Facile Direct Insertion of Nitrosonium Ion (NO^+) into Ruthenium–Aryl Bond

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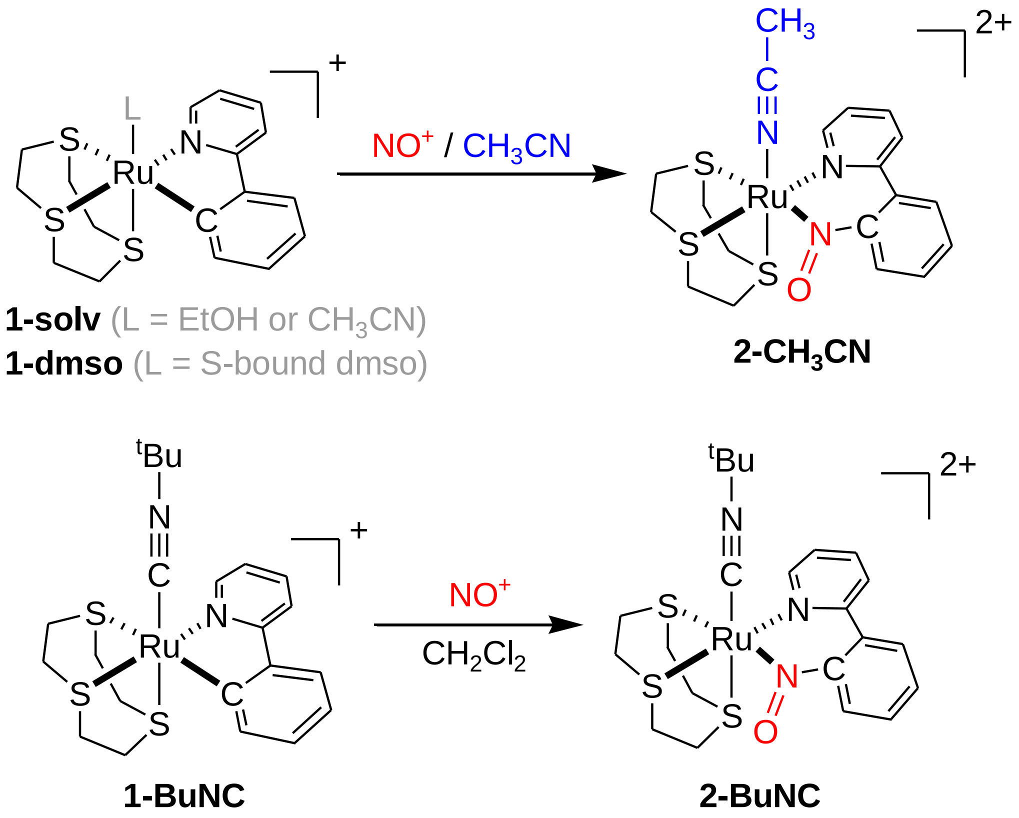
Summary: An insertion reaction of nitrosonium ion (NO^+) into the metal–carbon bond of cyclometalated ruthenium(II) complexes is presented. Experimental evidence support a bimolecular direct NO^+ insertion into the metal–carbon bond (i.e. $M–R + NO^+ \rightarrow [M–N(=O)–R]^+$) but not an intramolecular migratory insertion (i.e. $R–M–(NO) + L \rightarrow L–M–N(=O)R$) as the reaction mechanism. Theoretical calculations suggest that the direct NO^+ insertion into the M–C bond may be rationalized as a frontier orbital interaction between the [Ru–aryl]-dominated HOMO of the Ru(II) complexes and the LUMO of the NO^+.

