

# Synthesis of Alkyl- and Aryl[hydrotris(pyrazolyl)borato]carbonylruthenium Complexes by Decarbonylation of Alcohols. Synthesis of $\text{TpRuH}(\text{H}_2)(\text{PPh}_3)$ [ $\text{Tp} = \text{Hydrotris}(\text{pyrazolyl})\text{borate}$ ], an Observable Intermediate in the Decarbonylation Reaction

Yu-Zhong Chen, Wai Chung Chan, Chak Po Lau,\* Hei Shing Chu, and Hin Ling Lee

Department of Applied Biology & Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

Guochen Jia\*

Department of Chemistry, Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong

Received September 25, 1996<sup>®</sup>

Treatment of  $\text{TpRuCl}(\text{PPh}_3)(\text{CH}_3\text{CN})$  ( $\text{Tp} = \text{hydrotris}(\text{pyrazolyl})\text{borate}$ ) with  $\text{NaBH}_4$  in ethanol did not yield the expected hydride complex  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  (**2**) but rather the methyl carbonyl complex  $\text{TpRu}(\text{CH}_3)(\text{CO})(\text{PPh}_3)$  (**1b**). Formation of **1b** was due to decarbonylation of ethanol by **2** generated in situ by  $\text{NaBH}_4$  reduction of  $\text{TpRuCl}(\text{PPh}_3)(\text{CH}_3\text{CN})$ . Analogous reactions in the presence of other primary alcohols  $\text{RCH}_2\text{OH}$  ( $\text{R} = \text{H}$ ,  $\text{C}_2\text{H}_5$ ,  $n\text{-C}_3\text{H}_7$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{CH}_3$ -4, and  $\text{C}_6\text{H}_4\text{Cl}$ -4) led to the corresponding  $\sigma$ -organyl complexes  $\text{TpRuR}(\text{CO})(\text{PPh}_3)$ . A common feature of the reactions is that the R groups of alcohols  $\text{RCH}_2\text{OH}$  become the  $\sigma$ -organyl groups in the final metal complexes. A mechanism involving metal- $\eta^2$ -aldehyde and  $-\eta^2$ -dihydrogen intermediates is proposed for the decarbonylation reaction. This is supported by the observation of the  $\eta^2$ -dihydrogen complex  $\text{TpRuH}(\text{H}_2)(\text{PPh}_3)$  (**3**) during the decarbonylation reaction. **3** was synthesized independently by heating a THF solution of **2** under 40 atm of  $\text{H}_2$  at 60 °C for 48 h or by heating **2** in  $\text{CH}_3\text{OH}$  at 60 °C under 6 atm of  $\text{H}_2$  for 5–6 h.

## Introduction

It is well established that reactions of certain transition metal complexes with primary alcohols can lead to decarbonylation of the alcohols.<sup>1</sup> Such reactions usually result in the formation of CO-containing complexes and degraded fragments of the alcohols, that is,  $\text{RH}$  from  $\text{RCH}_2\text{OH}$ . While the presence of base is required for decarbonylation of alcohols in most cases, it is noted that  $\text{RuH}_4(\text{PPh}_3)_3$ <sup>2</sup> and  $\text{RuH}(\text{BH}_4)(\text{PMe}_2\text{Ph})_3$ <sup>3</sup> react with ethanol to give  $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$  and  $\text{RuH}_2(\text{CO})(\text{PMe}_2\text{Ph})_3$  under neutral condition.

During our attempts to prepare  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  [ $\text{Tp} = \text{hydrotris}(\text{pyrazolyl})\text{borate}$ ] from the reaction

of  $\text{TpRuCl}(\text{PPh}_3)(\text{CH}_3\text{CN})$  with  $\text{NaBH}_4$  in EtOH, we found that  $\text{TpRu}(\text{CH}_3)(\text{CO})(\text{PPh}_3)$  instead of the expected  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  was produced. Formation of this product corresponds to decarbonylation of EtOH during the reaction. Also, reaction of  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  with EtOH produces the same complex. To explore the scope and mechanism of these unusual reactions, we have studied the reactions of  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  with various primary alcohols  $\text{RCH}_2\text{OH}$  and with  $\text{CH}_3\text{CHO}$ . The results illustrate that the decarbonylation reactions are quite general and that they may involve molecular dihydrogen complexes<sup>4</sup> as intermediates. Incorporation of the R group of  $\text{RCH}_2\text{OH}$  into the final metal complex is unusual, as the R group is usually not retained on the metal in most of the known decarbonylation reactions. Here we report the synthesis of  $\text{TpRuR}(\text{CO})(\text{PPh}_3)$  via these interesting decarbonylation reactions. The mechanism of the reactions is also discussed.

## Results and Discussion

**Syntheses of  $\text{TpRuR}(\text{CO})(\text{PPh}_3)$ .** Reactions of  $\text{TpRuCl}(\text{PPh}_3)(\text{CH}_3\text{CN})$  with  $\text{NaBH}_4$  in alcohols ( $\text{RCH}_2\text{OH}$ )

<sup>®</sup> Abstract published in *Advance ACS Abstracts*, February 15, 1997.

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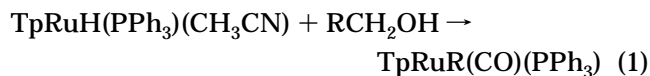
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OH) produce air-stable  $\text{TpRuR}(\text{CO})(\text{PPh}_3)$  ( $\text{R} = \text{H}$  (**1a**), Me (**1b**), Et (**1c**), Pr (**1d**), Ph (**1e**),  $\text{C}_6\text{H}_4\text{CH}_3$ -4 (**1f**),  $\text{C}_6\text{H}_4\text{-Cl}$ -4 (**1g**)) for which NMR and IR data are collected in Table 1. For  $\text{R} = \text{H}$ , the product is only observed if the reaction is carried out in a sealed tube.

