Chelation-assisted Facile C–N Bond Oxidative Addition of Spironaphthoxazines by Ru(η^4-cycloocta-1,5-diene)(η^6-naphthalene)

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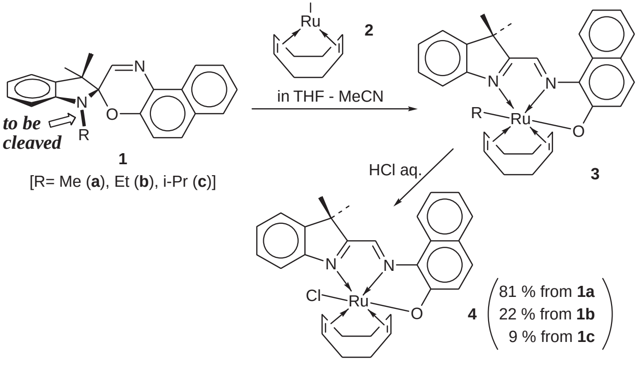
β-Spironaphthoxazines **1** undergo oxidative addition of the C–N bond of the indoline moiety at ambient temperature upon treatment with the labile Ru(0) precursor, Ru(η^4-cycloocta-1,5-diene)(η^6-naphthalene) (**2**), to give the Ru(II) complex with the naphtholato-tethered 1,4-diazabuta-1,3-diene ligand **3**. The reaction should be triggered by chelation of the isomeric azanaphthoquinone structure, which should bring the C–N bond to the position suitable for the oxidative addition.

Activation of chemical bonds under mild reaction conditions has been one of the major research subjects in the field of organometallic chemistry.[1a] In contrast to the challenging C–H and C–C bond activation and the rather well-encountered C–O bond activation,[1] little attention has been paid to C–N bond activation, and only a limited number of examples have been reported so far.[2] Furthermore, in the previous studies, for example, a highly azophilic low valent early transition metal is involved as the active metal species,[2b,2c] and strained molecules (e.g. aziridine)[2d] or pincer ligands having the N–C bond to be cleaved in the central part[2e–2g] are used as the substrates. During the course of our study on metal-complexation of photochromic compounds,[3] we have found facile oxidative addition reaction of the C–N bond in β-spironaphthoxazines **1** to the labile Ru(0) species, Ru(η^4-cycloocta-1,5-diene)(η^6-naphthalene) (**2**), which is the subject of the present report.

Treatment of *N*-methyl-β-spironaphthoxazine **1a** with **2** in THF–MeCN at ambient temperature resulted in exclusive formation of a new product **3a** (Scheme 1).[4,5] Because **3a** was too unstable to be isolated in a pure form, **3a** was characterized on the basis of its spectroscopic data as well as the structure of a degradation product (see below). Key spectral features of **3a** compared with **1a** are (1) a large upfield shift of the N–Me signal (δ_H 2.44 → 0.62) suggesting formation of a Ru–Me species, (2) a downfield shift of the HC=N signal (δ_H 7.62 → 8.69), and (3) FD-MS data consistent with the adduct formation ($m/z = 538$ (**1a** + Ru(cod))). In addition, disappearance of the ^{1}H NMR signals for the naphthalene ligand revealed replacement of the naphthalene ligand in **2** by **1a**.[5]



Scheme 1.

Because the structure of highly functionalized molecules such as **3** and **1** could not be determined by spectroscopic data alone, the product **3a** was further treated with aqueous HCl solution and, as a result, green chlorinated product **4** could be isolated and characterized by X-ray crystallography[6] (Figure 1). Complex **4** contains the octahedral Ru center coordinated by the κ^3-chelating ligand derived from **1a** in addition to the κ^1-Cl and two η^2-olefin (cod) ligands. Taking into account the bond alternation associated with the π-conjugated chelating moiety, the κ^3-ligand is described as a mononegative 1,4-diazabuta-1,3-diene ligand with the naphtholato tether on one N atom and the fused indoline moiety on the other side. In accord with the structure, (1) the ^{1}H NMR signal for **3a** at δ_H 0.62 disappears, (2) the molecular ion peaks ($m/z = 558$) are detected by FD-MS, and (3) quantitative liberation of methane is confirmed by GC-MS analysis. The spectral data for **3a** being similar to those of **4** with the exception of the Ru–X (X = Cl and Me) signals reveals that adduct **3a** is the corresponding methylruthenium complex. The ethyl (**1b**) and isopropyl derivatives (**1c**) were also converted to the same product **4** after HCl treatment, supporting cleavage of the N–R bond in the initial step. Thus, the reaction shown in Scheme 1 can be regarded as an oxidative addition reaction of the N–C bond in **1** to the Ru(0) species **2** leading to the Ru(II)–R complex **3**, and subsequent protonolysis with aqueous HCl solution gives the chloro complex **4** with elimination of R–H.

