Unusual Formation of Cyclometallated *C,H-trans*-Hydridoruthenium(II) Complexes and Their Isomerization into *C,H-cis*-Types

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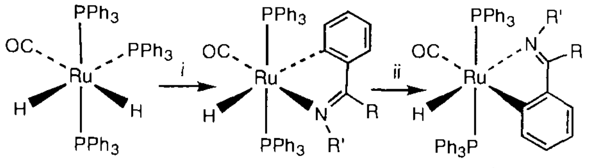
The aromatic C-H bonds of *N*-benzylideneaniline and 2-phenylpyridine are cleaved by $[RuH_2(CO)(PPh_3)_3]$ and triethoxyvinylsilane at 70-110 °C to give the corresponding cyclometallated hydridoruthenium(II) complexes. The X-ray structure analyses of these complexes reveal that the hydrido ligand is initially situated *trans* to aryl group of the cyclometallated moiety and these two ligands are moved mutually into *cis*-sites by heating.

Ruthenium complex-catalyzed C-H/olefin coupling and its related reactions have been widely recognized as useful synthetic processes for carbon-carbon bond formation.[1] Generation of an active ruthenium(0) species from a dihydridoruthenium(II) complex $[RuH_2(CO)(PPh_3)_3]$ (**1**) and successive activation of the C-H bond are considered as the key-steps of these catalytic reactions.[1] However, in spite of the usefulness of these reactions, neither real active species nor intermediary cyclometallated hydridoruthenium species have been characterized so far. From this standpoint, we have been working on identification and characterization of the ruthenium species related to the catalytic C-H/olefin coupling.[2] Here we report isolation and characterization of cyclometallated hydridoruthenium(II) complexes derived from the reactions of **1** with some nitrogen-containing aromatic compounds such as *N*-benzylideneaniline and 2-phenylpyridine in the presence of olefin.

A benzene suspension (6 cm^3) containing the complex **1** (0.1 mmol), *N*-benzylideneaniline (0.2-0.4 mmol) and triethoxyvinylsilane (0.2-0.4 mmol) was sealed under vacuum. After heating the suspension at 70 °C for 12 h, the seal was broken and successively the reaction mixture was concentrated under reduced pressure. Addition of hexane to the concentrated mixture precipitated the powder of $[Ru(C_6H_4\text{-}CH{=}NC_6H_5)H(CO)(PPh_3)_2]$, (**2a**)[3] (Scheme 1).



Scheme 1. i) Triethoxyvinylsilane and *N*-benzylideneaniline (for **2**) or 2-phenylpyridine (for **3**) at 70 °C; ii) At 110 °C.

Its isomer **2b**[3] was obtained when the reaction among **1**, triethoxyvinylsilane and *N*-benzylideneaniline was carried out at 110 °C for 2 h. Similarly, 2-phenylpyridine reacted with **1** and triethoxyvinylsilane at 70 °C for 12 h and at 110 °C for 3 h to afford the corresponding cyclometallated hydridoruthenium(II) complexes, $[Ru(C_6H_4\text{-}C_5H_4N)H(CO)(PPh_3)_2]$ (**3a**[3] and **3b**[3], respectively).

The $^{31}P\{^1H\}$ NMR spectrum of **2a** showed a singlet at δ 49.8, whereas that of **2b** did a singlet at a slightly lower field (at δ 52.1).[4] In the ^1H NMR spectra, the hydrido signal of **2a** was observed as a triplet at δ -4.76, whereas that of **2b** resonated as a triplet at a higher field (at δ -11.77). These spectroscopic features are commonly recognized for complexes **3a** and **3b**.[4] Therefore, the NMR data indicate that the isomers of these cyclometallated hydridoruthenium(II) complexes are classified into two types of the structure; one type includes **2a** and **3a** formed by the reaction at 70 °C and the other does **2b** and **3b** formed at 110 °C. When the formation of **3b** was traced at 110 °C by the $^{31}P\{^1H\}$ NMR spectra, it was observed that **3a** was formed initially and subsequently converted into **3b** along with the reaction time.

When **1** was treated with 2-phenylpyridine without triethoxyvinylsilane, **1** did not change at all at 70 °C, but reacted slowly with 2-phenylpyridine at 110 °C. The yields of **3a** and **3b** were 7.4 and 2.2% respectively, after the reaction period of 3 h. Accordingly, the relative reaction rate for the formation of **3b**