Several ( $\sigma$ -organyl)ruthenium complexes with hydrotris(pyrazolyl)borate have been reported.  $\text{TpRu}(\text{C}_6\text{H}_4\text{-CH}_3$ -4)(CO)(PPh<sub>3</sub>) and a series of  $\sigma$ -vinyl derivatives have been prepared via the reaction of KTp with  $\text{Ru}(\text{C}_6\text{H}_4\text{CH}_3$ -4)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> and  $\text{Ru}(\text{CR}=\text{CHR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , respectively.<sup>5</sup> The cyanoethyl complex  $[\text{TpRu}\{\text{CH}(\text{CN})\text{CH}_3\}(\text{CO})(\text{PPh}_3)]$  was prepared from the chlorobridged dimer  $[\text{Ru}_2(\mu\text{-Cl})_2\{\text{CH}(\text{CN})\text{CH}_3\}_2(\text{CO})_2(\text{PPh}_3)_4]$ .<sup>6</sup> It is worth pointing out that the carbonyl hydride complex **1a** has been prepared previously by treatment of  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  with sodium hydrotris(pyrazolyl)borate in refluxing toluene.<sup>7</sup> All the ( $\sigma$ -organyl)[hydrotris(pyrazolyl)borato]ruthenium complexes reported to date have been prepared by reacting KTp or NaTp with ruthenium complex precursors containing the  $\sigma$ -organyl groups.

Thus, reactions of  $\text{TpRuCl}(\text{PPh}_3)(\text{CH}_3\text{CN})$  with  $\text{NaBH}_4$  in alcohols provide an alternative simple route to ( $\sigma$ -organyl)[hydrotris(pyrazolyl)borato]ruthenium complexes. Formation of  $\text{TpRuR}(\text{CO})(\text{PPh}_3)$ , instead of  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$ , from the reactions of  $\text{TpRuCl}(\text{PPh}_3)(\text{CH}_3\text{CN})$  and  $\text{NaBH}_4$  in the presence of  $\text{RCH}_2\text{OH}$  is unexpected, especially in view of the fact that  $\text{NaBH}_4$  reduction of metal halides in alcoholic solutions is one of the most common routes to transition metal hydride complexes.

**Synthesis of  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  (**2**) and Its Reaction with Ethanol.** We have attempted to elucidate the mechanism of these interesting decarbonylation reactions. As many hydride complexes [e.g.  $\text{RuH}_4(\text{PPh}_3)_3$  and  $\text{RuH}(\text{BH}_4)(\text{PMe}_2\text{Ph})_3$ ] are able to decarbonylate alcohols, it was suspected that hydride species and  $\text{RCHO}$  were involved in our decarbonylation reactions. Therefore, we prepared  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  (**2**) and studied its reaction with EtOH and  $\text{CH}_3\text{CHO}$ . This complex, prepared by  $\text{NaBH}_4$  reduction of  $\text{TpRuCl}(\text{PPh}_3)(\text{CH}_3\text{CN})$  in THF, was characterized by elemental analysis and <sup>1</sup>H NMR spectroscopy ( $\text{CD}_2\text{Cl}_2$ ). A doublet at  $\delta$  -13.91 ppm ( $d$ ,  $^2J_{\text{PH}} = 28$  Hz) is assignable to the hydride ligand cis to the triphenylphosphine, and a singlet at  $\delta$  1.69 ppm is assignable to the coordinated acetonitrile. Complex **2** reacts with alcohols to afford **1a–g** as the final products (eq 1).



We have monitored the reaction of  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  with ethanol by <sup>1</sup>H NMR spectroscopy. Heating of a THF-*d*<sub>8</sub> solution of  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  and ethanol in a Wilmad pressure NMR tube at 70 °C for 1 h led to the emergence of three new hydride signals as doublets at  $\delta$  -9.99 ppm ( $^2J_{\text{PH}} = 17.0$  Hz), -12.14 ppm ( $^2J_{\text{PH}} = 27.2$  Hz), and -12.40 ppm ( $^2J_{\text{PH}} = 29.0$  Hz). All three signals collapsed to singlets upon phosphorus decoupling. Pressurizing the NMR tube with 10 atm of H<sub>2</sub>

and heating at 60 °C for another 1 h resulted in disappearance of the two doublets at  $\delta$  -12.14 and -12.40 ppm. The hydride peak of  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  at  $\delta$  -13.78 ppm also greatly diminished in intensity while that of the doublet at  $\delta$  -9.99 ppm was greatly enhanced. This NMR study indicates that, under H<sub>2</sub> pressure,  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  and the species that correspond to the two doublets at  $\delta$  -12.14 and  $\delta$  -12.40 ppm are converted to the complex which shows the doublet at  $\delta$  -9.99 ppm. Releasing the H<sub>2</sub> pressure and further heating the NMR tube eventually led to disappearance of all the hydride signals, with appearance of signals due to  $\text{TpRu}(\text{CH}_3)(\text{CO})(\text{PPh}_3)$ . The doublet at  $\delta$  -12.14 ppm is probably due to the acetaldehyde complex  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CHO})$ , while the hydrido-dihydrogen complex  $\text{TpRuH}(\text{H}_2)(\text{PPh}_3)$  (**3**) gives rise to the doublet at  $\delta$  -9.99 ppm. The doublet at  $\delta$  -12.40 ppm is tentatively assigned to the ethanol complex  $\text{TpRuH}(\text{PPh}_3)(\text{EtOH})$ . The assignment of the signal at  $\delta$  -12.40 ppm to  $\text{TpRuH}(\text{PPh}_3)(\text{EtOH})$  is supported by the fact that the signal only appears at the early stage of the reaction and it does not show up in the reaction of  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  with  $\text{CH}_3\text{CHO}$  (see below).

**Reaction of  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  (**2**) with Acetaldehyde.** Dehydrogenation of primary alcohols by transition metal complexes produce aldehydes,<sup>1h,i,8</sup> and decarbonylation of aldehydes can be affected by transition metal complexes, yielding metal carbonyls.<sup>1i,8b,9</sup> Expulsion of the coordinated CO from the carbonyl complexes will render the decarbonylation reactions catalytic.<sup>10</sup> A complex formulated as  $\text{RuH}_2(\eta^2\text{-HCHO})(\text{PPh}_3)_3$  was suggested as an intermediate in the decarbonylation of methanol with  $\text{RuHCl}(\text{PPh}_3)_3$ ,<sup>1e</sup> and a well-characterized  $\eta^2$ -formaldehyde complex,  $\text{WH}_2(\text{PMe}_3)_4(\eta^2\text{-HCHO})$ , formed by addition of methanol to  $\text{WH}(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_3)_4$  has been reported.<sup>11</sup> Detailed mechanistic study of a  $\beta$ -hydride elimination from iridium alkoxo complexes has been carried out.<sup>12</sup> In this process, a transient aldehyde complex is suggested as the immediate product of  $\beta$ -hydrogen elimination. It is thus reasonable to speculate that our alcohol decarbonylation proceeds via a metal-aldehyde intermediate. Indeed, we have been able to prepare  $\text{TpRu}(\text{CH}_3)(\text{CO})(\text{PPh}_3)$  (**1b**) by reacting  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  with acetaldehyde. The <sup>1</sup>H NMR spectrum of a THF-*d*<sub>8</sub> solution of  $\text{TpRuH}(\text{PPh}_3)(\text{CH}_3\text{CN})$  and excess acetaldehyde at 70 °C after 10 min showed a small doublet at -12.14 ppm ( $^2J_{\text{PH}} = 27$  Hz) which was also observed in the <sup>1</sup>H NMR study

