Dihydrogen Complex Formation and C−C Bond Cleavage from Protonation of Cp*RuH(diene) Complexes

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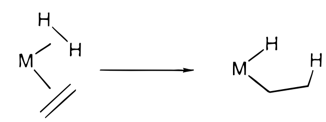
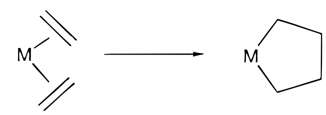
*Summary: Reaction of Cp*RuH(COD) with $HBF_4 \cdot OEt_2$ at −76 °C produced $[Cp^*Ru(H_2)(COD)]BF_4$, which transformed to $[Cp^*Ru(\eta^6\text{-}1,3,5\text{-}COT)]BF_4$ on warming to room temperature. Reaction of Cp*RuH(NBD) with $HBF_4 \cdot OEt_2$ produced a mixture of nortricyclene and the novel bimetallic complex $[(Cp^*Ru)_2(\mu\text{-}H)(\mu\text{-}C_5H_5{-}CH{=}CH_2)]BF_4$.*

Since the first report of dihydrogen complexes by Kubas et al. in 1984,[1] this unique class of complexes have been intensively investigated, especially their preparation, characterization, and structural and catalytic properties.[2] A relatively less explored aspect of the chemistry of dihydrogen complexes is their reactivities toward organic ligands (e.g., alkyls, vinylidenes, olefins, and acetylenes), although such a study should help to clarify the mechanisms of reactions mediated by dihydrogen complexes and to further develop new catalytic reactions based on dihydrogen complexes. Previous studies have shown that a coordinated dihydrogen ligand in $L_nM(H_2)R$ could transfer one of the protons of the dihydrogen ligand to the α-carbons of alkyl or vinyl ligands R to form L_nMH and RH. Such a reactivity has been invoked to explain the catalytic activity of $[FeH(H_2)(PP_3)]^+$ ($PP_3 = P(CH_2CH_2PPh_2)_3$)[3] and $RuHCl(PPh_3)_3$[4] for hydrogenation of acetylenes and olefins and to account for the reactions of some d^0 alkyl complexes with H_2 to give hydride complexes and alkanes.[5] Proton transfer from coordinated H_2 to the α-carbon of the acetylide ligand in $[Ru(H_2)(C{\equiv}CPh)(dippe)_2]^+$ (dippe = $(i\text{-}Pr)_2PCH_2CH_2P(i\text{-}Pr)_2$) has been observed.[6] Proton transfer from H_2 to β-carbons of vinylidene ligands has been proposed for the reaction of $OsH_2Cl_2(P(i\text{-}Pr)_3)_2$ with HC≡CR to give the carbyne complexes $OsHCl_2({\equiv}C\text{-}CH_2R)(P(i\text{-}Pr)_3)_2$ via the intermediates $OsCl_2(H_2)(C{=}CHR)(P(i\text{-}Pr)_3)_2$.[7]

In principle, a coordinated dihydrogen ligand may also undergo oxidative coupling reactions with unsaturated substrates such as olefins and acetylenes as illustrated in eq 1. The reaction is analogous to the well-known



(1)



(2)

oxidative coupling reactions of coordinated olefins and acetylenes as illustrated in eq 2.[8] Although interesting, examples of reactions shown in eq 1 or even olefin dihydrogen complexes are still very rare. The complexes $M(H_2)(NBD)(CO)_3$ (M = Cr, Mo, and W) and $M(H_2)(NBD)(CO)_4$ (M = Mo and W), which have been detected by IR spectroscopy, have been proposed as the intermediates for photocatalytic hydrogenation of norbornadiene using $M(CO)_6$.[9] Olefin dihydrogen complexes have also been proposed (but not detected) as the intermediates in the catalytic hydrogenation of olefins using $[TpRu(PPh_3)_x(CH_3CN)_{3-x}]^+$ (Tp = hydrotris(pyrazolyl)borate, $x = 1, 2$).[10] To model the reactions shown in eq 1, we have investigated the protonation reaction of L_nMH(olefin) complexes, with the hope of detecting the olefin dihydrogen complexes $[L_nM(H_2)(olefin)]^+$ or of observing the subsequent proton-transfer reactions between coordinated dihydrogen and olefin ligands. In this paper we wish to report the protonation reactions of Cp*RuH(diene) (diene = COD, NBD).