The discovery that nitric oxide plays many fundamental physiological roles arouses the interest in the structures, electronic properties, and reactivities of metal–nitrosyl complexes.[1-13] The chemistry between NO and organometallic complexes, especially reactions that lead to new carbon–nitrogen bond formations, is of considerable attention because organic nitroso compounds have been demonstrated as a class of attractive electrophiles in many carbon–nitrogen and/or carbon–oxygen bond forming reactions.[14-20] In the past decades, investigations on the insertion of NO into metal–alkyl and metal–aryl bonds to form *C*-nitroso complexes provided insightful results for the development of metal-mediated organic transformation reactions,[21-36] and the alkyl/aryl moiety migration to the coordinated NO ligand, i.e. R–M–(NO) + L → L–M–N(=O)R, has been demonstrated to be a critical step for the carbon–nitrogen bond formation. Nitrosonium ion (NO^+), a close relative of NO, is known to react substitutionally with metal complexes to give metal–nitrosyl systems,[8,37-44] although there are several examples proposing that NO^+ can insert into metal–carbon bonds in an intermolecular fashion.[25-27,31] We herein present a systematic investigation on the reaction between NO^+ and 2-phenylpyridine anion (phpy)-ligated cyclometalated ruthenium(II) complexes, which demonstrates for the first time that NO^+ inserts into a Ru(II)–$aryl_{phpy}$ bond to give 2-(2-nitrosophenyl)pyridine (NO-phpy)-coordinated complexes. Experimental evidence support a direct bimolecular NO^+ insertion mechanism, i.e. M–R + NO^+ → $[M–N(=O)–R]^+$, but not an intramolecular migratory insertion mechanism for the insertion reactions in this work. Moreover, theoretical calculations reveal that the direct NO^+ insertion into the Ru–C bond may be rationalized as a frontier orbital interaction between the [Ru–aryl]-based HOMO of the Ru(II) complexes and the LUMO of the NO^+.

Unlike many literature examples, non-NO-ligated complexes $[Ru(phpy)([9]aneS3)(L)]^+$ ([9]aneS3 = 1,4,7-trithiacyclononane) were employed to react with NO^+ in this study; this can reduce ambiguity in mechanism evaluations. When excess $[NO][BF_4]$ (5-fold) was added to $[Ru(phpy)([9]aneS3)(solv)]^+$ (**1-solv**; solv = CH_3CN or EtOH) in CH_3CN under argon at room temperature, the color of the solution changed from yellow to dark red immediately. The dark red product isolated (85% yield) was characterized to be $[Ru(NO\text{-}phpy)([9]aneS3)(CH_3CN)]^{2+}$ (**2-CH$_3$CN**; NO-phpy = 2-(2-nitrosophenyl)pyridine) by ^1H and ^{13}C NMR spectroscopies, X-ray crystallography and elemental analysis (Scheme 1). This reactivity is different from that for other ruthenium(II) complexes that react with NO^+ substitutionally to give the ligand-substituted Ru-nitrosyl products.[37,38,40,41,43] Reaction between the S-bound dmso complex $[Ru(phpy)([9]aneS3)(dmso)]^+$ (**1-dmso**) and $[NO][BF_4]$ in CH_3CN also gave **2-CH$_3$CN** in 80% yield.

Scheme 1.



The X-ray crystal structure for [**2-CH$_3$CN**](PF$_6$)$_2$•CH$_3$CN represents the first example of NO-phpy-ligated metal complex, where the NO-phpy behaves as a bidentate ligand via the two N atoms (Figure 1). The Ru–N$_{NO}$ distance (1.936(2) Å) is significantly shorter than those for Ru–N$_{py}$ and Ru–N$_{acetonitrile}$ (2.101(2) and 2.060(2) Å, respectively), and is comparable to the Ru–N$_{NO}$ distance in a similar ruthenium complex [TpRuCl{N(=O)–CH=CH–(NC$_5$H$_3$Me)-κ^2}] (1.9069(15) Å).[34] The angles around the N$_{NO}$ atom are consistent with sp^2 hybridization. The N$_{NO}$–O bond distance of 1.236(3) Å reveals the double-bond character of the NO moiety, whereas the N$_{NO}$–C(9) bond is essentially single (1.437(3) Å). Note that the phenyl and pyridyl rings are not coplanar (angle between the planes = 26.1°), which is different from those in [**1-dmso**](ClO$_4$) (3.7°) and [Ru(phpy)([9]aneS3)(^{t}BuNC)](PF$_6$) ([**1-BuNC**](PF$_6$), 6.8°).