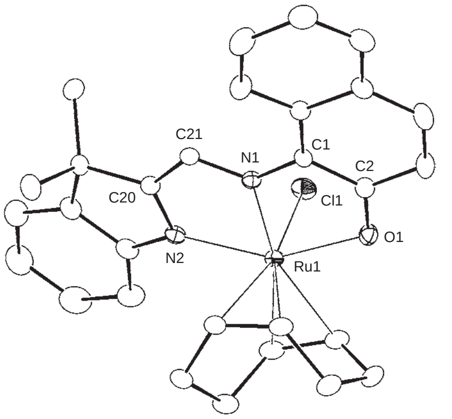
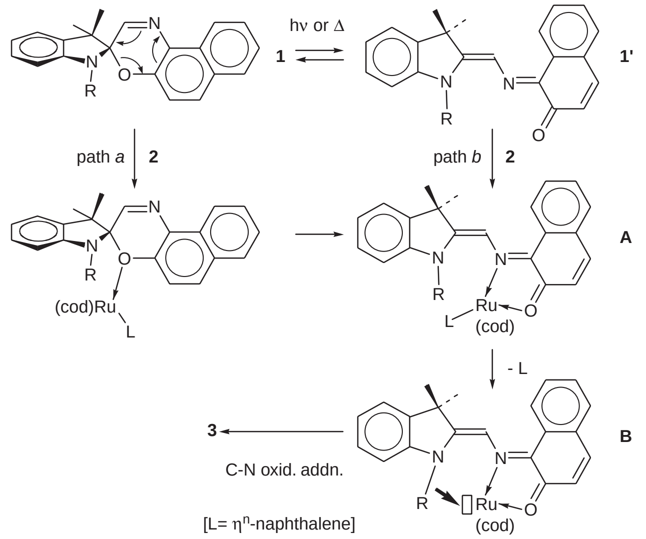


Figure 1. An ORTEP plot of **4** drawn with thermal ellipsoids at the 30% probability level. Selected interatomic distances (in Å): Ru1–Cl1: 2.403(1), Ru1–O1: 2.069(2), Ru1–N1: 2.036(3), Ru1–N2: 2.139(3), Ru1–C(cod): 2.175(4)–2.225(4), C11–N2: 1.423(4), N2–C20: 1.321(4), C20–C21: 1.426(4), C21–N1: 1.323(4), N1–C1: 1.374(4), C1–C2: 1.414(5), C2–O1: 1.304(4).



Scheme 2.

Spironaphthoxazine **1** is a photochromic molecule (Scheme 2).[7] In the spiro form **1**, the two aromatic π systems are separated by the central sp^3-hybridized spiro-carbon atom to show absorptions only in the UV region. UV irradiation, however, causes heterolysis of the central spiro-C–O bond to convert the spiro sp^3-carbon atom into the sp^2-carbon atom (**1′**), through which the two aromatic systems are conjugated with each other to show absorptions in the visible region. Because the backward ring closing process is promoted by visible light irradiation (or a thermal process), the molecule shows photochromic behavior. The structure of the κ^3-chelating ligand moiety in **3** reminds ones of the colored open form **1′**, which suggests two plausible formation mechanisms of **3** shown in Scheme 2. The common κ^2-chelated Ru(0) key intermediate **A** can be formed either by coordination of the oxygen atom in the naphthoxazine moiety in **1** followed by ring-opening and chelation of the resultant azanaphthoquinone form (path *a*) or by coordination of **1′** (path *b*), but path *b* can be eliminated because of **1′** not being detected with the naked eye. Judging from the molecular structure of **4a**, the N,O-coordination in **A** should bring the N–R bond of the indoline moiety to the proximity of the coordinatively unsaturated site of the Ru center in **B**; the arrangement of the N–C bond suitable for the oxidative addition. In accord with this mechanism, (1) a bulky N-substituent (e.g. Et and *i*-Pr) hinders approach of the N–C bond to the active site to result in lower yields, (2) the reactions of **1b** and **1c** are substantially slower than that of **1a**, and (3) no apparent effect of irradiation on the present transformation is noted.[8] It is also notable that stabilization of the organic fragment formed by the oxidative addition (e.g. η^3-allyl coordination) is not always a requisite for a smooth C–N bond activation.

