Ligand Exchange Reaction on a Ru(II)−Pheox Complex as a Mechanistic Study of Catalytic Reactions

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ABSTRACT: A ligand exchange of one of the acetonitrile ligands of the (acetonitrile)₄Ru(II)−phenyloxazoline complex (Ru(II)−Pheox) by pyridine was demonstrated, and the location of the exchange reaction was examined by density functional theory (DFT) calculations to study the mechanism of its catalytic asymmetric reactions. The acetonitrile was smoothly exchanged with a pyridine to afford the corresponding (pyridine)(acetonitrile)₃Ru(II)−Pheox complex with a trans orientation (C−Ru−N(pyridine)) in a quantitative yield, and the complex was analyzed by single-crystal X-ray analysis. DFT calculations indicated that the most eliminable acetonitrile is the trans group, which is consistent with the X-ray analysis. The direction of the ligand exchange is thus determined on the basis of the energy gap of the ligand elimination instead of the stability of the metal complex. These results suggested that a reactant in a Ru=Pheox-catalyzed reaction should approach trans to the C−Ru bond to generate chirality on the Ru center.

1. INTRODUCTION

Development of transition-metal-catalyzed carbene transfer reactions, such as cyclopropanation of a π bond and C−H insertion reactions, have recently attracted great interest.1 Recently, we reported that (acetonitrile)₄Ru(II)−phenyloxazoline complex (Ru(II)−Pheox), which has a unique C₁-symmetric structure, is an efficient catalyst for carbene transfer reactions. We successfully demonstrated that a series of Ru(II)−Pheox complexes could promote catalytic asymmetric intra- and intermolecular cyclopropanations of a wide variety of olefins and asymmetric Si−H insertion reactions with diazo compounds to give the desired products in high yields with high enantioselectivities.2 On the other hand, details on the stability of the metal complex. These results suggested that a reactant in a Ru=Pheox-catalyzed reaction should approach trans to the C−Ru bond to generate chirality on the Ru center.

2. RESULTS AND DISCUSSION

The ligand exchange from acetonitrile to pyridine on Ru(II)−Pheox proceeded smoothly in the presence of pyridine (1 equiv) in CH₂Cl₂ at room temperature, and the desired Ru(II)−Pheox complex with one pyridine ligand and three acetonitrile ligands was obtained in quantitative yield. Surprisingly, compared with the (acetonitrile)₄Ru(II)−Pheox complex, (pyridine)(acetonitrile)₃Ru(II)−Pheox has a high crystallinity and pure single crystals were obtained. The results of single-crystal X-ray analysis of the (pyridine)(acetonitrile)₃Ru(II)−Pheox complex are shown in Figure 1 and Tables S1−S6. The site selectivity of the elimination of acetonitrile and coordination of pyridine might be affected by the trans effect of the C−Ru−ligand and proceed selectively at (A). On the basis of the experimental results, we examined the stability of various Ru(II)−Pheox complex with ligands by density functional theory (DFT) using the Gaussian 16 program.3 The LanL2DZ basis set for Ru and 6-31G(d) for other atoms in combination with the B3LYP hybrid functional were used for all calculations.

Initially, we investigated the structural stability of (pyridine)(acetonitrile)₃Ru(II)−Pheox. The most stable structure is d,
which has a pyridine in the (D) direction. One of the optimized structures a, which has the same complex as the X-ray structure in Figure 1, is slightly higher in energy than b, c, and d (Figures 2 and S3, Table S7). In addition, other calculation levels also give the same results (Tables S8 and S9). These results suggested that the (pyridine)(acetonitrile),Ru(II)−Pheox complex is formed by kinetic control not thermodynamic controlled product.

