CHEMISTRY LETTERS, pp. 1219-1222, 1980. © The Chemical Society of Japan 1980

NOVEL RUTHENIUM(II) OLEFIN COMPLEX WITH A COORDINATED ALICYCLIC CARBON-HYDROGEN BOND

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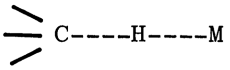
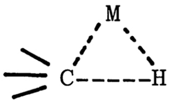
Chloro(η^2,η^2-norbornadiene)[η^1,η^2-3-endo-(3'-nortricyclyl)norborn-5-en-2-endo-yl]ruthenium(II), **1a**, prepared by zinc reduction of $[RuCl_2(norbornadiene)]_n$ in the presence of norbornadiene and suitable proton sources such as alumina or ammonium chloride in acetonitrile, involves a coordinated alicyclic carbon-hydrogen bond.

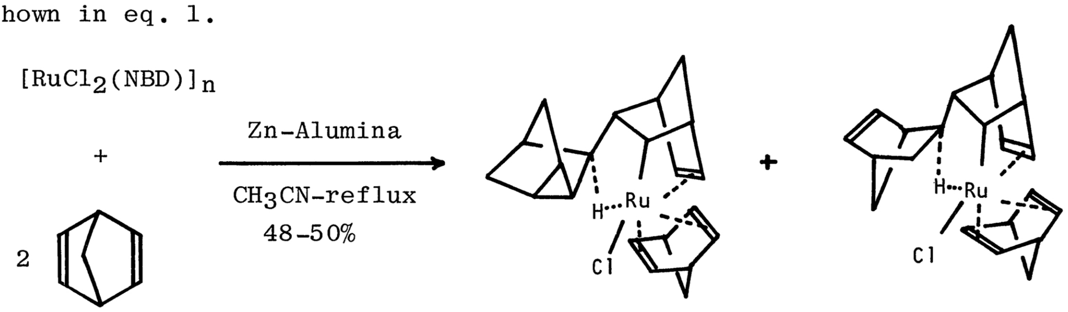
Activation of a carbon-hydrogen bond by transition metal complexes has attracted considerable interest in recent years1). Apparent cleavage of C-H bonds of aromatic hydrocarbons2), vinyl groups3), and those of coordinated phosphine or nitrogen ligands4) has been reported by means of a wide range of transition metal complexes. Little has been known, however, about the activation of aliphatic or alicyclic C-H bonds which are less activated5).
The primary step of such activation involves the metal approaching the C-H bond within the coordination sphere of the transition metal complexes5).





This communication deals with the preparation and preliminary spectroscopic results on the ruthenium(II) complex which contains the first example of substantial interaction between a C-H bond of an inert alicyclic hydrocarbon ligand. When an acetonitrile(10 ml) suspension of $[RuCl_2(norbornadiene)]_n$ (480 mg), zinc powder(4 g), and alumina(Merck 1097; 1 g) was refluxed under dinitrogen with norbornadiene(NBD; 140 mg) for 30 min, the color of the mixture turned to deep orange. Additional NBD(140 mg) was added to the above mixture, and reflux was continued for further 15 min. After filtration the mixture was evaporated in vacuo to give reddish yellow oil, which was chromatographed under dinitrogen with alumina(Merck 1097; diethyl ether). The orange band was collected, and its evaporated residue was subjected to recrystallization from a dichloromethane-diethyl ether mixed solvent. Orange crystals of $Ru(Cl)(C_{14}H_{17})(C_7H_8)$, **1**, Mp 136-137°(dec) were obtained in 48-50% yield6). The X-ray structure determination of **1**7) suggested that **1** was composed of a mixture of chloro(η^2,η^2-norbornadiene)[η^1, η^2-3-endo-(3'-nortricyclyl)norborn-5-en-2-endo-yl]ruthenium(II), **1a**(86%), and chloro(η^2, η^2-norbornadiene)[η^1, η^2-3-endo-

(norborn-5'-en-2'-endo-yl)norborn-5-en-2-endo-yl]ruthenium(II), **1b**(14%), as shown in eq. 1.