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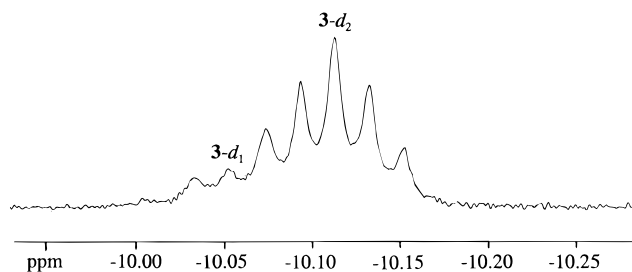
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of the reaction between TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CN) and ethanol described above. Pressuring the NMR tube with 10 atm of H<sub>2</sub> led to the disappearance of the doublet at  $\delta$  -12.14 ppm and the emergence of the doublet at  $\delta$  -9.99 ppm. Releasing the H<sub>2</sub> pressure and further heating of the NMR solution eventually led to the formation of TpRu(CH<sub>3</sub>)(CO)(PPh<sub>3</sub>). We assign the doublet at  $\delta$  -12.14 ppm to TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CHO),<sup>13</sup> as this signal appears at the early stage in both reactions of EtOH and CH<sub>3</sub>CHO with TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CN). Unfortunately we were unable to isolate and to fully characterize the compound because of its ready decomposition to give TpRu(CH<sub>3</sub>)(CO)(PPh<sub>3</sub>). The acetaldehyde complex TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CHO) is not unusual as there are numerous examples of  $\eta^1$ - and  $\eta^2$ -aldehyde complexes.<sup>14,15</sup>

**Synthesis and Characterization of TpRuH(H<sub>2</sub>)(PPh<sub>3</sub>) (3).** Heating a THF solution of TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CN) under 40 atm of H<sub>2</sub> at 60 °C for 48 h gave TpRuH<sub>3</sub>(PPh<sub>3</sub>) (3). The complex was also prepared by heating TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CN) in CH<sub>3</sub>OH at 60 °C under 6 atm of H<sub>2</sub> for 5–6 h in a sealed tube. The <sup>1</sup>H NMR (THF-*d*<sub>8</sub>) spectrum of the compound shows a doublet (<sup>2</sup>J<sub>PH</sub> = 17.0 Hz) which integrates to three hydrogens, at  $\delta$  -9.99 ppm. This doublet shows no sign of decoalescence down to -110 °C. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a singlet at  $\delta$  75.31 ppm in CD<sub>2</sub>Cl<sub>2</sub>. That <sup>2</sup>J<sub>PH</sub> (17.0 Hz) in **3** is significantly smaller than those observed for TpRuH(PPh<sub>3</sub>)(L) (L = CO, <sup>2</sup>J<sub>PH</sub> = 26.4 Hz; L = CH<sub>3</sub>CN, <sup>2</sup>J<sub>PH</sub> = 28.0 Hz) indicates that **3** may contain a dihydrogen ligand. The presence of a dihydrogen ligand in complex **3** is confirmed by the small *T*<sub>min</sub> (34 ms at 216 K and 400 MHz) for the hydride signal at  $\delta$  -9.99 ppm and *J*<sub>HD</sub> for its isotopomer TpRuH<sub>x</sub>D<sub>3-x</sub>(PPh<sub>3</sub>). The HD isotopomers of **3** were generated by heating a methanol-*d*<sub>4</sub> solution of TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CN) under 6 atm of H<sub>2</sub> for 5 h. As shown in Figure 1, the <sup>1</sup>H{<sup>31</sup>P} NMR (THF-*d*<sub>8</sub>, 298 K) shows, in the hydride region, a 1:2:3:2:1 quintet for



**Figure 1.** Hydride region of the <sup>1</sup>H{<sup>31</sup>P} NMR spectrum of a mixture of TpRuH<sub>2</sub>D(PPh<sub>3</sub>) (**3-d**<sub>1</sub>) and TpRuHD<sub>2</sub>(PPh<sub>3</sub>) (**3-d**<sub>2</sub>).

TpRuHD<sub>2</sub>(PPh<sub>3</sub>) (**3-d**<sub>2</sub>) and a 1:1:1 triplet for TpRuH<sub>2</sub>D(PPh<sub>3</sub>) (**3-d**<sub>1</sub>) (the triplet is partially obliterated by the quintet). The observed *J*<sub>HD</sub> values for both multiplets are identical at 7.9 Hz. An upfield isotopic shift of 60 ppb is observed for **3-d**<sub>2</sub> relative to **3-d**<sub>1</sub>. Assuming rapid fluxionality between hydride and dihydrogen and little deuterium site preference in **3**, the no-exchange coupling of the (HD) ligand, *J*<sub>HD</sub>, is approximately 3*J*<sub>HD/obs</sub> and is therefore equal to 29.7 Hz. This value is typical for  $\eta^2$ -HD coordinated to a transition metal center. It is noted that the analogous  $\eta^5$ -cyclopentadienide complex, ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)RuH<sub>3</sub>(PPh<sub>3</sub>), is a classical trihydride.<sup>16</sup> The reasons for this difference could be the poor electron-donating ability of hydrotris(pyrazolyl)borate and its preference for forming octahedral complex. Other examples of hydrotris(pyrazolyl)borate ligands favoring dihydrogen coordination have been reported, for example, [TpIrH(H<sub>2</sub>)(PMe<sub>3</sub>)]<sup>+</sup>,<sup>17</sup> Tp<sup>\*</sup>RhH<sub>2</sub>(H<sub>2</sub>)<sup>18</sup> [Tp<sup>\*</sup> = hydrotris(3,5-dimethylpyrazolyl)borate], LRuH(H<sub>2</sub>)<sub>2</sub>,<sup>19</sup> and LRuH(H<sub>2</sub>)L' <sup>19</sup> [L = Tp, Tp<sup>\*</sup>, or hydrotris(3-isopropyl-4-bromopyrazolyl)borate (Tp<sup>\*</sup>); L' = PCy<sub>3</sub>, THT, py, and NHET<sub>2</sub>].