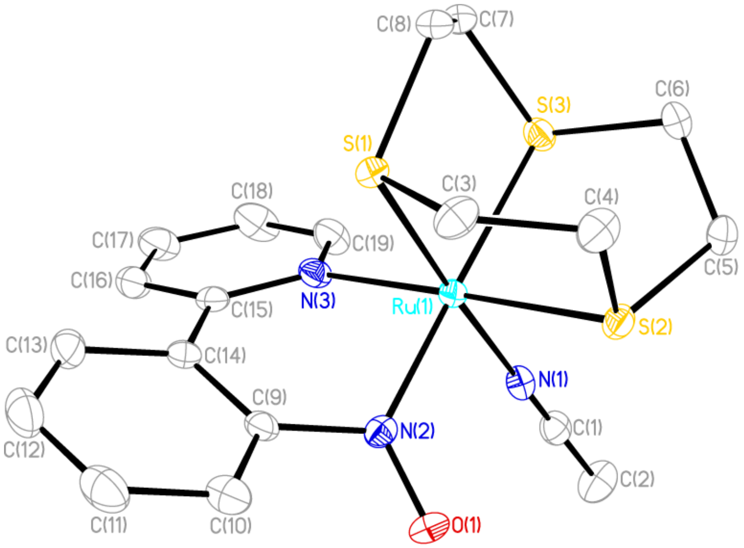
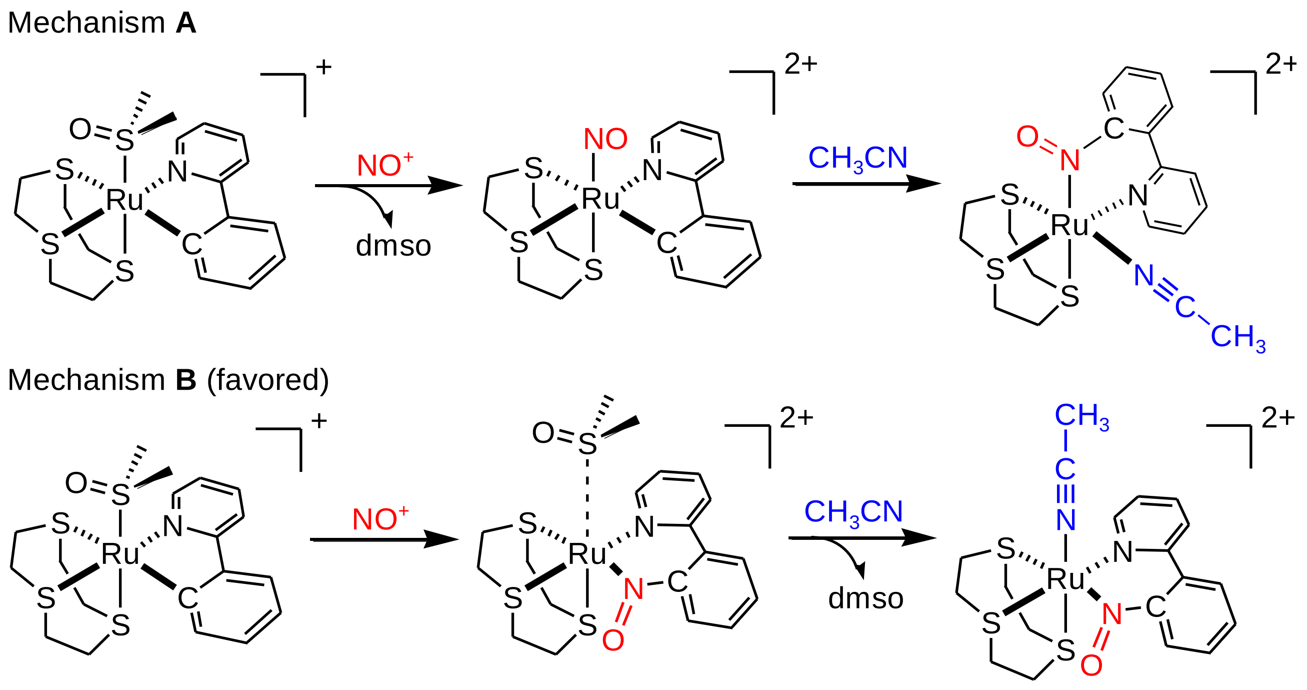


