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Reactivity of a Methoxido Ruthenium Complex bearing a Pincer-type Bis(carbene) Ligand toward Thiocyanate, Carbon disulfide, and Isothiocyanate


Abstract: Thiocyanate linkage isomers and two insertion complexes were prepared from a methoxido ruthenium complex bearing a 2,6-bis(3-tert-butylimidazol-2-ylimidene)pyridine (CNC) and a bipyridine ligands. In the linkage isomers obtained from the substitution reaction, a linear N-bound and a bent S-bound isomers were crystallographically determined, and the equilibrium between them at elevated temperature was revealed. On the other hand, in the reactions with carbon disulfide CS2 and phenyl isothiocyanate PhNCS, the S=C bond was inserted into the Ru–OMe bond, and the resulting ligands are bound to the ruthenium by sulfur.

Introduction

Recently, researchers have shown an increased interest in pincer complexes which consist of a pincer-type ligand and a metal center.[1] Of the pincer-type ligand, NHC (N-heterocyclic carbene)[2] has received considerable attention because of its superior σ-donation. We have reported preparations and reactivity of pyridine-based bis(carbene) complexes (CNC complexes),[3] including interesting capture of CO2 from air by ruthenium complexes.[3a] In this fixation of atmospheric carbon dioxide, intermediacy of a methoxido complex [(CNC)Ru(bpy)(OMe)]PF6 (1) was revealed. The observation of the reactive methoxido complex motivated us to investigate its reactivity, in particular, toward sulfur-containing reagents (ammonium thiocyanate NH4SCN, carbon disulfide CS2, and phenyl isothiocyanate PhNCS). To the best of our knowledge, interactions between the CNC complexes and sulfur-containing reagents have little explored. This research would provide a fundamental understanding of mechanism in catalytic reaction such as organotransformation reactions.

Results and Discussion

The reaction of [(CNC)Ru(bpy)(OMe)]PF6 (1) with NH4SCN in refluxing methanol for 2h afforded a mixture of two compounds (ca. 1:1 ratio) as determined by 1H NMR spectrum (Scheme 1).

Separation of these two compounds was successful by column chromatography with a silica gel. The ESI-MS spectra of the two compounds show the same signals at m/z 639.29 ([M-PF6]+), indicating linkage isomers. These compounds were also prepared from the reaction between a chlorido complex [(CNC)Ru(bpy)Cl]PF6 and NH4SCN. Finally, these structures were confirmed by the X-ray crystallographic analysis.

The column chromatographic purification afforded [(CNC)Ru(bpy)(NCS)]PF6 (2-N) from the first band and [(CNC)Ru(bpy)(SCN)]PF6 (2-S) from the second band. The X-ray crystal structures of 2 are shown in Figure 1. In both structures, the meridional CNC and bipyridine ligands are bound to the Ru atom, and the distorted octahedral geometry is completed by the thiocyanato ligand. As a distinct difference, a linear NCS form in

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2-N (Ru(1)–N(8)–C(30) = 168.94(19)°) and a bent SCN form in 2-S (Ru(1)–S(1)–C(30) = 104.76(8)°) are observed. The Ru–NCS distance (Ru(1)–N(8)) is 2.043(2) Å in 2-N and the Ru–SCN distance (Ru(1)–S(1)) is 2.4248(6) Å in 2-S are similar to those in the corresponding isomers of [(terpy)Ru(tbbpy)(thiocyanato)]SbF6[5] (terpy = 2,2′;6′,2″-terpyridine, tbbpy = 4,4′-di-tert-butyl-2,2″-bipyridine), where both linkage isomers have been crystallographically determined.

There is little difference in the structure of the thiocyanato moiety in 2-N and 2-S (N(8)–C(30) = 1.162(3) Å (2-N), 1.162(3) Å (2-S); S(1)–C(30) = 1.642(4) Å (2-N), 1.681(2) Å (2-S); S(1)–C(30)–N(8) = 178.5(2)° (2-N), 177.2(3)° (2-S)). The 1H NMR spectroscopy revealed that heating of a DMF-d6 solution of 2-N at 120°C for 2h gave a mixture of 2-N and 2-S at ca. 1:0.13 ratio, though the isomerisation did not proceed at room temperature. Heating did not affect the ratio of the two isomers. These results indicate the existence of equilibrium in the mixture. The 2-S isomer is thermodynamically unfavorable, which is the same trend as [(terpy)Ru(tbbpy)(thiocyanato)]SbF6[6]. The steric hindrance between a bent SCN ligand and two tBu moieties on the CNC ligand would be attributed to the lower stability of 2-S isomer.