1a(86%) **1b**(14%) (1)

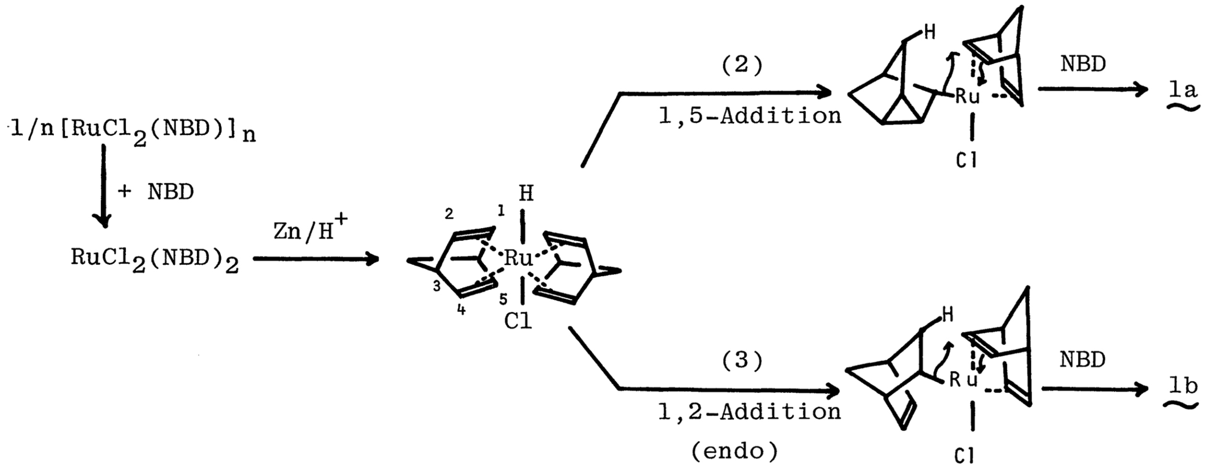
Careful repeated chromatographic separation followed by the recrystallization from diethyl ether results in the isolation of almost pure major isomer, **1a**. When we eliminated alumina during the above preparation, the yield of **1** decreased to 20-30% yield. Addition of ammonium chloride instead of alumina as a proton source, total yield of **1a** and **1b** increased dramatically to 80%. These facts indicate that the protonation of an anionic ruthenium intermediate to give a ruthenium(II) hydride involved in the formation of both **1a** and **1b**.

A particular feature of the ^1H NMR($CDCl_3$) spectrum of the major isomer(**1a**) is the appearance of an extremely highfield doublet at δ-3.74(J=12 Hz) indicative of interaction between a hydrogen atom of the C-H bonds of the nortricyclyl skeleton. The measurement of the ^{13}C NMR under a complete proton decoupling condition showed expected 21 carbon resonances$^{8)}$. The particular carbon resonance at 35.8 ppm was concluded to be ascribed to the signal due to the perturbed C-H bond because this signal increased its intensity on the selective irradiation of the proton signal at δ-3.74. Moreover, this signal showed the longest relaxation time(1.03 sec) suggesting the stretched C-H bond. The infrared spectrum of **1a**(KBr) also supported the perturbation of a C-H bond by the ruthenium atom since a particular ν(C-H) absorption was observed at 2580 cm^{-1} corresponding to the stretched C-H bond. The X-ray structure of **1a** by Jameson, Lewis, and Ibers$^{7)}$ indicated that one of the C-H bond of saturated nortricyclyl ring was extremely close to the ruthenium(II) moiety in the distance of d(Ru-H)= 2,10Å, and that it occupied the sixth coordination site of the distorted octahedral symmetry.

There have been two reports on the coordinated C-H bonds in the case of $(Et_2PBz)_2[(\eta^3\text{-}CH_2CPhCH_2)(CO)_2Mo]$ involving a coordinated α-C-H bond of the ethyl group in the pyrrazolylborate ligand$^{9)}$ and of $Fe[P(OMe)_3]_3(\eta^3$-cyclooctenyl) in which an α-C-H bond of the cyclooctenyl ligand located at the extremely short distance to the iron atom, d(Fe-H)=1.88Å$^{10)}$. In these examples, the interacting C-H bond had α-functionalities such as boron atom or η^3-allyl moiety. The present results of the ruthenium complex, **1a**, therefore, appears to be the first example of substantial interaction between a metal and an inert carbon-hydrogen bond of an alicyclic hydrocarbon ligand.