Figure 1. Perspective view of the cation in [Ru([9]aneS3)(NO-phpy)(CH_3CN)](PF_6)$_2$ (thermal ellipsoids are drawn at 50% probability). Selected bond lengths (Å) and angles (deg): Ru(1)–N(1) 2.060(2), Ru(1)–N(2) 1.936(2), Ru(1)–N(3) 2.101(2), Ru(1)–S(1) 2.3223(6), Ru(1)–S(2) 2.3243(6), Ru(1)–S(3) 2.3795(6), N(2)–O(1) 1.236(3), N(2)–C(9) 1.437(3), Ru(1)–N(2)–C(9) 118.73(15), Ru(1)–N(2)–O(1) 125.15(16).

The mechanism for the formation of **2-CH$_3$CN** is of fundamental interest. Scheme 2 depicts two plausible reaction pathways: (i) formation of nitrosyl complex [Ru(phpy)([9]aneS3)(NO)]$^{2+}$ followed by aryl group migration to the coordinated NO (Mechanism **A**); (ii) direct intermolecular NO$^+$ insertion into the Ru–C bond (Mechanism **B**). Although migration of bound alkyl/aryl moiety to coordinated NO in metal–nitrosyl complexes are well-documented and supported by kinetic and theoretical studies,[21-24,28,30,32,35,36] experimental findings suggest that mechanism **A** is not a favorable pathway for the reactions in this work. Firstly, the Ru–S bond in **1-dmso** is so strong that the bound dmso cannot be substituted by CH_3CN or excess ^{t}BuNC in refluxing CH_3CN for two days, and no exchange reaction of **1-dmso** with d^6-dmso has been observed for 1 week; these suggest that the formation of [Ru(phpy)([9]aneS3)(NO)]$^{2+}$ via ligand substitution is unlikely to occur. Similar argument can be made from the reaction between **1-BuNC** and [NO][BF_4] in CH_2Cl_2, which gave **2-BuNC** as the only product (Scheme 1). In addition, *in situ* infrared (IR) monitoring of the reactions showed no sign of formation of the [Ru(phpy)([9]aneS3)(NO)]$^{2+}$. Although partial liberation of the [9]aneS3 followed by NO$^+$

coordination and then aryl group migration seems to be a possible alternative mechanism, one should note that the coordination sphere of the complexes **1-solv/dmso/BuNC** would suffer from drastic structural changes in order to give **2-CH$_3$CN** or **2-BuNC** as the reaction product: (1) if the coordinated NO were *trans* to the phenyl ring, the phpy ligand would have to flip along the Ru–N bond by ca. 180° in order to perform the aryl migration; (2) if the coordinated NO were *trans* to the pyridyl ring, the migration would not only involve the phenyl ring but the pyridyl ring as well; (3) if the coordinated NO were *trans* to the solv/dmso/BuNC, large coordination sphere reorganization (especially for the [9]aneS3) would be required to keep the [9]aneS3 facially coordinating to the Ru(II) center in the final products, this point also holds for situations (1) and (2). Therefore, migratory insertion involving partial liberation of the [9]aneS3 is unlikely to occur.