As many complexes of the type $[(\eta^5\text{-}C_5R_5)RuH_2(L)(L')]^{+}$[11−14] are known to contain a dihydrogen ligand, especially when L or L′ is a π-accepting ligand such as CO or CNR, it is expected that protonation of Cp*RuH(COD) and Cp*RuH(NBD) might lead to dihydrogen complexes $[Cp^*Ru(H_2)(COD)]^+$ and $[Cp^*Ru(H_2)(NBD)]^+$, respectively. Reaction of Cp*RuH(COD)[15] (**1**) in CD_2-

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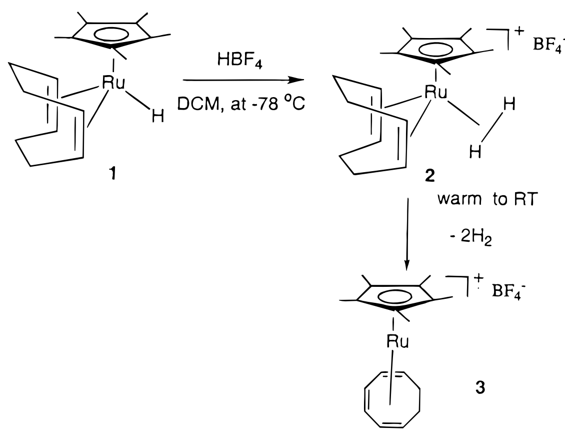
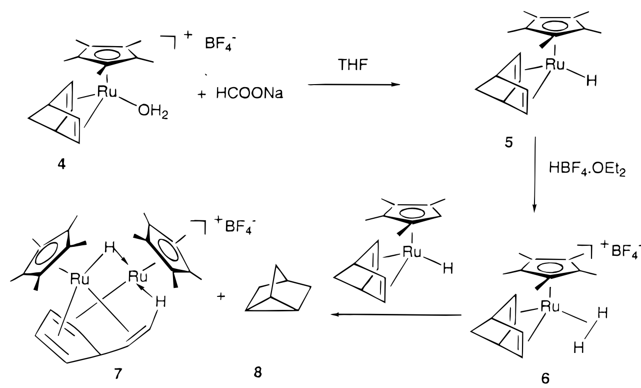
Scheme 1



Scheme 2



Cl_2 with $HBF_4{\cdot}OEt_2$ at −76 °C indeed produced [Cp*Ru(H_2)(COD)]BF_4 (**2**)[16] (Scheme 1). In the ^{1}H NMR spectrum at 200 K, the signal assignable to Ru(H_2) was observed as a broad singlet at δ −4.81 ppm, which has a T_1 value of 12 ms at 200 K and 9.9 ms at 180 K (on 300.13 MHz). The short T_1 values for the hydride signal are a good indication of the presence of the dihydrogen ligand in **2**. In support of the dihydrogen formation, a ^1J(HD) value of 29.3 Hz was observed for the isotopomer [Cp*Ru(η^2-HD)(COD)]BF_4, which was synthesized by protonation of Cp*RuH(COD) with DBF_4. The presence of the COD ligand in **2** is clearly indicated by the ^{1}H and ^{13}C NMR spectra. The dihydrogen complex **2** represents a very rare example of dihydrogen complexes with only hydrocarbon ligands. Previously reported dihydrogen complexes usually contained auxiliary ligands such as phosphines, CO, CNR, hydrides, and halides.[2]

The dihydrogen complex [Cp*Ru(H_2)(COD)]BF_4 is only stable at low temperature. Warming a solution of **2** in CD_2Cl_2 to room temperature led to the formation of the dehydrogenated complex [Cp*Ru(η^6-1,3,5-COT)]-BF_4 (**3**). No hydrogenated COD products could be detected by NMR spectroscopy. Complex **3**, which could also be synthesized by treatment of Cp*RuCl(COD) with $AgBF_4$ in ethanol, has ^{1}H and ^{13}C NMR data very similar to those of the known compound [Cp*Ru((η^6-1,3,5-COT)]Cl, which was prepared by the reaction of $[Cp{*}RuCl_2]_x$ with 1,3-COD in ethanol in the presence of Zn.[17]

The previously unknown complex Cp*RuH(NBD) (**5**)[18] was prepared by the reaction of [Cp*Ru(OH_2)(NBD)]BF_4 (**4**)[19] with sodium formate in THF (Scheme 2). In this reaction, the hydride complex **5** was presumably formed via extrusion of CO_2 from the formate intermediate Cp*Ru(O_2CH)(NBD).[20] Protonation of Cp*RuH(NBD) in dichloromethane with $HBF_4{\cdot}OEt_2$ produced a 1:1 mixture of nortricyclene (**8**) and the novel bimetallic complex **7**, in which the two ruthenium centers are bridged by vinylcyclopentadiene formed by skeletal rearrangement of NBD involving C−C/C−H bond cleavage reactions. The expected dihydrogen complex [Cp*Ru(H_2)(NBD)]BF_4 (**6**), which could be the intermediate for the formation of **7** and **8**, was not detectable by NMR even though the reaction was carried out at −76 °C.