When zinc reduction of $RuCl_3 \cdot H_2O$ was undertaken in the presence of an excess NBD in benzene at room temperature overnight, only **1b** was isolated in 41% yield$^{11)}$. This bisnorbornenyl isomer **1b** showed the signal of an interacting C-H bond at relatively lower field than 1a at δ-2.87 as a broad multiplet. This finding indicates that the coordination of the ruthenium moiety of 1b is slightly weaker than the isomer 1a. Other differences in the ^{13}C NMR of 1b are the absence of the cyclopropyl carbon resonances around 10-16ppm, and the appearance of the non-coordinated olefin resonances at 140.8 and 130.4 ppm in $CDCl_3$.

The mechanism of the formation of both major isomer(1a) and minor isomer (1b) is explained reasonably in terms of a common ruthenium(II) hydride intermediate, "$Ru(H)(Cl)(NBD)_2$", which is consistent with the requirement of a proton source on preparation. The insertion of a coordinated NBD to the ruthenium hydride either in a 1,5-addition to a nortricyclyl ruthenium intermediate(eq.2) or in an endo-1,2-addition to an endo-norbornenyl complex(eq.3), followed by the second insertion of another coordinated NBD ligand yields the correct endo stereochemistry observed in final products, 1a and 1b, respectively.



The full details of spectroscopic results based on the decoupling technique will be published with a combined form with the X-ray structure determination as a full paper in near future.

Acknowledgement. The author(K. I.) is indebted to the Ministry of Education, Japan for a grant in aid(No. 555332).

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6) Complex **1**: Anal. Calcd. for $C_{21}H_{25}ClRu$: C, 60.93; H, 6.09. Found: C, 61.04 H, 6.14. IR(KBr):ν(C-H---Ru) 2580, ν(Ru-Cl) 239 cm^{-1}. ^{1}H NMR of **1a** in $CDCl_3$: Coordinated NBD, Olefinic, δ3.96(1H,t, J=4Hz), 3.76(1H,m), 3.56(2H,m): Bridgehead, 2.94(1H,br), 3.12(1H,t); Bridge, 1.52(2H,br): Norbornenyl, Olefinic, 4.11(1H,m), 6.21(1H,dt); Bridgehead, 3.72(1H,m), 3.41(1H,m); Bridge, 1.29(2H, br), 2.43(1H, ddd, J=14, 4, 1-2Hz); Methine 0.90(1H,d, J=1-2Hz): Nortricyclyl, Methylene, 1.5-2.0(2H,brm); Methine 1.98(1H,br), -3.74(1H,d, J=14Hz), Cyclopropane, 1.1-0.6(3H,m).

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8) ^{13}C NMR of **1a** in $CDCl_3$(Relaxation time: sec), Coordinated NBD, Olefinic, 65.9 (0.89), 60.9(0.80), 50.0(0.81), 48.8(0.87); Bridgehead, 45.2(0.83), 44.0 (0.82); Bridge, 56.3(0.45); Norbornenyl, Olefinic, 90.7(0.73), 121.2(0.67); Bridgehead, 53.4(0.77), 46.8(0.70); Bridge, 54.6(0.45), Methine, 52.2(0.93); Ru-C, 19.5(0.85); Nortricyclyl, Methylene, 34.0(0.44), 26.1(0.36); Methine 35.8(1.03), 34.7(0.81); Cyclopropane, 15.4(0.75), 12.5(0.89), 10.7(0.81). All chemical shifts were measured in ppm units downfield from internal TMS.

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11) ^{1}H NMR of **1b** in $CDCl_3$: Coordinated NBD, Olefinic, δ3.89(2H,m), 3.57(2H,m); Bridgehead, 3.40(1H,m), 3.16(1H,t); Bridge, 1.52(2H,m). Two Norbornenyl Skeletons, Free Olefin, 6.25(2H,m); Coordinated Olefins, 4.13(1H,t), 5.92 (1H,m); Bridgehead, 2.82(1H,br), 2.73(1H,m), 2.05(2H,m); Bridge, 1.35(4H,m); Methine and Methylenes; 2.32(1H,m), 0.90-1.30(3H,m), -2.87(1H,m).

(Received July 28, 1980)