Scheme 2.



To explore the feasibility of mechanism **B**, the reaction between **1-BuNC** and NO$^+$ in CH$_3$CN was studied by stopped-flow technique. The kinetic experiments revealed a second-order rate law, and the measured second-order rate constant (k_2) at 298 K is $(2.153 \pm 0.024) \times 10^3$ dm^3 mol^{-1} s^{-1}. Figure 2 depicts the spectrophotometric changes when **1-BuNC** (2.7×10^{-4} M) was mixed with [NO][BF$_4$] (1.7 ×

10^{-3} M) at 298 K, which shows that well-defined isosbestic points at 289, 340, and 368 nm were maintained throughout the reaction. The final spectrum is the same as that for **2-BuNC**. This suggests that the formation of **2-BuNC** from **1-BuNC** and NO^+ is a clean reaction.

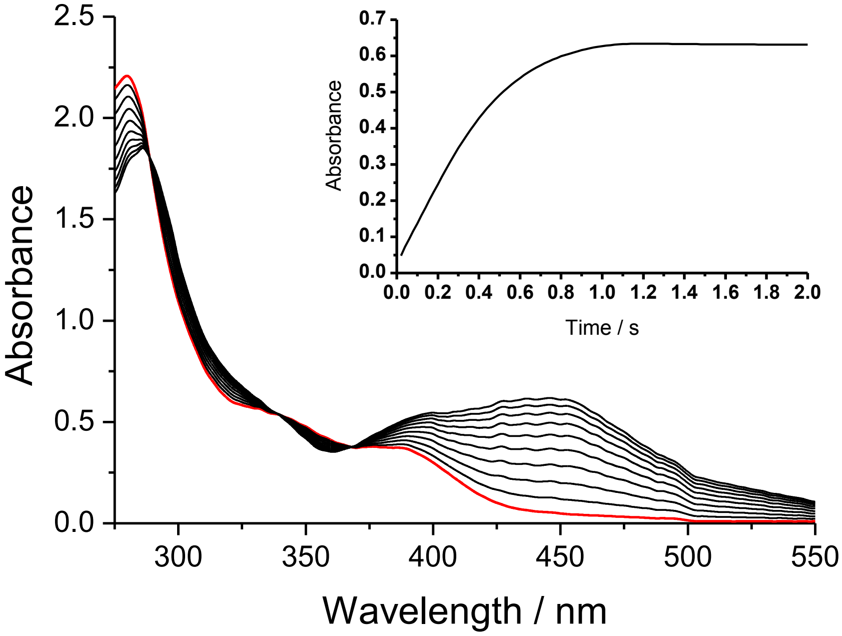


Figure 2. Spectrophotometric changes for the reaction between **1-BuNC** (2.7×10^{-4} M) and $[NO][BF_4]$ (1.7×10^{-3} M) in CH_3CN at 298 K (spectra collected at 0.05 s intervals using a stopped-flow spectrophotometer under argon; initial trace shown in red). The inset shows the absorbance-time trace at 450 nm for the reaction between **1-BuNC** (2.3×10^{-4} M) and $[NO][BF_4]$ (1.4×10^{-3} M) in CH_3CN at 298 K.

Since NO^+ is a well-known 1-electron oxidant, the possibility for the insertion reaction proceeds via an outer-sphere electron transfer from **1-L** to NO^+ with subsequent recombination of the oxidized **1-L**$^+$ and NO· should not be excluded. To investigate the possibility of such pathway, excess radical trap (2,2,6,6-tetramethyl-piperidin-1-yl)oxyl (TEMPO) was introduced into the solvent prior to the addition of **1-L** and NO^+. However, it was observed that the presence of TEMPO did not quench the reaction between **1-L** and NO^+, suggesting that the insertion reaction may not proceed in a way as aforementioned.