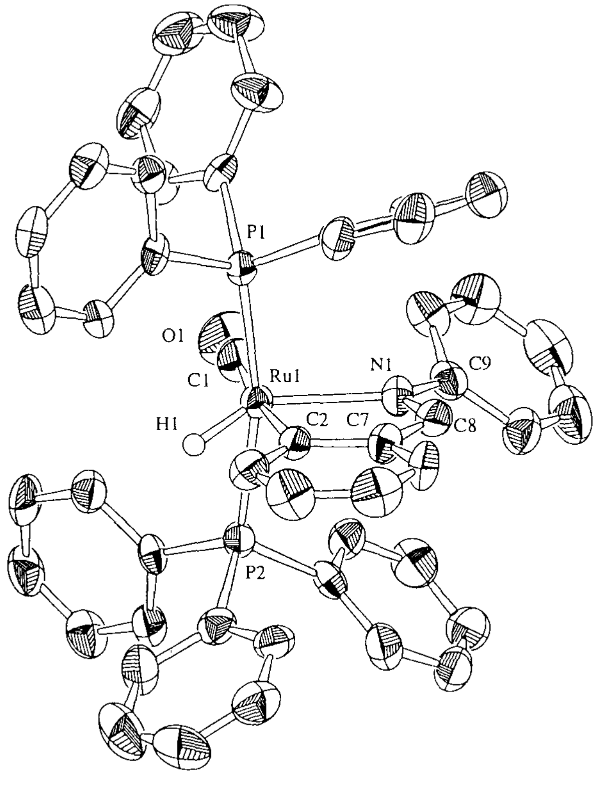


Figure 1. The molecular structure of **2b**. Hydrogen atoms are omitted for clarity except for H1. Selected bond lengths (Å) and angles (°): Ru1-P1, 2.342(3); Ru1-P2, 2.330(3); Ru1-N1, 2.223(9); Ru1-C1, 1.89(1); Ru1-C2, 2.14(1); Ru1-H1, 1.4(1); O1-C1, 1.17(1); P1-Ru1-P2, 165.90(10); N1-Ru1-C2, 78.7(4); N1-Ru1-H1, 140(4); C2-Ru1-H1, 67(4); Ru1-C1-O1, 176(1).

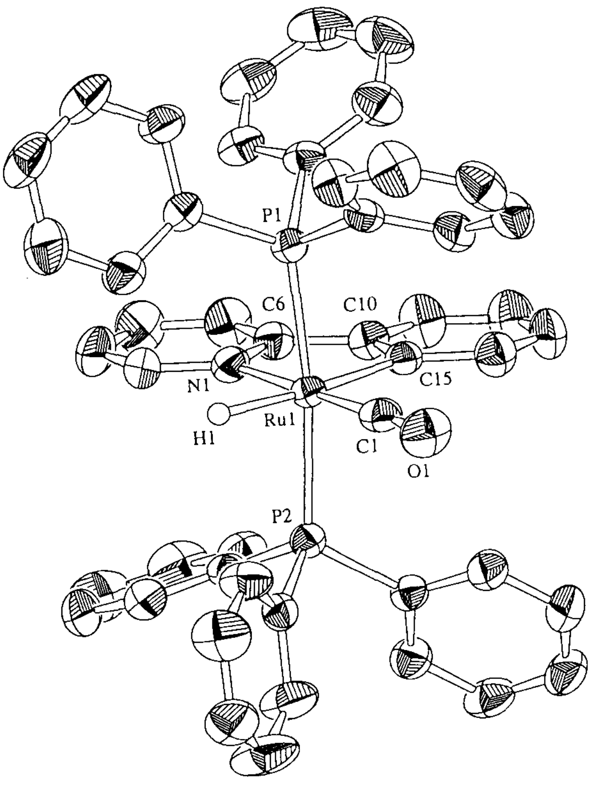


Figure 2. The molecular structure of **3a**. Hydrogen atoms are omitted for clarity except for H1. Selected bond lengths (Å) and angles (°): Ru1-P1, 2.355(1); Ru1-P2, 2.322(1); Ru1-N1, 2.158(4); Ru1-C1, 1.845(5); Ru1-C15, 2.133(5); Ru1-H1, 1.61(4); O1-C1, 1.156(6); P1-Ru1-P2, 170.09(5); N1-Ru1-C15, 77.1(2); N1-Ru1-H1, 86(1); C15-Ru1-H1, 163(1); Ru1-C1-O1, 178.0(5).

was about 20:1 in the presence and absence of the silane. Then, α-olefin such as triethoxyvinylsilane is necessary to obtain **3a** and **3b** in good yields separately and smoothly.

Single-crystal X-ray analyses of **2b**[5] and **3a**[6] reveal that the aryl and the hydrido ligands are laid mutually *cis* in the equatorial plane of **2b** (Figure 1); in contrast, these ligands are situated *trans* to each other in **3a** (Figure 2). Interestingly, a series of the *C,H-trans*-isomers of the cyclometallated hydrido-ruthenium(II) complexes (**2a** and **3a**) is formed initially at 70 °C and isomerize into the *C,H-cis*-isomers (**2b** and **3b**) in the severer conditions. It is noteworthy that the initial activation of the C-H bond of the nitrogen-containing aromatic compounds on the ruthenium center at 70 °C yields the *C,H-trans*-complexes, in contrast with ordinary oxidative addition which locates the resulting cleaved moieties at *cis*-sites on a metal center. The unusual formation of the *C,H-trans*-complexes of the aromatic compounds means either that the oxidative addition of the C-H bond gives other type of a *C,H-cis*-complex, which is immediately rearranged to the *C,H-trans*-one[7] or that the C-H activation on the ruthenium center does not proceed *via* the ordinary oxidative addition. Previously, Cole-Hamilton and Wilkinson[8] reported that $[RuH_2(PPh_3)_4]$ reacted with benzophenone at 100 °C to give a cyclometallated hydridoruthenium(II) complex, $[Ru\{C_6H_4C(=O)C_6H_5\}H(PPh_3)_3]$ which was ascribed to a *C,H-cis* type.

