

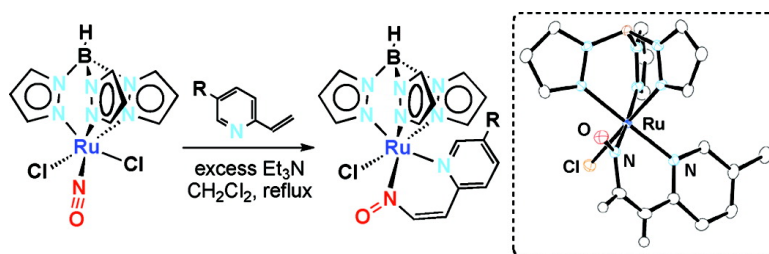
Communication

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N–C Bond Formation of NO Ligands on Ruthenium Complexes with Concurrent Vinylic C–H Activation and Subsequent Proton-Induced Reactivities of the Resulting Nitrosovinyl Species

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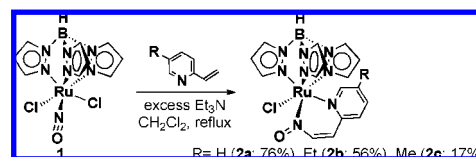
Direct C–H bond functionalizations on transition metals are a promising approach for transformations of simple molecules into valuable organic compounds.¹ These functionalizations consist of combination of C–H bond activation and subsequent coupling reaction, but use of a NO molecule as a coupling partner is rare, and the regulated N–C bond-formation to form nitroso-alkane and -alkene has been a subject of considerable interest over these decades.² Their strategies involve NO insertion reactions^{2a–c} and reactions of M–NO with ketones under strong base,^{2f–h} alkenes,^{2i,j} and alkynes.^{2k} Interesting reports are the nitrosation of aromatic compounds with electron-donating substituents by use of [RuX(bpy)₂(NO)](PF₆)₂ (X = Cl, NO₂; bpy = 2, 2'-bipyridyl).³ In this work, we describe unprecedented N–C coupling of the NO ligand attended by concurrent vinylic C–H activation to form nitrosovinyl derivatives. We have investigated the chemistry of nitrosylrutheniums supported by Tp (= hydrotris(pyrazolyl)borate) ligand⁴ and recently found interesting N–N coupling of NO ligands on dinuclear Tp ruthenium complexes.^{4b} Furthermore, we show here that the resulting nitroso-alkene complexes are chemically versatile and potentially valuable species. These transformations are of significance since exploitation of their reactivities has not been sufficiently developed.⁵

Treatments of TpRuCl₂(NO) (**1**) with 2-vinylpyridines in the presence of excess Et₃N in refluxing CH₂Cl₂ gave the nitrosovinyl complexes TpRuCl{N(=O)–CH=CH–(NC₅H₃R)-κ²} (R = H (**2a**), Et (**2b**), Me (**2c**)) (Scheme 1). The IR spectra of **2** exhibit disappearance of a characteristic ν(N=O) band. The MS spectra show the parent molecular ion signals, and furthermore the structure was confirmed by an X-ray crystallographic analysis of **2c** (Figure S1, Supporting Information). The structure of **2c** verified the presence of a nitrosovinylpyridine chelate in which two nitrogen atoms of nitroso and pyridyl groups are coordinated to the central ruthenium atom.

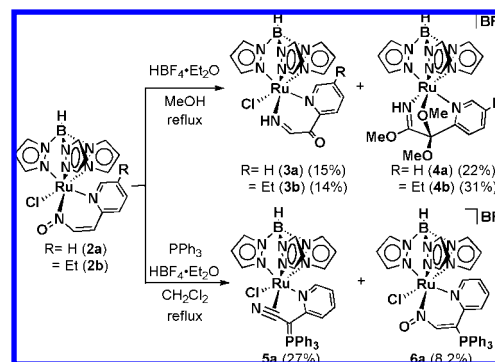
The observed N–C bonding indicates occurrence of the vinylic C–H bond activation. Concerning vinylic C–H activation, there are literature-described five-membered cycloruthenation reactions of 2-vinylpyridine⁶ and vinyl N-heterocyclic carbene (NHC),⁷ where initial coordination of pyridine or NHC group has been proposed. Thus, we presume that the formation mechanism of **2** begins with coordination of the pyridine nitrogen and dissociation of the chloride ion. Intramolecular activation of a vinyl C–H bond, accompanying formal HCl elimination with the aid of the base Et₃N, should give a cyclometalated intermediate, followed by insertion of the NO ligand into the resulting Ru–alkenyl bond to afford the six-membered ruthenacycle **2**.^{8,9}

The scarcity of the isolated nitrosovinyl complexes prompted us to investigate the chemical reactivities of **2**. Treatments of **2a** and **2b** with HBF₄·Et₂O in refluxing MeOH for 2 h afforded the ketoimine isomers TpRuCl{NH=CH–C(O)–(NC₅H₃R)-κ²} (R =

Scheme 1



Scheme 2

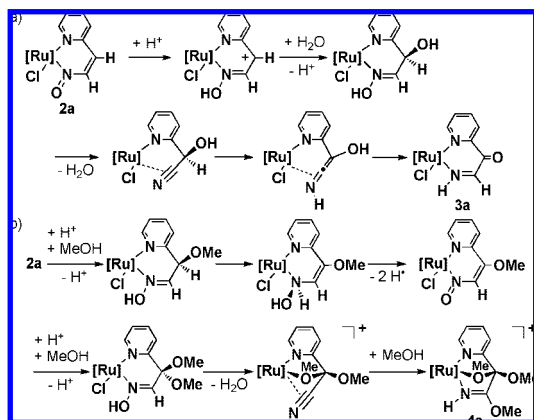


H (**3a**), Et (**3b**)) and the alcohol-incorporated complexes [TpRu{NH=C(OMe)–C(OMe)₂–(NC₅H₃R)-κ³}]BF₄ (R = H (**4a**), Et (**4b**)) (Scheme 2).