In conclusion, our study reveals that C–N bonds are readily susceptible to oxidative addition to a low valent late transition-metal species under mild reaction conditions, when the C–N bond in the substrate is exposed to the coordinatively unsaturated metal site in an appropriate arrangement. In the present system, the N,O-chelation of the open form (**B**) controls the arrangement of the C–N bond to be cleaved with respect to the active site on the metal fragment.

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References and Notes

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4 Selected spectroscopic data for **3a**: δ_H (C_6D_6) 0.62 (s, Ru–Me), 0.98, 1.10 (s × 2, CMe$_2$), 8.69 (s, HC=N), FD-MS $m/z = 538$ (M$^+$); for **3b**: δ_H (C_6D_6) 0.91 (t, $J = 7$ Hz, Ru–CH$_2$CH$_3$), 1.09, 1.13 (s × 2, CMe$_2$), 8.76 (s, HC=N), FD-MS $m/z = 552$ (M$^+$); for **4**: δ_H (CDCl$_3$) 1.54, 1.65 (s × 2, CMe$_2$), 8.59 (s, HC=N). FD-MS $m/z = 558$ (M$^+$), Anal. Calcd for $C_{29}H_{29}N_2OClRu$ (**4**•(CH$_2$Cl$_2$)$_{1/2}$): C, 58.99; H, 5.04; N, 4.67%. Found: C, 58.72; H, 4.97; N, 4.38%. The CH$_2$ signal of **3b** was overlapped with the other signals, but no hydride signal in high field could be located leading to the characterization as an ethyl complex. Signals for **3c** could not be located owing to a low conversion. A typical procedure for isolation of **4**: To a mixture of **1a** (103 mg, 0.312 mmol) and **2** (314 mg, 0.931 mmol) dissolved in THF (15 mL) was added MeCN (0.2 mL), and the resultant mixture was stirred for 24 h. After removal of the volatiles the residue was dissolved in acetone (10 mL) and cooled at −78 °C. To the resultant solution was added aqueous HCl (12 M, 0.16 mL) dissolved in acetone (16 mL; cooled at −78 °C) over a period of 10 min. Stirring was continued for 4 h at the same temperature and then for 4 h at ambient temperature. The volatiles were removed under reduced pressure, and chromatographic separation of the residue (alumina; eluted with CH$_2$Cl$_2$:MeOH = 50:1) gave the product **4** (140 mg, 0.25 mmol, 81% yield) as green solid.

5 A small amount of a transient species, which could be assigned as a η^6-arene adduct, was detected (δ_H for the coordinated arene ring: ≈5) but finally converted into the most thermodynamically stable chelated species **3a**. E. P. Kündig, *Transition Metal Arene π-Complexes in Organic Synthesis and Catalysis*, Springer, Berlin, **2004**.

6 Crystal data for **4** (at −60 °C): $C_{29}H_{29}N_2OClRu$, fw 558.08, monoclinic, space group $P2_1/c$, $a = 10.979(2)$ Å, $b = 14.621(3)$ Å, $c = 15.617(4)$ Å, $\beta = 102.063(9)°$, $V = 2451.5(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.51$ g·cm^{-3}, $R1 = 0.046$ (refined on F^2) for 4638 data ($I > 2\sigma(I)$) and 423 parameters.

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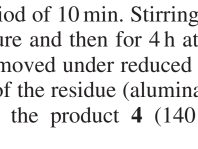
8 One of the reviewers suggested an S$_N$2-type reaction on the zwitterionic intermediate (**C**) formed by interaction of **1′** with **2**, but these mechanisms could not be discriminated by the results obtained so far.



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