The nortricyclene produced in this reaction has been isolated and characterized by ^{1}H and ^{13}C NMR spectroscopy.[21] The structure of the bimetallic complex **7** was deduced from its ^{1}H, ^{13}C NMR (including ^{1}H−^{1}H, ^{1}H−^{13}C COSY experiments), and MS spectroscopic data and elemental analysis.[22] The bimetallic nature of the compound is indicated by elemental analysis and the FAB MS, which showed the molecular ion peak at *m/z* 565, corresponding to $(Cp{*}Ru)_2C_7H_9^+$. Consistent with the proposed structure, the ^{1}H NMR spectrum displayed two Cp* signals at 1.81 and 1.87 ppm, the bridging

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(16) The complex [Cp*Ru(H_2)(COD)]BF_4 was prepared as follows. $HBF_4{\cdot}Et_2O$ was added through a microsyringe to an NMR tube charged with Cp*RuH(COD) and CD_2Cl_2 precooled at −76 °C. The ^{1}H and ^{13}C NMR spectra were collected immediately at 200 K. Selected characterization data for the dihydrogen complex are as follows. ^{1}H NMR (CD_2Cl_2, 300.13 MHz, 200 K): δ −4.81 (br, 2 H, Ru(H_2)), 1.80 (s, 15 H, CH_3), 2.0−2.3 (m, 8 H, CH_2), 4.08 (m, 2 H, CH), 4.40 (m, 2 H, CH). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz, 200 K): δ 10.1 (s, C_5Me_5), 29.1 (s, CH_2), 29.4 (s, CH_2), 79.4 (s, CH), 88.4 (s, CH), 97.1 (s, C_5Me$_5$). [Cp*Ru-(HD)(COD)]BF_4 was prepared similarly except that DBF_4 was used instead of $HBF_4{\cdot}Et_2O$. The DBF_4 was prepared in situ by mixing $HBF_4{\cdot}Et_2O$ and D_2O in a ratio of 1:3 in volume. ^{1}H NMR (CD_2Cl_2): δ −4.80 (t, 1:1:1, J(HD) = 29.3 Hz, Ru(HD)).

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(18) The complex Cp*RuH(NBD) was prepared as follows. A mixture of [Cp*Ru(H_2O)(NBD)]BF_4 (0.62 g, 1.4 mmol) and HCOONa (0.40 g, 5.9 mmol) in 40 mL of THF was stirred at room temperature for 2 h to give a yellow solution. The solvent was then removed under vacuum. The residue was extracted with 20 mL of diethyl ether. Removal of the ether under vacuum produced a yellow powder. Yield: 0.40 g, 86%. Selected characterization data are as follows. ^{1}H NMR (C_6D_6, 300.13 MHz): δ −4.84 (s, 1 H, RuH), 1.24 (t, J(HH) = 1.50 Hz, 2 H, CH_2), 1.99 (s, 15 H, CH_3), 2.38 (t, J(HH) = 4.2 Hz, 2 H, =CH), 3.47 (m, 1 H, CH), 3.58 (t, J(HH) = 4.2 Hz, 2 H, =CH), 3.91 (m, 1 H, CH). ^{13}C {^{1}H} NMR (C_6D_6, 75.5 MHz): δ 12.0 (s, C_5Me_5), 32.1 (s), 42.3 (s), 47.1(s), 51.1(s), 56.7 (s), 92.9 (s, C_5Me$_5$). Anal. Calcd for $C_{17}H_{24}$Ru: C, 61.98; H, 7.34. Found: C, 61.89; H, 6.49.

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(21) ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ 1.09 (br s, 3 H), 1.28 (br d, J(HH) = 1.4 Hz, 6 H), 2.01 (m, 1 H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 9.4 (s), 29.2 (s), 32.6 (s). The ^{13}C NMR data are similar to those reported in the literature. See: Fresenius, W.; Huber, J. F. K.; Pungor, E.; Rechnitz, G. A.; Simon, W.; West, T. S. In *Tables of Structural Data for Structure Determination of Organic Compounds*, 2nd ed.; Springer-Verlag: Berlin, 1989; p C75.

hydride signal at −14.24 ppm (d, J(HH) = 2.4 Hz), the agostic proton signal at −9.16 ppm (td, J(HH) = 5.4, 2.4 Hz), the sp^3 methine CH signal at 3.49 ppm, and six additional signals assignable to the protons of the coordinated olefins in the region 2.08−3.91 ppm. The coupling constants among the CHH(agostic) protons and the bridging hydride for **7** are close to those observed for Cp*Ru(μ-H)(μ-η^3,η^1-*i*-PrNCC(Me)=CHH(agostic))-RuCp* reported by Caulton et al.[23] The presence of the bridging vinylcyclopentadiene ligand is further evidenced by the appearance of seven carbon signals in the region 9.8−76.3 ppm in the ^{13}C NMR spectrum. The framework of the vinylcyclopentadiene ligand in complex **7** is fully supported by the ^{1}H−^{1}H and ^{1}H−^{13}C COSY spectra.

