yne** contributes significantly to the stability.

In summary, we have demonstrated that reactions of $[Cp^*Ru(H_2O)(NBD)]^+$ with H_2 and MeC≡CPh lead to formal [2 + 2 + 2] cycloaddition between the substrates and the coordinated NBD, while a similar reaction is not observed for the reaction with styrene. Theoretical calculations support the proposal that $[Cp^*Ru(substrate)(NBD)]^+$ is the active species in the observed reactions. The similarity of the alkyne reaction to the H_2 one has been attributed to the extra $\pi_\perp$ bond of alkynes. The extra $\pi_\perp$ bond has been found to play a key role in stabilizing the relevant reaction intermediate as well as lowering the reaction barriers. In the olefin reaction, the absence of the extra $\pi_\perp$ bond leads to the instability of the corresponding intermediate as well as the high reaction barriers. We are now continuing our effort in comparatively studying the reactivity of σ-bonding electron pair donors (e.g. η^2-H_2, η^2-H−Si, η^2-H−B) and π-bonding electron pair donors (e.g. alkynes and olefins), both experimentally and theoretically.

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Supporting Information Available: Spectroscopic data, experimental, computational, and crystallographic details, and tables of bond distances and angles, atomic coordinates and equivalent isotropic displacement coefficients, and anisotropic displacement coefficients for **4** and **5BPh$_4$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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