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NO Insertion Reaction of Ethyl(nitrosyl)ruthenium Complex Having Hydrotris(pyrazolyl)borate and Conversion to Acetaldoxime and Acetonitrile Complexes

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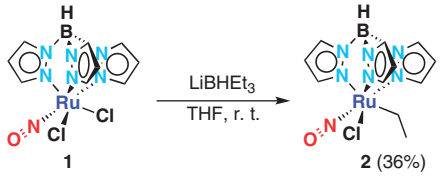
Ethyl(nitrosyl)ruthenium [TpRuCl(Et)(NO)] (**2**) was isolated from the reaction of [TpRuCl$_2$(NO)] (**1**) with LiBHEt$_3$. NO insertion of **2** was observed from heating a solution of **2**. In the presence of PPh$_3$, nitrosoethane complex [TpRuCl{N(=O)Et}(PPh$_3$)] (**3**) was isolated, but the absence of PPh$_3$ led to nitrosoethane-bridged dimer [(TpRuCl)$_2${μ-N(=O)Et}$_2$] (**6**). Also, in complex **3**, conversion of the nitrosoethane moiety to acetaldoxime and acetonitrile was observed.

The important roles of *C*-nitroso compounds in various biochemical metabolic processes have been realized, which have stimulated wide interest in the chemistry and also in the biochemical aspects of *C*-nitroso compounds.[1] In addition, they have intriguing coordination chemistry.[2] One of their preparative methods is metal-assisted NO incorporation reactions.[3] In our continuing research of nitrosylruthenium chemistry,[4] we have described *C*-nitroso complexes from the reaction of [TpRuCl$_2$(NO)] (**1**) (Tp; BH(pyrazolyl)$_3$) with 2-vinylpyridines, where chelation-assisted C–H bond activation of a vinyl substituent on pyridine ring was involved.[4b] Here, we report isolation of an ethyl(nitrosyl)ruthenium complex, its NO insertion reactions, and subsequent isomerization and dehydration processes.

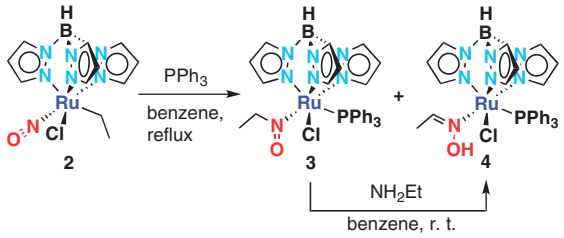
We first attempted to synthesize a hydrido(nitrosyl)ruthenium complex from the reaction of **1** with 1.5 equiv of LiBHEt$_3$. This reaction did not give the desired hydrido complex, but instead ethyl(nitrosyl)ruthenium [TpRuCl(Et)(NO)] (**2**) was isolated (Scheme 1). In the ^{1}H NMR spectrum, characteristic diastereotopic methylene signals were observed. Moreover, complex **2** was characterized by X-ray structural analysis (Figure S1).[5,6] Unfortunately, the crystallographic disorder between Et and NO groups causes uncertainty of the metric structural parameters. Other examples of ethyl group rather than hydride incorporation by use of LiBHEt$_3$ have been reported.[7]

Heating a solution of **2** induced NO insertion. When a benzene solution of **2** was refluxed in the presence of PPh$_3$, a nitrosoethane complex [TpRuCl{N(=O)Et}(PPh$_3$)] (**3**) was isolated in 94% yield along with the acetaldoxime isomer [TpRuCl{N(OH)=CHMe}(PPh$_3$)] (**4**) as a minor product (4%) (Scheme 2).[8] For complex **3**, the N≡O stretching band disappeared in the IR spectrum, and in the ^{1}H NMR spectrum diastereotopic methylene signals remained. Finally, the structure of **3** was confirmed by X-ray analysis (Figure 1). In spite of uncertainty of the metric structural parameters due to crystallographic disorder, structural analysis of **3** determined the bond lengths of O1–N1 and N1–C1 in the nitrosoethane group to be 1.204(13) and 1.509(19), respectively. On the other hand, the ^{1}H NMR spectrum of **4** shows one characteristic down-field singlet signal for the acidic oxime proton at δ 10.9. Unfortunately, uncertainty of the oxime conformation (*syn*- or *anti*-form) remains, owing to the lack of X-ray structural determinations. But the *anti*-form would be supported by the X-ray analysis of the nitrosobenzene analog (vide infra). Although silica gel column separation accelerates moderately the isomerization of **3** to **4**, treatment of **3** with excess EtNH$_2$ afforded **4** quantitatively. In the case of diethyl(nitrosyl)ruthenium [Cp*Ru(Et)$_2$(NO)], its thermolysis in the presence of PMe$_3$ has been described to give oximate complexes.[3c]

The acetaldoxime complex **4** was dehydrated to give an acetonitrile complex [TpRuCl(NCMe)(PPh$_3$)] (**5**), which has



Scheme 1.



Scheme 2.