The bond length of Ru−N1 by X-ray analysis of (pyridine)(acetonitrile),Ru(II)−Pheox is clearly longer than that of the other three Ru−N bonds although pyridine nitrogen can coordinate to Ru(II) more strongly than acetonitrile nitrogen. These suggest that the rate for elimination of acetonitrile on site (A) differs from that for others. Thus, we calculated the energy gap for the elimination of acetonitrile from (acetonitrile)4Ru(II)−Pheox. The result of DFT calculation shows as e (Figure 3(1)). Each of the Ru−N(acetonitrile) bond lengths in (acetonitrile)4Ru(II)−Pheox complex e were scanned in CH2Cl2 solvent (using polarizable continuum model (PCM)) to determine the kinetically most favorable ligand elimination pathway (Figure 3(2), Tables S11 and S12).

The results showed that the energy gap of the elimination of acetonitrile at (A) is the lowest energy pathway.

Furthermore, these energies were also calculated for Ru(II)−Pheox complexes with three acetonitrile ligands and one vacant coordination site on the ruthenium atom ((acetonitrile)3Ru(II)−Pheox) by the DFT calculations. As a result, the energy of the structure with the three acetonitriles shows the same result with Figure 3(2) and the elimination of acetonitrile at (A) is clearly lower (by more than 12 kcal/mol) than the energies of the other structures (Figure 4, Table S10). These results indicate that (A) is the most eliminable position in this complex. The elimination of acetonitrile and insertion of pyridine into Ru(II)−Pheox should proceed from (A) on the basis of the stability of the elimination by kinetic control in the initial stage of the catalytic cycle. The selectivity may be due to the trans effect of the C−Ru ligand and accordingly affect the enantioselectivity of carbene transfer reactions using Ru(II)−Pheox complexes.

3. CONCLUSIONS

We demonstrated the ligand exchange reaction of an acetonitrile of (acetonitrile)4Ru(II)−phenyloxazoline (Ru(II)−Pheox) with a pyridine and examined the reaction by DFT calculations. This ligand exchange reaction proceeded site selectively from the position trans to C−Ru bond (A). DFT calculations show that the direction of the ligand exchange is determined on the basis of the energy gap of the ligand elimination instead of the stability of the metal complex.
The results provide important information for understanding the behavior around the Ru atom in an organometallic complex, which will allow the design of new and more efficient C₆₅-symmetric catalyst systems.

4. EXPERIMENTAL SECTION

To a solution of (acetonitrile)₃Ru(II)–Pheox complex 1 (67.4 mg, 0.1 mmol) in 2.0 mL of CH₂Cl₂, was added pyridine (8.1 mL, 0.1 mmol) in one portion. The mixture was stirred for 5 min at room temperature. The resulting mixture was concentrated under reduced pressure to give (pyridine)-(acetonitrile)₃Ru(II)–Pheox complex 2 (68.6 mg, >99% yield) as a yellow solid.

1H NMR (500 MHz, CDCl₃): 8.60–8.56 (2H, m, ArH), 7.86 (1H, br s, ArH), 7.76–7.70 (1H, m, ArH), 7.61 (1H, d, J = 7.3 Hz, ArH), 7.42–7.37 (2H, m, ArH), 7.27–7.22 (1H, m, ArH), 7.13 (1H, t, J = 7.3 Hz, ArH), 7.04 (2H, t, J = 7.6 Hz, ArH), 6.97 (1H, br t, J = 7.0 Hz, ArH), 6.77 (2H, d, J = 6.9 Hz, ArH), 5.09–5.01 (2H, m, CH₂), 4.60 (1H, dd, J = 14.1, 10.7 Hz, CH), 2.46 (3H, s, CH₃), 2.29 (3H, s, CH₃), 2.02 (3H, s, CH₃) (Figure S1).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01510.

Values for type 1 and type 2 compounds (XYZ)

Crystallographic data for (pyridine)(acetonitrile)₃Ru(II)–phenyloxazoline obtained using SHELXL-97 method (CIF)

Experimental result (1H NMR spectral), X-ray analysis (figures of crystal and crystal data), computational data (details of calculation result of Figure 2, additional calculation results, tables of energies and bond lengths, figures of optimized structures) (PDF)

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The manuscript was written through contributions from all authors. All authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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