**Mechanism for Alcohol Decarbonylation with TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CN) (2).** Isolation of TpRuR(CO)(PPh<sub>3</sub>) from the reactions of TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CN) (**2**) with primary alcohols reveals that the alcohols are decarbonylated by TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CN) in neutral solutions. A proposed mechanism for the decarbonylation reactions based on the observations is depicted in Scheme 1. The dihydrogen complex TpRuH(H<sub>2</sub>)(PPh<sub>3</sub>) (**3**) observed at the early stage of the reaction of **2** with ethanol in a sealed NMR tube is probably formed by substitution of L in TpRuH(PPh<sub>3</sub>)L (L = CH<sub>3</sub>CN, RCH<sub>2</sub>OH, or RCHO) by H<sub>2</sub> produced during the reaction. Intermediates of the ruthenium–alcohol complex (**4**) and ruthenium–aldehyde complex (**5**) are inferred by the <sup>1</sup>H NMR study of the reactions of TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CN) with ethanol and acetaldehyde in sealed NMR tubes, as described above. The coordinated alcohol in **4** can either undergo oxidative addition to form the ruthenium alkoxide dihydride intermediate or it can protonate the metal hydride to generate a ruthenium alkoxo dihydrogen intermediate. We prefer the alkoxo

(13) The bonding mode of the acetaldehyde is probably  $\eta^2$  because there is no sign of aldehydic proton of  $\eta^1$ -coordinated acetaldehyde in the low-field region. The aldehydic proton of free acetaldehyde in THF-*d*<sub>8</sub> appears as a singlet at  $\delta$  9.63 ppm; it is expected that the aldehydic proton of  $\eta^1$ -coordinated acetaldehyde will be slightly shifted downfield from that of the free aldehyde. Aldehydic protons in  $\eta^2$  complexes are usually shifted significantly upfield, but unfortunately in the present system, the large number of strong peaks in the 4–8 ppm region renders observation of the aldehydic proton of  $\eta^2$ -coordinated acetaldehyde impossible. Usage of <sup>13</sup>C NMR measurement to confirm the coordination mode of the acetaldehyde is excluded because the acquisition time of such measurement is too long, and TpRuH(PPh<sub>3</sub>)(CH<sub>3</sub>CN) reacts with acetaldehyde to yield the final product TpRuCH<sub>3</sub>(CO)(PPh<sub>3</sub>) before the acquisition time is over.

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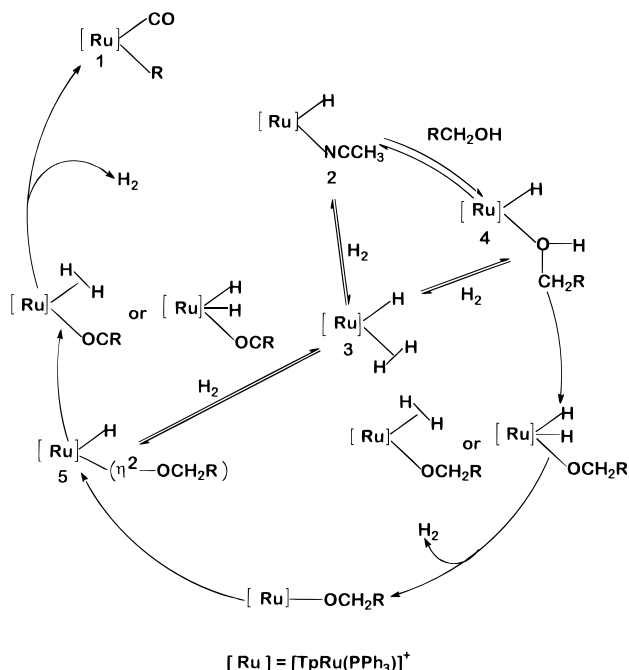
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**Scheme 1. Proposed Mechanism for Decarbonylation of  $RCH_2OH$  with  $TpRuH(PPh_3)(CH_3CN)$  (**2**)**



dihydrogen intermediate as the fragments  $[TpRuL(PPh_3)]^0$  or  $1^+$  ( $L = H, PPh_3^{20}$  or  $CH_3CN^{20}$ ) all form dihydrogen complexes with  $H_2$ . Intramolecular protonation of  $TpRuH(PPh_3)(RCH_2OH)$  is reasonable as the acidity of alcohol coordinated on metal is enhanced, and  $M-H$  can be very effective proton acceptor.<sup>21</sup> There are examples of intramolecular and intermolecular protonations of  $M-H$  by  $R-O-H$ ,  $R-S-H$ , and  $RR'N-H$ .<sup>21</sup> For similar reasons, we prefer the formation of the acyl dihydrogen intermediate over the acyl dihydride from **5**. It should be noted that, in the catalytic dehydrogenation of alcohols with  $RuH_2(N_2)(PPh_3)_3$ , the trihydride intermediate  $[RuH_3(PPh_3)_3]^-$  was protonated by ethanol to give the molecular dihydrogen complex  $RuH_2(H_2)(PPh_3)_3$ , which readily lost  $H_2$  to generate the unsaturated species  $RuH_2(PPh_3)_3$ .<sup>8e</sup>

Consistent with the mechanism, it was observed that the decarbonylation product  $TpRuH(CO)(PPh_3)$  was not obtainable when the reaction of  $TpRuH(PPh_3)(CH_3CN)$

with  $CH_3OH$  was carried out in an open reactor under a constant bubbling of dinitrogen. According to the mechanism depicted in Scheme 1, the intermediate product of methanol decarbonylation will be formaldehyde, which, being very volatile, would escape from the open system. If the reaction is conducted in a sealed tube for an extended period of time, the formaldehyde remains in the system and the reaction sequence in Scheme 1 is thus followed.

The role of the dihydrogen complexes in the decarbonylation reactions is interesting. Formation of  $TpRu(OCH_2R)(H_2)(PPh_3)$  and  $TpRu(COR)(H_2)(PPh_3)$  facilitates the production of  $RCHO$  and  $TpRuR(CO)(PPh_3)$ . However, formation of  $TpRuH(H_2)(PPh_3)$  retards the decarbonylation. Thus it was observed that the reflux of a solution of **2** in ethanol under a slow stream of  $N_2$  led to the formation of  $TpRu(CH_3)(CO)(PPh_3)$  (**1b**) at a faster rate than in a sealed tube. In the former case, the stream of  $N_2$  carries away the  $H_2$  and the accumulation of  $TpRuH(H_2)(PPh_3)$  is unlikely; hence, the decarbonylation reaction proceeds. In the sealed tube reaction, the  $H_2$  accumulates and the decarbonylation reaction is blocked by the generation of  $TpRuH(H_2)(PPh_3)$ .