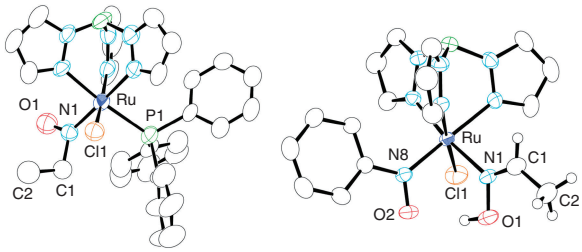
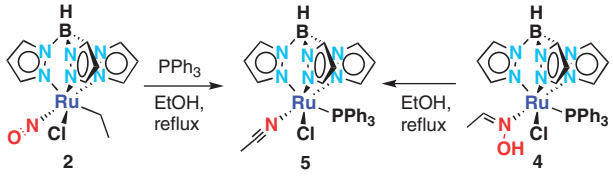
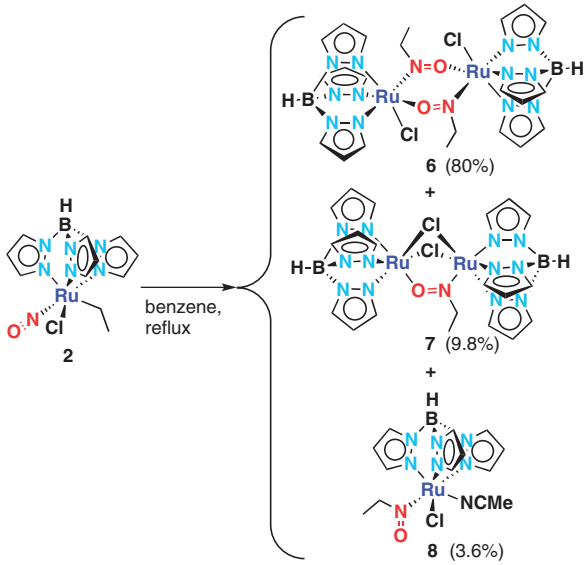


Figure 1. Crystal structures of **3** (left) and **9** (right). Minor sets of the disordered atoms of **3** and hydrogen atoms except for the acetaldoxime group of **9** are omitted for clarity. Selected bond distances (Å) and angles (°) are as follows. For **3**: Ru–P = 2.377(2), O1–N1 = 1.204(13), N1–C1 = 1.509(19); Ru–N1–O1 = 122.4(7), Ru–N1–C1 = 129.1(10). For **9**: Ru–N1 = 2.0949(16), Ru–N8 = 1.9309(15), O1–N1 = 1.383(2), O2–N8 = 1.261(2), N1–C1 = 1.273(2); Ru–N1–O1 = 119.70(13), Ru–N8–O2 = 119.15(12).



Scheme 3.

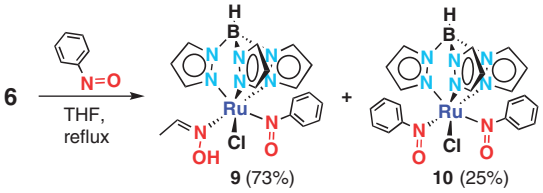


Scheme 4.

been already prepared.[9] Although the dehydration was assisted by silica gel column procedures, conversion of **4** to **5** was clearly observed in refluxing EtOH (Scheme 3). Also, treatment of **2** with PPh_3 in refluxing EtOH gave **5** in one-step (68%).

On the other hand, in the absence of PPh_3, refluxing of a benzene solution of **2** afforded a nitrosoethane-bridged dimer $[(TpRuCl)_2\{\mu\text{-}N(=O)Et\}_2]$ (**6**) as a major product (80%) (Scheme 4). In the ^{1}H NMR spectrum of **6**, diastereotopic methylene signals were also observed. The structure was preliminary revealed by X-ray structural analysis (Figure S1).[6] The FAB-MS spectrum does not show the parent molecular ion signal, but there appear fragment signals due to the loss of one Cl atom or N(=O)Et group. Under these reaction conditions, a mono(nitrosoethane)-bridged dimer $[(TpRu)_2\{\mu\text{-}N(=O)Et\}(\mu\text{-}Cl)_2]$ (**7**) and an acetonitrile complex [TpRuCl(NCMe)-{N(=O)Et}] (**8**) were also obtained in low yields. Complex **7** was prepared from refluxing a THF solution of **6** in the presence of Zn (66%).[10]

Finally, reactivity of **6** was examined. Treatment of **6** with 5 equiv of nitrosobenzene in refluxing THF afforded acetaldoxime complex [TpRuCl{N(OH)=CHMe}{N(=O)Ph}] (**9**) and bis-(nitrosobenzene) complex $[TpRuCl\{N(=O)Ph\}_2]$ (**10**) (Scheme 5). The ^{1}H NMR spectrum of **9** showed the acidic oxime proton at δ 13.9. The molecular structure of **9** was determined by a single-crystal X-ray structural analysis (Figure 1). The bond length of 1.273(2) Å (N1–C1) is regarded to be a typical N–C double bond. The O1–N1 bond distance of 1.383(2) Å is longer than that of **3**. For the acetaldoxime group of **9**, the X-ray crystal structural analysis indicated a mutual *E*-



Scheme 5.

configuration of the Me group and the Ru atom with respect to the N=C double bond.

In conclusion, we prepared the ethyl(nitrosyl)ruthenium **2** from the reaction of **1** with $LiBHEt_3$. In the formation of **3**, isolation of the nitrosoethane-bridged dimer **6** would indicate that initial NO insertion into Ru–Et bond occurred, followed by phosphine coordination. Also, transformation of nitrosoethane to acetaldoxime, finally to acetonitrile on ruthenium was found.

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5 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-782237–782239. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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10 Thermolysis of **6** in the absence of Zn also afforded **7**, but in low yield. The role of Zn remains unclear.