On the other hand, in the reaction with CS2 and PhNCS, insertion reactions were observed (Scheme 2). Treatment of [(CNC)Ru(bpy)(OMe)]PF6 (1) with CS2 and PhNCS gave rise to [(CNC)Ru(bpy)(SC(S)OMe)]PF6 (3) and [(CNC)Ru(bpy)(SC(NPh)OMe)]PF6 (4), respectively. A ν(C=S) stretching band at 1620 cm−1 is observed in the IR spectrum of 3. The ESI-MS spectra of 3 and 4 exhibit the molecular ion signals at m/z 688.1(3) and m/z 747.3 (4), which show Cs2 and PhNCS mass increments, respectively, as compared to [(CNC)Ru(bpy)(OMe)]+, indicating their incorporation. Although reaction of 1 with tBuNCS proceeded, isolation of the products was unsuccessful. The molecular structures of 3 and 4 were determined by the X-ray crystallographic analyses (Figure 2 and 3).

Scheme 2. Insertion reactions of 1 with CS2 and PhNCS.

The μ1-coordinated xanthato ligand in 3 and monodentate sulfur-coordination in 4 are revealed, along with coordination of the CNC and bpy ligands to the Ru atom. The sulfur-coordination in 4 indicates that the S=C bond rather than N=C was inserted into the ruthenium–methidoxo bond. Similar insertion reactions have been observed in other alkoxido-metal complexes,[8] probably due to the HSAB principle, with the soft ruthenium center preferring the softer sulfur atom. The Ru–S bond length of 3 (2.3776(7) Å) is shorter than that of 4 (2.4279(11) Å). The former is similar to that of a monodentate xanthato ruthenium complex [Ru(CO)(PEt3)2(η1-S2COiPr)(η2-S2COEt)][9] (2.3915(8) Å) [7]. The S–C distances for the coordinated and uncoordinated sulfur atoms of the xanthato ligand of 3 (1.7148(16) and 1.6694(19) Å, respectively) are almost identical to the distances found in trans-[Ru(CO)(PEt3)2(η1-S2COiPr)(η2-S2COEt)][7] (2.3915(8) Å) [7].
complex 4, the bond distances S(1)–C(30) (1.741(4) Å) and N(8)– C(30) (1.285(5) Å) are consistent with single and double bonds, respectively. The planarity of the sulfur-coordinated ligands in 3 and 4 is supported by the sum of angles (360º) around the C(30).

The insertion reactions giving 3 and 4 should proceed via a four-membered ring transition state without requirement of a binding site for the substrate prior to insertion. In sharp contrast to this, the formation mechanism of a xanthato complex [TtRu(PPh3)3(S2COCH3)] is a MeOH attack on a coordinated CS2 ligand.

Conclusions

We reported reactivity of the methoxydibrid ruthenium complex having the pyridine-based bis(N-tet-butyl substituted N-heterocyclic carbene) (CNC) and a bipyridine toward the sulfur-containing heterocarbenes. In the reaction with NH2SCN, thioacetylene ligand isomers from the substitution reaction have been obtained, structures of which (linear NCS and bent SCN) were determined by the X-ray crystallographic analyses. In contrast, the product of insertion of isothiocyanate into ruthenium–alkoxido bond was characterized by elemental analyses (C, H, and N) were performed on a Perkin Elmer 2400II elemental analyzer. Infrared spectra in KBr pellets were obtained on a Varian Gemini-300 and a JEOL JNM-AL-400 spectrometers. 1H and 13C{1H} NMR chemical shifts are quoted with respect to the solvent signals.

Experimental Section

Materials and General Procedures: All reactions were carried out under N2 or Ar unless otherwise noted, and subsequent work-up manipulations were performed in air. The starting complex ([CNC]Ru(bpy)(OMe))PF6 (1) was prepared according to the previously reported method. Organic solvents and all other reagents were commercially available and used without further purification. NMR spectra in acetone-d6 were recorded on a Varian Gemini-300 and a JEOL JNM-AL-400 spectrometers. 1H and 13C{1H} NMR chemical shifts are quoted with respect to the solvent signals. Infrared spectra in KBr pellets were obtained on JASCO FT-IR-4100 spectrometer. Electrospray mass spectroscopies (ESI-MS) were carried out on a Waters ACQUITY SQD MS system. Elemental analyses (C, H, N) were performed on a Perkin Elmer Elan 2400II elemental analyzer.

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integrated using a Rigaku CrystalClear program package, and the data sets were corrected for absorption using a REQAB program.

The calculations were performed with a CrystalStructure software package. The structures were solved by direct methods, and refined on F² by the full-matrix least squares methods. For 3-ether and 4-ether, a diethyl ether crystallization solvent is included. Therefore, a SQUEEZE/PLATON technique was applied. Anisotropic refinement was applied to all non-hydrogen atoms. Hydrogen atoms for all structures were put at calculated positions. Full-matrix least squares methods. For 2-N 2-S 2-S contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgements

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Keywords: Bis(carbene) ligand • Linkage isomers • Insertion • Methoxide • Ruthenium


Thiocyanate linkage isomers and two insertion complexes were prepared from a methoxido ruthenium complex bearing a pyridine-based bis(carbene) (CNC) and a bipyridine ligands. In the linkage isomers obtained from the substitution reaction, a linear N-bound and a bent S-bound isomer were crystallographically determined. On the other hand, in the reactions with carbon disulfide CS₂ and phenyl isothiocyanate PhNCS, the S=C bond was inserted into the Ru–OMe bond.