## Conclusion

Reactions of  $TpRuCl(PPh_3)(CH_3CN)$  with  $NaBH_4$  in primary alcohols or  $TpRuH(PPh_3)(CH_3CN)$  (**2**) with primary alcohols produce  $TpRuR(CO)(PPh_3)$  via decarbonylation of the primary alcohols. Unlike most transition metal complex promoted alcohol decarbonylation reactions, which are usually carried out in basic conditions, decarbonylation of primary alcohols with **2** proceeds smoothly in nonbasic solutions. Another feature of our alcohol decarbonylation reactions is that the  $R$  groups of  $RCH_2OH$  become the  $\sigma$ -organyl groups of the final metal complexes, instead of forming the usual  $RH$  byproducts in most alcohol decarbonylation reactions. We propose that the decarbonylation of alcohols by **2** proceeds via metal- $\eta^2$ -aldehyde and -dihydrogen complexes. We have been able to identify a dihydrogen complex observed in the early stage of the decarbonylation reaction, by carrying out its independent syntheses.

## Experimental Section

Ruthenium trichloride,  $RuCl_3 \cdot 3H_2O$ , and lithium tetrafluoroborate were obtained from Aldrich. Pyrazole, sodium borohydride, and tetrafluoroboric acid in ethereal solution ( $HBF_4 \cdot Et_2O$ , 54%) were purchased from Fluka. Triphenylphosphine was obtained from Merck and was recrystallized from ethanol before use. 4-Methylbenzyl alcohol and 4-chlorobenzyl alcohol were prepared respectively from reduction of their corresponding 4-substituted benzaldehydes using  $NaBH_4$  in ethanol, and the solid products obtained were recrystallized from petroleum ether (80–100 °C). The complex  $TpRuCl(PPh_3)_2$ <sup>22</sup> was synthesized according to published procedures. Solvents were distilled under dry nitrogen atmosphere with appropriate drying agents (solvent/drying agent): methanol/ $Mg-I_2$ , acetonitrile/ $P_2O_5$ , dichloromethane/ $P_2O_5$ , tetrahydrofuran/ $Na$ -benzophenone, diethyl ether/ $CaH_2$ ,  $n$ -hexane/ $Na$ .<sup>23</sup> All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques unless otherwise specified.

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**Table 1.** NMR and IR Spectroscopic Data for TpRuR(CO)(PPh<sub>3</sub>)

R	$\delta(^1\text{H})$ (ppm) <sup>a</sup>	$\delta(^{13}\text{C}\{^1\text{H}\})$ (ppm) <sup>a</sup>	$\delta(^{31}\text{P}\{^1\text{H}\})$ (ppm) <sup>a</sup>	$\nu(\text{CO})$ (KBr, cm <sup>-1</sup> )	$\nu(\text{B-H})$ (KBr, cm <sup>-1</sup> )	$\nu(\text{Ru-H})$ (KBr, cm <sup>-1</sup> )
<b>1a<sup>b</sup></b> H	-11.99 (d, <sup>2</sup> J <sub>PH</sub> = 26.4 Hz, 1H, Ru-H); 9H of Tp, <sup>c</sup> 5.68 (t, 1H), 5.96 (t, 1H), 6.12 (t, 1H), 6.54 (d, 1H), 6.72 (d, 1H), 7.53 (d, 1H), 7.56 (d, 1H), 7.68 (d, 1H), 7.80 (d, 1H); 7.24–7.35 (m, 15H of PPh <sub>3</sub> )	206.6 (d, <sup>2</sup> J <sub>PC</sub> = 17.1 Hz, Ru-CO)	68.10 (s)	1928 (vs)	2479 (br)	1985 (w)
<b>1b</b> Me	0.11 (d, <sup>3</sup> J <sub>PH</sub> = 3.0 Hz, 3H, Ru-CH <sub>3</sub> ); 9H of Tp, <sup>c</sup> 5.82 (t, 1H), 5.87 (t, 1H), 6.15 (t, 1H), 6.65 (d, 1H), 6.73 (d, 1H), 7.57 (d, 1H), 7.60 (d, 1H), 7.65 (d, 1H), 7.68 (d, 1H); 7.17–7.33 (m, 15H of PPh <sub>3</sub> )	-5.8 (d, <sup>2</sup> J <sub>PC</sub> = 9.2 Hz, Ru-CH <sub>3</sub> ); 207.9 (d, <sup>2</sup> J <sub>PC</sub> = 18.0 Hz, Ru-CO)	55.63 (s)	1923 (vs)	2517 (br)	
<b>1c</b> Et	1.05 (t, J <sub>HH</sub> = 6.9 Hz, 3H, Ru-CH <sub>2</sub> CH <sub>3</sub> ); 0.95, 1.15 (m, 2H, Ru-CH <sub>2</sub> CH <sub>3</sub> ); 9H of Tp, <sup>c</sup> 5.79 (t, 1H), 5.81 (t, 1H), 6.10 (t, 1H), 6.69 (d, 1H), 6.73 (d, 1H) 7.51 (d, 1H), 7.57 (d, 1H), 7.59 (d, 1H), 7.69 (d, 1H); 7.09–7.29 (m, 15H of PPh <sub>3</sub> )	8.7 (d, <sup>2</sup> J <sub>PC</sub> = 9.8 Hz, Ru-CH <sub>2</sub> CH <sub>3</sub> ); 20.8 (s, Ru-CH <sub>2</sub> CH <sub>3</sub> ); 8.5 (d, <sup>2</sup> J <sub>PC</sub> = 19.6 Hz, Ru-CO)	55.60 (s)	1916 (vs)	2494 (br)	
<b>1d</b> Pr	0.75 (t, J <sub>HH</sub> = 7.0 Hz, 3H, Ru-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ); 0.95–1.76 (m, 4H, Ru-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ); 9H of Tp, <sup>c</sup> 5.86 (t, 1H), 5.89 (t, 1H), 6.17 (t, 1H), 6.79 (d, 1H), 6.83 (d, 1H), 7.53 (d, 1H), 7.64 (d, 1H), 7.66 (d, 1H), 7.72 (d, 1H); 7.12–7.37 (m, 15H of PPh <sub>3</sub> )	20.3 (s, Ru-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) 20.5 (d, <sup>2</sup> J <sub>PC</sub> = 8.9 Hz, Ru-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ); 30.4 (s, Ru-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ); 208.0 (d, <sup>2</sup> J <sub>PC</sub> = 16.7 Hz, Ru-CO)	55.66 (s)	1916 (vs)	2465 (br)	
<b>1e</b> Ph	9H of Tp, <sup>c</sup> 5.80 (t, 1H), 5.84 (t, 1H), 5.92 (t, 1H), 6.58 (d, 1H), 6.67 (d, 1H), 7.08 (d, 1H), 7.51 (d, 1H), 7.57 (d, 1H), 7.67 (d, 1H); 6.72–6.77, 6.81–6.87, 7.11–7.17, 7.28–7.33 (m, 15H of PPh <sub>3</sub> , 5H of Ph)	163.2 (d, <sup>2</sup> J <sub>PC</sub> = 11.1 Hz, ipso C of Ru-C <sub>6</sub> H <sub>5</sub> ); 206.9 (d, <sup>2</sup> J <sub>PC</sub> = 15.7 Hz, Ru-CO)	48.87 (s)	1916 (vs)	2494 (br)	
<b>1f</b> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -4	2.25 [s, 3H, Ru-(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -4)]; 6H of Tp, <sup>c</sup> 5.86 (t, 1H), 5.90 (t, 1H), 6.00 (t, 1H), 7.58 (d, 1H), 7.63 (d, 1H), 7.74 (d, 1H); 6.61–6.65, 6.81–6.87, 7.11–7.16, 7.30–7.32 [m, 3H of Tp, 4H of Ru-(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -4), 15H of PPh <sub>3</sub> ]	20.8 [s, Ru-(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -4)]; 157.5 [d, <sup>2</sup> J <sub>PC</sub> = 12.6 Hz, ipso C of Ru-(C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> -4)]; 206.6 (d, <sup>2</sup> J <sub>PC</sub> = 15.6 Hz, Ru-CO)	52.95 (s)	1928 (vs)	2468 (br)	
<b>1g</b> C <sub>6</sub> H <sub>4</sub> Cl-4	9H of Tp, <sup>c</sup> 5.88 (t, 1H), 5.90 (t, 1H), 6.01 (t, 1H), 6.63 (d, 1H), 6.81 (d, 1H), 7.00 (d, 1H), 7.58 (d, 1H), 7.65 (d, 1H), 7.74 (d, 1H); 6.71–6.74, 6.77–6.80, 6.82–6.87, 7.14–7.17, 7.30–7.34 [m, 4H of Ru-(C <sub>6</sub> H <sub>4</sub> Cl-4), 15H of PPh <sub>3</sub> ]	161.7 [d, <sup>2</sup> J <sub>PC</sub> = 12.4 Hz, ipso C of Ru-(C <sub>6</sub> H <sub>4</sub> Cl-4)]; 206.6 (d, <sup>2</sup> J <sub>PC</sub> = 15.6 Hz, Ru-CO)	52.72 (s)	1933 (vs)	2465 (br)	