Complex **3** was characterized by spectral data and elemental analysis. In the EI-MS spectra, the parent molecular ion signals of **3** indicate the mass value remains unaltered during their formation. The structure of **3b** was confirmed by an X-ray diffraction study (Figure S2, Supporting Information). In the nitrosovinylpyridine-derived bidentate ligands, the nitroso group is transformed into the imine group on ruthenium and simultaneously the keto group appears. On the other hand, isolation of **4** indicates incorporation of solvent molecules (MeOH). The ¹H NMR spectra of **4** exhibit a characteristic broad NH proton and three inequivalent methoxy signals. Finally, the structure was revealed by an X-ray crystallographic analysis of **4a** (Figure S2), in accord with its FAB-MS spectral data. In the iminotri(methoxy)ethyl substituent on the pyridine, two MeO groups are linked to 1'-C carbon and the remaining MeO group constitutes the iminoester form. Conversion from **3a** to **4a** was not observed when a MeOH solution of **3a** was refluxed under acidic condition.

Isolation of **3** and **4** indicates significant complexity in these reaction mechanisms. To obtain a clue to the mechanism, protonation of **2a** in the presence of PPh₃ as an alternative nucleophile was carried out. From the reaction with PPh₃, the ((phosphonio)cyanomethanidyl)pyridine complex TpRuCl{η²-N≡C–C(=PPh₃)-(NC₅H₄)-κ} (**5a**) and the {nitroso(phosphonio)ethenyl}pyridine complex

Scheme 3



[TpRuCl{N(=O)–CH=C(PPh₃)–(NC₅H₄)–κ²}]BF₄ (**6a**) were isolated in 27% and 8.2% yields, respectively (Scheme 2).¹⁰ Complex **5a** and **6a** were characterized by spectral data and elemental analyses, and moreover their structures were determined by X-ray diffraction studies (Figure S3 and S4, Supporting Information). The remarkable feature is the presence of the π -coordinated C≡N group and phosphorus ylide moiety in **5a**. In the ¹³C {¹H} NMR spectrum of **5a**, the characteristic phosphorus ylide carbon atom resonated at $\delta = 42.1$ as a doublet ($J_{PC} = 125$ Hz). On the other hand, for **6a**, although insufficient quality of the crystals obtained and the crystallographic disorder between two coordination sites of the N(=O)–C moiety and Cl atom cause the uncertainty of the metric parameters, the linkage of PPh₃ with the 1'-C carbon in the nitrosoethenylpyridine was established.

Concerning the reaction mechanism to **3** and **4**, initial protonation on the N=O oxygen atom was considered.^{5c} Protonation of **2** in CH₂Cl₂ (nonalcoholic solvent) afforded an uncharacterized red solid, but presumable as the protonated species. Actually, treatment of the separated red solid with PPh₃ gave **5a** and **6a**. For the formation of **3** in MeOH, protonation of the N=O oxygen formed aldoxime and also induced nucleophilic addition of adventitious H₂O molecule on the 1'-C carbon atom (Scheme 3a), followed by dehydration of the aldoxime to give a nitrile intermediate¹¹ such as **5a**, which is converted to the ketenimine form¹² and finally to the ketoimine species **3**. On the other hand, for the formation of **4**, the oxidative process would be essential, and one probable elementary process is hydroxylamine oxidation.¹³ With this oxidative process in mind, a reasonable mechanism is described in Scheme 3b. In analogy with the formation mechanism of **3**, addition of the MeOH nucleophile on the 1'-C carbon atom would also occur. In competition with dehydration process of the aldoxime to the nitrile intermediate, hydroxylamine intermediate would be generated by 1,3-H shift, followed by some oxidative process to give the nitroso(methoxy)ethenylpyridine species such as **6a**, although the oxidizing species is presently unclear. Once again proton-induced MeOH addition on the 1'-C carbon atom, dehydration similar to that above-described, and subsequent further MeOH addition to the nitrile moiety¹⁴ would afford **4**.

In conclusion, we have obtained the chemically versatile nitrosovinyl complexes **2** from one-pot reactions of **1** with 2-vinylpyridines, through vinylic C–H activation and N–C bond formation of the NO ligands. Furthermore, we found novel transformation of the nitrosovinyl complexes **2** by protonation in refluxing alcohol to afford unusual alcohol-incorporated products **4** concomitant with

the ketoimine isomers **3**, and their formation mechanisms are revealed from the comparative investigation of an alternative proton-induced PPh₃ addition reaction.

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Supporting Information Available: Full experimental and spectroscopic details for all new compounds, ORTEP drawing, and X-ray structural data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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