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Mechanism of asymmetric sulfimidation with *N*-alkoxycarbonyl azide in the presence of (OC)Ru(salen) complex

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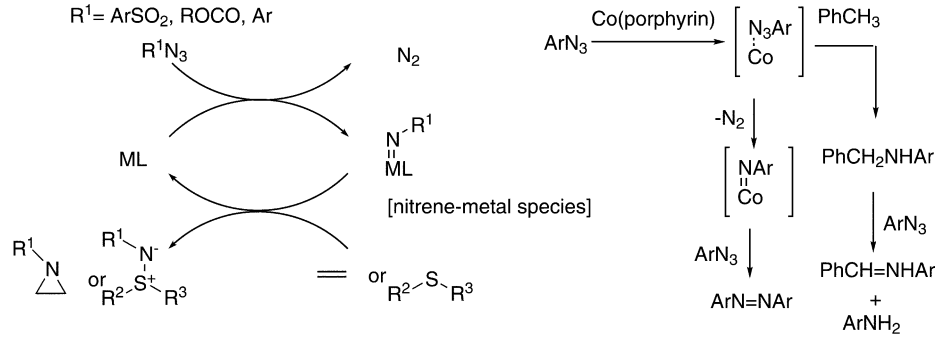
Abstract—Spectroscopic analysis of imidation of alkyl aryl sulfides with *N*-2,2,2-trichloro-1,1-dimethylethyloxycarbonyl azide **2** in the presence of (OC)Ru(salen) complex **1** strongly suggests that an addition compound of the azide **2** to **1** is the active species for the imidation, while the addition compound undergoes the undesired intramolecular C–H insertion onto the salen ligand of the complex in the absence of sulfide, directly or via the corresponding nitrene–ruthenium species.

Transition metal-catalyzed asymmetric nitrogen atom transfer reactions such as aziridination, C–H amination, and imidation of sulfides are useful tools for the preparation of optically active nitrogen compounds.[1–3] *N*-Arylsulfonylphenyliodinanes ($ArSO_2N{=}IPh$) have been used as the nitrene source for most of these nitrogen atom transfer reactions and the reactions have been proposed to proceed through the corresponding nitrene–metal species ($ArSO_2N{=}ML$),[1] except for a few examples that have been considered to proceed via an addition compound ($ArSO_2N{=}IPh{\cdot\cdot}ML$).[3] On the other hand, several groups have recently reported that azide compounds can be used as nitrene sources. Jacobsen et al. disclosed that an optically active (diimine)copper(I) complex catalyzed asymmetric aziridination with moderate enantioselectivity in the presence of arylsulfonyl azides under photo-irradiating conditions.[4] Bach and Körber found that iron(II) chloride was a good catalyst for sulfimidation using *N*-alkoxycarbonyl azides as the nitrene source.[5] Cenini et al. also reported nitrene transfer reaction using *p*-nitrophenyl azide as the nitrene source in the presence of metalloporphyrin, though high reaction temperature was required.[6] These reactions have been postulated to proceed via the corresponding nitrene–metal species (Scheme 1). However, Cenini et al. have recently proposed that the C–H amination catalyzed by a Co(porphyrin) complex proceeds via an addition product of aryl azide to the Co



Scheme 1.

Keywords: (OC)Ru(salen) complex; asymmetric catalysis; sulfimidation; *N*-alkoxycarbonyl azide; intramolecular C–H amination.
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complex and the arylnitrene–Co species gives the corresponding diazene product, on the basis of kinetic studies (Scheme 1).[7] Recently, we found that highly enantioselective sulfimidation of alkyl aryl sulfides using toluenesulfonyl azide (TsN_3) or *N*-2,2,2-trichloro-1,1-dimethylethyloxycarbonyl azide **2** as the nitrogen source was effected by Ru(CO)-salen complex **1**.[8,9] However, aziridination with **2** was found not to be effected by complex **1**,[10] though aziridination with toluenesulfonyl azide was effected by complex **1** with high enantioselectivity.[11] This suggested that these two azides gave a different active species, respectively. Since *N*-sulfonylnitrene-[12] and *N*-acylnitrene–metal species[13] are known to undergo aziridination, the above results strongly indicated the participation of an active species other than a nitrene–metal species in the sulfimidation using **2** in the presence of complex **1**. In order to explain this unprecedented behavior of **2**, we studied the reaction mechanism of the sulfimidation with **2** by spectroscopic means.