<sup>a</sup> CDCl<sub>3</sub>. <sup>b</sup> In CD<sub>2</sub>Cl<sub>2</sub> solution. <sup>c</sup> All coupling constants for pyrazolyl proton resonances were about 2 Hz.

Infrared spectra were obtained from a Nicolet Magna 750 FT-IR spectrophotometer or a Perkin-Elmer 983 IR spectrophotometer. <sup>1</sup>H NMR spectra were obtained from a Bruker ARX-300 or a Bruker ARX-400 spectrometer. Chemical shifts ( $\delta$ , ppm) were reported relative to tetramethylsilane (TMS). <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker ARX-400 instrument at 161.70 MHz or on a Bruker ARX-300 instrument at 121.49 MHz. <sup>31</sup>P chemical shifts were externally referenced to 10% P(OMe)<sub>3</sub> solution in CDCl<sub>3</sub> ( $\delta$  140.4 ppm). <sup>13</sup>C{<sup>1</sup>H} NMR spectra were taken on a Bruker ARX-300 instrument at 75.47 MHz or on a Bruker ARX-400 spectrometer at 100.54 MHz; chemical shifts were internally referenced to CDCl<sub>3</sub> ( $\delta$  77.0 ppm). Elemental analyses were performed by Butterworth Laboratories Ltd., London, U.K., and Institute of Chemistry, Academia Sinica, Beijing, China.

NMR and IR spectroscopic data of TpRuR(CO)(PPh<sub>3</sub>) (**1a–g**) are collected in Table 1.

**Preparation of TpRuCl(PPh<sub>3</sub>)(CH<sub>3</sub>CN).** A 0.50 g (0.59 mmol) amount of TpRuCl(PPh<sub>3</sub>)<sub>2</sub> in a two-necked round bottom flask fitted with a condenser was evacuated and flushed with nitrogen. A degassed solution of tetrahydrofuran and acetonitrile (9:1, 30 mL) was added via syringe. The solution was heated at 60 °C for 6 h with stirring under nitrogen and then concentrated to a few milliliters. A yellow solid precipitated out and was collected by filtration and washed with diethyl ether and then hexane. It was dried under vacuum at room temperature. Yield = 0.26 g (67%). Anal. Calcd for C<sub>29</sub>H<sub>28</sub>BCIN<sub>7</sub>PRu: C, 53.35; H, 4.32; N, 15.02. Found: C, 53.80; H, 4.65; N, 14.92. IR (KBr, cm<sup>-1</sup>):  $\nu(\text{C}\equiv\text{N})$  2278 (sh, w),  $\nu(\text{B-H})$  2474 (br, med). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C):  $\delta$  2.10 (s, 3H, CH<sub>3</sub>CN), 5.75 (t, 1H), 5.84 (t, 1H), 6.22 (t, 1H), 6.62 (d, 1H), 6.94 (d, 1H), 7.63 (d, 1H + 1H), 7.64 (d, 1H), 8.07 (d, 1H) (9H of Tp, all coupling constants for pyrazolyl proton reso-

nances were about 2 Hz); 7.23–7.37 (m, 15 H of PPh<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 121.49 MHz, 25 °C):  $\delta$  51.7 (s).

**Preparation of TpRuH(CO)(PPh<sub>3</sub>) (**1a**).** A 100 mL Schlenk tube loaded with TpRuCl(PPh<sub>3</sub>)(CH<sub>3</sub>CN) (0.20 g, 0.31 mmol) and NaBH<sub>4</sub> (0.10 g, 2.6 mmol) was degassed and filled with nitrogen, for three cycles. Freshly distilled methanol (20 mL) was added, and the tube was then sealed. The mixture was stirred at 70 °C for 14 h, and then the solvent was removed by vacuum. The white residue was treated with 10 mL of 1-propanol. A white solid was collected, washed with a few portions of diethyl ether, and dried in vacuo. Yield = 0.13 g (69%). Anal. Calcd for C<sub>28</sub>H<sub>26</sub>BN<sub>6</sub>OPRu: C, 55.54; H, 4.33; N, 13.88. Found: C, 55.82; H, 4.18; N, 13.65.