The nortricyclene and the bimetallic complex **7** are likely formed via the dihydrogen complex [Cp*Ru(H_2)-(NBD)]$^+$ (**6**), although the latter complex was not detected in the NMR experiments. Intramolecular transfer of H_2 to NBD in [Cp*Ru(H_2)(NBD)]$^+$ would lead to the formation of nortricyclene (**8**). Transferring proton(s) from H_2 to NBD in **6** would generate coordinatively unsaturated ruthenium species, which could attack Cp*RuH(NBD) to cause the skeletal rearrangement of NBD to give the bimetallic complex **7**. Skeletal rearrangements of NBD or norbornenyl ligands on coordinated unsaturated metal centers to form organic ligands with a five-membered ring are known, for example, in the reaction of Cp*RuCl(NBD) with $AgBF_4$ to give Cp*Ru(η^6-C_5H_4=$CHCH_3$)]BF_4[19] and in the reaction of CpCo(NBD) with HBF_4 to form [CpCo(C_5H_6−CH=CH_2)]BF_4.[24] Initial formation of the dihydrogen intermediate [Cp*Ru(H_2)(NBD)]$^+$ is reasonable especially in view of the fact that the analogous dihydrogen complex [Cp*Ru(H_2)(COD)]$^+$ has been observed from the protonation reaction of Cp*RuH(COD). Intramolecular transfer of H_2 to NBD has been proposed for the photocatalytic hydrogenation of NBD to give nortricyclene with $Mo(CO)_6$.[9] Consistent with the involvement of the [Cp*Ru(H_2)(NBD)]$^+$ intermediate in the formation of nortricyclene, it was demonstrated by NMR experiments that [Cp*Ru(H_2O)(NBD)]$^+$ also reacted with pressurized H_2 gas (50 bar) to give nortricyclene. In addition, [Cp*Ru(H_2O)(NBD)]$^+$ was observed when Cp*RuH(NBD) was protonated with aqueous HBF_4.

In summary, reaction of Cp*RuH(COD) with HBF_4·OEt_2 at −76 °C produced [Cp*Ru(H_2)(COD)]BF_4, a very rare example of dihydrogen complexes with only hydrocarbon ligands. In contrast, reaction of Cp*RuH(NBD) with HBF_4·OEt_2 produced a mixture of nortricyclene and the novel bimetallic complex [(Cp*Ru)$_2$(μ-H)(μ-C_5H_5−CH=CH_2)]BF_4, which are likely formed via the intermediate [Cp*Ru(H_2)(NBD)]BF_4. We are in the process of investigating the detailed mechanism for the latter reaction and studying the protonation reactions of other olefin hydride complexes with the aims of preparing olefin dihydrogen complexes [L_nM(H_2)(olefin)]$^+$ and observing proton-transfer reactions between coordinated dihydrogen and olefin ligands.

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(22) Selected characterization data for **7**. ^{1}H NMR (CD_2Cl_2, 300.13 MHz): δ −14.24 (d, J(HH) = 2.4 Hz, Ru(μ-H)Ru), −9.16 (td, J(HH) = 5.4, 2.4 Hz, CH*H*(agostic)), 2.08 (t, J(HH) = 5.4 Hz, C*H*H(agostic)), 2.47 (m, J(HH) = 3.6, 3.9 Hz), 2.82 (m, J(HH) = 3.3, 3.6 Hz), 3.49 (m, J(HH) = 3.9, 4.5, 8.9 Hz), 3.55 (m, J(HH) = 3.3, 4.2 Hz), 3.71 (m, J(HH) = 5.4, 8.9 Hz), 3.91 (m J(HH) = 4.2, 4.8 Hz). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 9.7 (s, C_5Me_5), 9.8 (s, CH_2), 10.1 (s, C_5Me_5), 34.8 (s), 43.1 (s), 57.6 (s), 59.3 (s), 67.2 (s), 76.3 (s), 94.9 (s, C_5Me_5), 95.6 (s, C_5Me_5). Anal. Calcd for $C_{27}H_{39}BF_4Ru_2$: C, 49.70; H. 6.02. Found: C, 48.92; H, 5.70.

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