Kakiuchi et al.[1b] reported that the reaction among **1**, triethoxyvinylsilane, and acetophenone-d_5 at 50 °C gave no coupling product, but gave rise to H-D scrambling at the three olefinic hydrogen atoms of recovered triethoxyvinylsilane. These facts are interpreted well by the initial formation of the *C,H-trans*-complexes which could not yield the coupling product (see later), but cause the H-D scrambling *via* insertion of the olefin into the H-Ru bond and subsequent β-elimination.

Reductive elimination of a coupling product requires *cis*-arrangement of two leaving ligands. Our results stated above elucidate that cyclometallated *C,H-trans*-hydridoruthenium(II) complexes are isomerized into the corresponding *C,H-cis*-ones near 110 °C, at which the catalytic C-H/olefin coupling reactions have been carried out.[1] This is the reason why the catalytic C-H/olefin coupling reactions need the high temperature near 110 °C.

Complexes **2** and **3** involve both the cyclometallated moiety and the hydrido ligand, which have been suggested as essential parts of the intermediary species in the ruthenium complex-catalyzed C-H/olefin coupling.[1] Especially, *N*-benzylideneaniline is a similar aromatic imine to *N*-(2-methylbenzylidene)-*tert*-butylamine, which has allowed to be coupled with triethoxyvinylsilane under the similar reaction conditions.[9] Therefore, it is reasonable to consider **2a** and **2b** as structural models for the intermediates in the catalytic cycle. Furthermore, **3a** and **3b** are very similar to an intermediate proposed for rhodium complex-catalyzed coupling of 2-phenylpyridine and olefin in spite of differences of the central metal and its oxidation number.[10] Further studies to elucidate the mechanisms for the formation of the *C,H-trans*-complexes and for the *trans-cis* isomerization and the successive reaction with an olefin are now in progress.

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References and Notes

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3 a) Yield: **2a** 44%, **2b** 48%, **3a** 55%, **3b** 45%. b)IR data (KBr): **2a** 1930 sh (Ru-H), 1915 vs (C≡O), 1580 s cm^{-1} (C=N). **2b** 1996 m (Ru-H), 1915 vs (C≡O), 1575 s cm^{-1} (C=N).

4 Selected NMR data ($CDCl_3$): **2a**: ^1H δ -4.76 (t, $^2J_{HP}$ = 21.3 Hz, RuH), $^{31}P\{^1H\}$ δ 49.8 (s); **2b**: ^1H δ -11.77 (t, $^2J_{HP}$ = 23.4 Hz, RuH), $^{31}P\{^1H\}$ δ 52.1 (s); **3a**: ^1H δ -4.96 (t, $^2J_{HP}$ = 22.7 Hz, RuH), $^{31}P\{^1H\}$ δ 51.5 (s); **3b**: ^1H δ -11.30 (t, $^2J_{HP}$ = 21.3 Hz, RuH), $^{31}P\{^1H\}$ δ 53.0 (s).

5 Crystal data for **2b**: $C_{50}H_{41}NOP_2Ru$, FW = 834.90, monoclinic, space group $P2_1/n$ (# 14), a = 13.336(2), b = 19.212(2), c = 16.591(1) Å, β = 110.486(6)°, V = 3981.9(7) Å^3, Z = 4, D_{calc} = 1.393 gcm^{-3}, $F(000)$ = 1720.00, μ(MoKα) = 5.14 cm^{-1}, T = 293 K. Of 7254 unique reflections measured, 3010 ($I > 3\sigma(I)$) were used in refinement. R = 0.057, R_w = 0.054.

6 Crystal data for **3a**: $C_{48}H_{39}NOP_2Ru \cdot C_6H_6$, FW = 886.97, triclinic, space group $P1$ (# 2), a = 12.4081(9), b = 17.998(1), c = 10.743(1) Å, α = 100.679(7)°, β = 109.683(7)°, γ = 91.472(6)°, V = 2209.8(3) Å^3, Z = 2, D_{calc} = 1.333 gcm^{-3}, F(000) = 916.00, μ(MoKα) = 4.67 cm^{-1}, T = 293 K. Of 10415 unique reflections measured, 6620 ($I > 3\sigma(I)$) were used in refinement. R = 0.044, R_w = 0.041.

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