**Preparation of TpRu(CH<sub>3</sub>)(CO)(PPh<sub>3</sub>) (**1b**).** TpRuCl(PPh<sub>3</sub>)(CH<sub>3</sub>CN) (0.15 g, 0.23 mmol) and sodium borohydride (0.08 g, 2.3 mmol) were combined in a two-necked round bottom flask fitted to a condenser. The flask was evacuated and filled with nitrogen for three cycles. Distilled, degassed ethanol (40 mL) was added via a cannula, and the resulting reaction mixture was heated under reflux for 6 h. The solution was concentrated to ca. 8 mL to give a white solid, which was then filtered out. The solid was washed with a few 20 mL portions of ethanol (95%) and diethyl ether and was then vacuum-dried at room temperature for 6 h. Yield = 0.07 g (49%). Anal. Calcd for C<sub>29</sub>H<sub>28</sub>BN<sub>6</sub>OPRu: C, 56.22; H, 4.56; N, 13.57. Found: C, 55.91; H, 4.42; N, 13.31.

**Preparation of TpRu(C<sub>2</sub>H<sub>5</sub>)(CO)(PPh<sub>3</sub>) (**1c**).** This complex was prepared by using the same procedure as for preparation of **1b**, except that 1-propanol (40 mL) was used. Yield = 0.10 g (69%). Anal. Calcd for C<sub>30</sub>H<sub>30</sub>BN<sub>6</sub>OPRu: C, 56.87; H, 4.78; N, 13.27. Found: C, 56.50; H, 4.90; N, 13.41.

**Preparation of TpRu(*n*-C<sub>3</sub>H<sub>7</sub>)(CO)(PPh<sub>3</sub>) (**1d**).** This complex was prepared by the same procedure as for the

preparation of **1b**, except that 1-butanol (40 mL) was used. Yield = 0.09 g (60%). Anal. Calcd for  $C_{31}H_{32}BN_6OPRu$ : C, 57.50; H, 4.98; N, 12.98. Found: C, 57.68; H, 4.82; N, 13.06.

**Preparation of  $TpRu(C_6H_5)(CO)(PPh_3)$  (**1e**).** The preparation procedures were similar to that for the preparation of **1b**, except benzyl alcohol was used in place of ethanol and the reflux time was extended to 12 h. The yield of the white solid obtained was 0.100 g (64%). Anal. Calcd for  $C_{34}H_{30}BN_6OPRu$ : C, 59.91; H, 4.45, N, 12.33. Found: C, 60.06; H, 4.55; N, 12.56.

**Preparation of  $TpRu(C_6H_4CH_3-4)(CO)(PPh_3)$  (**1f**).** A 2-necked pear-shaped flask loaded with  $TpRuCl(PPh_3)(CH_3CN)$  (0.30 g, 0.46 mmol),  $NaBH_4$  (0.16 g, 4.2 mmol), and 4-methylbenzyl alcohol (5.0 g, 0.041 mol) was degassed and filled with nitrogen, for three cycles. Freshly distilled THF (20 mL) was added, and the mixture was stirred under reflux for 3 days. The mixture was then filtered, and the filtrate was concentrated to 2–3 mL. A white solid precipitated out after the addition of ethanol (5 mL). The solid was collected by filtration and washed with ethanol (5 mL  $\times$  2) and then dried in vacuo for 8 h at 80 °C. Yield = 0.17 g (53%). Anal. Calcd for  $C_{33}H_{32}BN_6OPRu$ : C, 60.43; H, 4.64, N, 12.08. Found: C, 59.92; H, 4.26, N, 12.20.

**Preparation of  $TpRu(C_6H_4Cl-4)(CO)(PPh_3)$  (**1g**).** This complex was prepared by using a similar procedure as for the preparation of **1f**, except that 4-chlorobenzyl alcohol (6.5 g, 0.046 mol) was used and the reflux time was extended to 5 days. Yield of the white solid obtained: 0.23 g (70%). Anal. Calcd for  $C_{34}H_{29}ClBN_6OPRu$ : C, 57.03; H, 4.08; N, 11.74. Found: C, 56.62, H, 4.27; N, 11.40.

**Preparation of  $TpRuH(PPh_3)(CH_3CN)$  (**2**).** A 50 mL 2-necked pear-shaped flask loaded with  $TpRuCl(PPh_3)(CH_3CN)$  (0.30 g, 0.46 mmol) and  $NaBH_4$  (0.16 g, 4.2 mmol) was degassed and then filled with nitrogen, for three cycles. Freshly distilled dry THF (20 mL) was added, and the mixture was stirred and refluxed under nitrogen for 3 days. The mixture was filtered, and to the filtrate was added 5 mL of acetonitrile; the solution was refluxed for 1 day. The solvent of the solution was removed, and a yellow powder was obtained. Dry diethyl ether (10 mL) was added to dissolve the solid, and the insoluble matter was filtered off. The filtrate was then concentrated to 1–2 mL, and 10 mL of dry pentane was added to precipitate out an air-sensitive yellow solid. It was vacuum-dried and stored under nitrogen. Yield = 0.18 g (52%). Anal. Calcd for  $C_{29}H_{29}BN_7PRu$ : C, 56.32, H, 4.73, N, 15.86. Found: C, 56.70; H, 4.90; N, 15.66. IR (KBr,  $cm^{-1}$ ):  $\nu(B-H)$  2461 (br, med);  $\nu(C\equiv N)$  2258 (w);  $\nu(Ru-H)$  1890 (w).  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz, 25 °C):  $\delta$  -13.91 (d, 1H,  $^2J_{PH}$  = 28.0 Hz, Ru-H); 1.69 (s, 3H,  $CH_3CN$ ); 5.60 (t, 1H), 5.93 (t, 1H), 6.14 (t, 1H), 6.50 (d, 1H), 7.11 (d, 1H), 7.53 (d, 1H), 7.60 (d, 1H), 7.66 (d, 1H), 7.75 (d, 1H) (9H of Tp, all coupling constants for pyrazolyl proton resonances were about 2 Hz); 7.12–7.28 (m, 15H of  $PPh_3$ ).  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ , 161.70 MHz, 25 °C):  $\delta$  77.62 (s).