Density functional theory (DFT) using B3LYP was employed to study the reaction of **1-dmso** and NO^+ in gas phase to discern the key features of the proposed direct NO^+ insertion mechanism which are difficult or impossible to be determined experimentally. The structure of the transition state (**TS**) connecting the reactants {**1-dmso** + NO^+} and product $[Ru(NO\text{-}phpy)([9]aneS3)(dmso)]^{2+}$ (**2-dmso**) was located by using the quadratic synchronous transit (QST) calculations,[45] and was confirmed by intrinsic reaction coordinate (IRC)[46] scan and frequency calculation (one imaginary frequency was found). The structure of **TS** is depicted in Figure 3a. The calculated $Ru–S_{dmso}$ distance in **2-dmso** (2.42 Å) is longer than that in **1-dmso** (2.33 Å), revealing that the $Ru–S_{dmso}$ bond is weakened upon NO^+ insertion; this is consistent with the experimental finding that **2-CH_3CN** rather than **2-dmso** was isolated in the reaction of **1-dmso** and NO^+ in CH_3CN. Regarding the energetics of the direct NO^+ insertion into **1-dmso**, the activation energy was calculated to be 13.6 kcal mol^{-1}, which is more than two times lower than that required for splitting **1-dmso** into $[Ru(phpy)([9]aneS3)]^+$ and dmso (32.7 kcal mol^{-1}). Thus direct NO^+ insertion (Mechanism **B**) is a more facile reaction pathway compared with Mechanism A, which requires $Ru–S_{dmso}$ bond cleavage.

Our DFT calculations also provide a clue to understand why NO^+ inserts into the Ru–C bond of the cyclometalated Ru(II) complexes instead of undergoes electrophilic aromatic substitution at other positions. Partitioning the molecular orbital composition of **TS** into the **1-dmso** and NO^+ fragments reveals that the major interaction between **1-dmso** and NO^+ in **TS** is the [HOMO(**1-dmso**) + $\pi^*(NO^+)$] interaction, as depicted in the surface plot of the HOMO for **TS** (Figure 3b). The HOMO of **1-dmso** is mainly contributed from the Ru(II) and the phenyl ring (Figure 3c). Importantly, the Ru–C bonding interaction in the HOMO is of π^* symmetry, which matches the symmetry of the $\pi^*(NO^+)$, as depicted in Figure 3b. Thus the direct NO^+ insertion into the Ru–C bond may be rationalized as an orbital symmetry controlled interaction between the [Ru–aryl]-dominated HOMO of the Ru(II) complexes and the LUMO of the NO^+. Indeed, the same rationalization also holds for **1-BuNC**: it reacts with NO^+ to give **2-BuNC** and at the same time its HOMO has the correct symmetry to interact with the $\pi^*(NO^+)$ (Figure 3d).