**Preparation of  $TpRuH(H_2)(PPh_3)$  (**3**).** **Method a.** The preparation was carried out in a 250 mL stainless steel autoclave. A 50 mL round bottom flask, loaded with 200 mg (0.32 mmol) of  $TpRuH(PPh_3)(CH_3CN)$  (**2**) and 20 mL of freshly distilled THF, was put into the autoclave. After the autoclave was flushed with hydrogen five times, the system was stirred at 60 °C and under 40 atm of  $H_2$ . At the end of the reaction time (48 h), the reactor was cooled rapidly and vented carefully. The solution was concentrated to 1–2 mL, and 30 mL of hexane was added. The solution was filtered under nitrogen, and the filtrate was collected. The solvent of the yellow filtrate was removed in vacuo to produce an air-sensitive yellow solid. Yield = 0.12 g (65%). Anal. Calcd for  $C_{27}H_{28}BN_6PRu$ : C, 55.96; H, 4.87, N, 14.51. Found: C, 56.12; H, 4.65; N, 14.37.  $^1H$  NMR ( $CD_2Cl_2$ , 400 MHz, 25 °C):  $\delta$  -9.97 (d,  $^2J_{PH}$  = 17 Hz, 3H, Ru- $F_3$ ); 5.92 (t, 2H), 6.05 (t, 1H), 6.85 (d, 2H), 7.45 (d, 1H), 7.56 (d, 1H), 7.68 (d, 2H) (9H of Tp, all

coupling constants for pyrazolyl proton resonances were about 2 Hz); 7.17–7.36 (m, 15H of  $PPh_3$ ).  $^{31}P\{^1H\}$  NMR ( $CD_2Cl_2$ , 161.70 MHz, 25 °C):  $\delta$  75.31 (s). Variable-temperature  $T_1$  measurements on the  $H_2$  signal were carried out by the inversion-recovery method using standard  $180^\circ-\tau-90^\circ$  pulse sequences.  $T_1$  (400 MHz,  $CD_2Cl_2$ , ms): 86 (293 K), 63 (273 K), 41 (243 K), 34 (223 K), 33 (213 K), 36 (203 K), 41 (193 K).  $T_{1min}$  (34 ms at 216 K and 400 MHz) was obtained from the “V”-shaped  $\ln T_1$  vs  $1000/T$  plot.<sup>24</sup>

**Method b.** Into a 10 mm  $\times$  80 mm thick-walled tube fitted with a threaded vacuum stopcock was loaded 600 mg (0.96 mmol) of  $TpRuH(PPh_3)(CH_3CN)$  (**2**). The tube was evacuated and then filled with  $N_2$ , for three cycles. A 2 mL volume of methanol was added under  $N_2$ , and the tube was then pressurized with 6 atm of  $H_2$  and heated at 60 °C. **2**, which was in fine powder form, was not completely dissolved in the methanol, but as the reaction proceeded, the powder gradually disappeared and yellow solids started crystallizing out. The reaction was stopped after 5 h, and more crystals formed as the tube cooled to room temperature. The tube was vented, and the solution above the crystals was decanted. The yellow crystals of  $TpRuH(H_2)(PPh_3)$  (**3**) were collected and dried in vacuo. Yield = 0.21 g (38%).

**Preparation of  $TpRuH_xD_{3-x}(PPh_3)$  ( $x = 2, 3-d_1$ ;  $x = 1, 3-d_2$ ).** Mixture of the isotopomers, **3-d<sub>1</sub>** and **3-d<sub>2</sub>** was prepared by following method b as for the preparation of **3**, except that methanol- $d_4$  was used. The  $^1H\{^{31}P\}$  NMR spectrum of the mixture (THF- $d_8$ , 400 MHz, 25 °C) showed a 1:2:3:2:1 quintet at  $\delta$  -10.11 ppm (due to **3-d<sub>2</sub>**) and a 1:1:1 triplet partially masked by the quintet, at  $\delta$  -10.05 ppm (due to **3-d<sub>1</sub>**).  $J_{HD/obs}$  for both the quintet and triplet was identical and was equal to 7.9 Hz.

**$^1H$  NMR Study of the Reaction of  $TpRuH(PPh_3)(CH_3CN)$  (**2**) with  $C_2H_5OH$ .** A Wilmad pressure NMR tube loaded with  $TpRuH(PPh_3)(CH_3CN)$  (~100 mg) was evacuated and then filled with  $N_2$ , for three cycles. Dry THF- $d_8$  (0.3 mL) was added to the tube under  $N_2$ , and the tube was then sealed and heated at 70 °C for 1 h. An  $^1H$  NMR spectrum was taken after cooling the tube to room temperature. Three small doublets were observed at  $\delta$  -9.90 (d,  $^2J_{PH}$  = 17.0 Hz), -12.14 (d,  $^2J_{PH}$  = 27.2 Hz), and -12.40 (d,  $^2J_{PH}$  = 29.0 Hz) ppm. The NMR tube was then pressurized with 10 atm of  $H_2$  and heated at 60 °C for another 1 h. After cooling of the sample to room temperature, an  $^1H$  NMR spectrum was again taken, and it was observed that the two doublets at  $\delta$  -12.14 and -12.40 ppm disappeared and the intensity of the one at  $\delta$  -9.99 ppm was greatly enhanced.

**$^1H$  NMR Study of the Reaction of  $TpRuH(PPh_3)(CH_3CN)$  (**2**) with  $CH_3CHO$ .** A Wilmad pressure NMR tube loaded with 100 mg of  $TpRuH(PPh_3)(CH_3CN)$  (**2**) was evacuated and then filled with  $N_2$ , for three cycles. A 0.3 mL volume of THF- $d_8$  and 0.1 mL of  $CH_3CHO$  were added under  $N_2$ . The tube was then sealed and heated at 70 °C for 10 min. After cooling of the sample to room temperature, an  $^1H$  NMR spectrum of the reaction mixture was taken; a small doublet was observed at  $\delta$  -12.14 ppm (d,  $^2J_{PH}$  = 27.2 Hz). Further heating of the tube at 70 °C for another 1 h led to the disappearance of the doublet at  $\delta$  -12.14 ppm, and the methyl peak of  $TpRu(CH_3)(CO)(PPh_3)$  (**1b**) was observed at  $\delta$  0.11 ppm.

**Acknowledgment.** This work was supported by the Hong Kong Research Grant Council Earmarked Grant HKP 91/94P. We thank Professor Richard Haynes for helpful discussion and proofreading the manuscript.

OM960817U

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