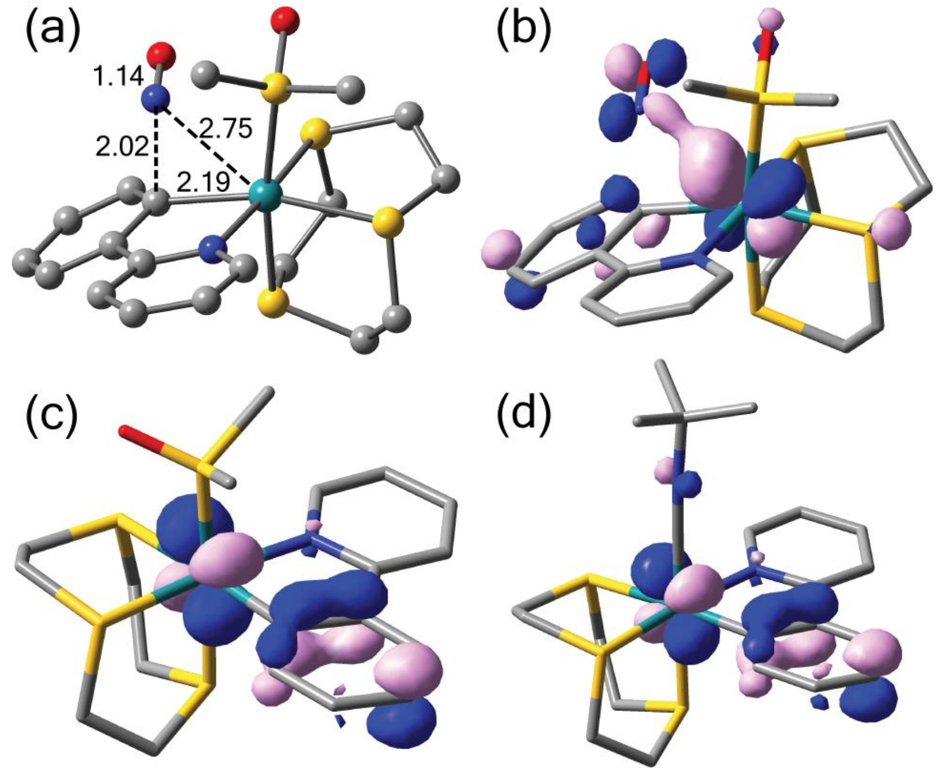


Figure 3. (a) Optimized structure and selected bond distances (Å) for TS. (b)–(d) HOMO surfaces for TS, 1-dmso, and 1-BuNC (surface isovalue = 0.06 au).

In summary, we have demonstrated an insertion reaction of NO^+ into the Ru–aryl bond of some cyclometalated ruthenium(II) complexes. Experimental evidences support a direct bimolecular NO^+ insertion mechanism and discount an intramolecular migratory insertion pathway. Furthermore, the selective nitrosation at the Ru–C bond can be rationalized as a frontier orbital interaction between the [Ru–aryl]-based HOMO of the Ru(II) complexes and the LUMO of the NO^+. This work highlights the opportunity for metal complexes mediated selective nitrosation of aromatic compounds, and further studies of this reaction will focus on extending the scope of this approach to other synthetically useful transformations.

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Supporting Information Available: Experimental procedures and analytical data for all the complexes; crystallographic information files (CIF) for [**1-dmso**](ClO_4), [**1-BuNC**](PF_6), and [**2-CH$_3$CN**](PF_6)$_2$•CH_3CN; details of theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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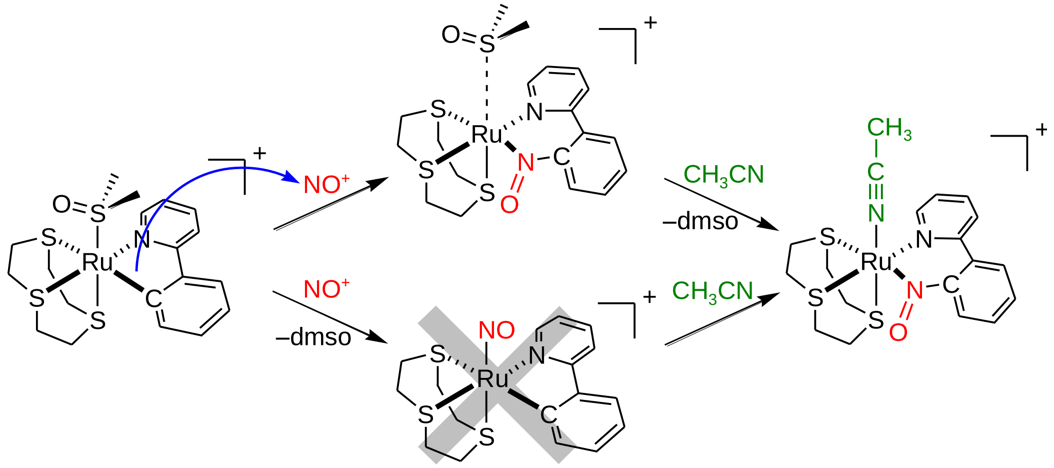

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