We traced the stoichiometric reaction of complex **1** and *N*-2,2,2-trichloro-1,1-dimethylethyloxycarbonyl azide **2** by visible absorption and ^1H NMR spectral analyses. Complex **1** was dissolved in $CDCl_3$ under argon atmosphere and then the azide **2** was added to the solution. Immediately after the mixing of **1** and **2**, visible absorption increased slightly (Fig. 1A, line b) and the chemical shifts of some aromatic protons in the ^1H NMR spectrum of **1** shifted slightly. Subsequent to this change, the mixture began to show slow isosbestic transformation (Fig. 1B) to give a new complex, HRFABMS analysis [*m*/*z* 1171.1854] of which revealed its molecular formula, $C_{66}H_{50}Cl_3N_3O_5Ru$ (calculated for this molecular formula: *m*/*z* 1171.1860). This meant that the newly formed complex was either nitrene–metal species **4** or intramolecular C–H insertion product **5** of the nitrene species. After complex **1** was consumed completely, methyl phenyl sulfide (1 equiv.) and azide **2** (1 equiv.) were added to the reaction mixture but no sulfimidation was observed. The new complex was isolated and mixed with azide **2** and methyl phenyl sulfide, but no change was observed. The measurement of the magnetic susceptibility of the new complex revealed that it was a diamagnetic substance. On the other hand, ^{13}C NMR analysis (DEPT) of the new complex showed that one methine or aromatic proton disappeared in the complex. Since ^1H NMR analysis proved that the cyclohexane unit of the complex remained intact, it was concluded that one aromatic carbon was oxidized by intramolecular nitrene insertion to an aromatic C–H bond during the reaction. These experimental results can be explained by assuming that the newly generated complex was not **4** but **5** (Scheme 2).[14] As there are so many aromatic carbons in the complex, we could not determine which aromatic carbon was oxidized.[15]

On the other hand, the small visible and NMR spectral changes observed right after the mixing of **1** and **2** strongly suggested the formation of an addition compound, which might undergo nitrene transfer reaction.[16] Thus, we examined sulfimidation by adding 1 equiv. of methyl phenyl sulfide to the mixture. Sulfimidation proceeded with high enantioselectivity of >95% ee to give the corresponding sulfimide in 30% (for 1 h) and quantitative yields (for 24 h). As the sulfide was consumed, the visible absorption spectrum became similar to that of complex **1**, but it did not completely agree with the spectrum of **1**, even after the sulfimidation was completed (Fig. 1C). The slight difference in the spectra of **1** and of the mixture at the end of the reaction was likely attributable to the fact that the resulting sulfimide was coordinated to the ruthenium ion, though the coordination should be reversible. These results indicate that the newly formed addition compound is the complex **3**.

After the 1:1 mixture of **1** and **2** was stirred in $CDCl_3$ for 1 h (ca. 16% of **1** was converted into **5** at this stage), 1.0 equiv. of methyl phenyl sulfide was added. The visible spectral change stopped upon the addition and the sulfide was converted to the corresponding sulfimide in 85% yield with high enantioselectivity (94% ee). In the controlled experiment in the absence of **1**, no sulfi-

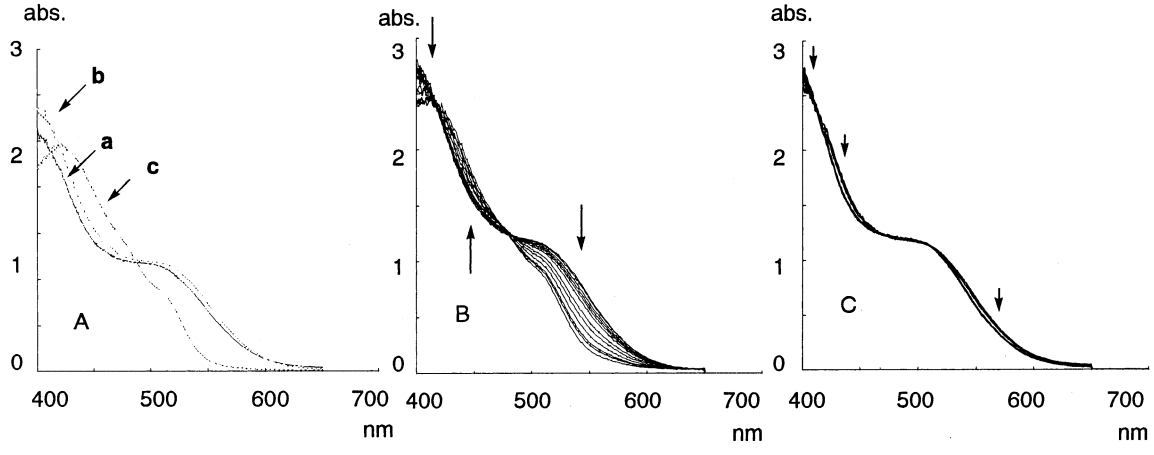
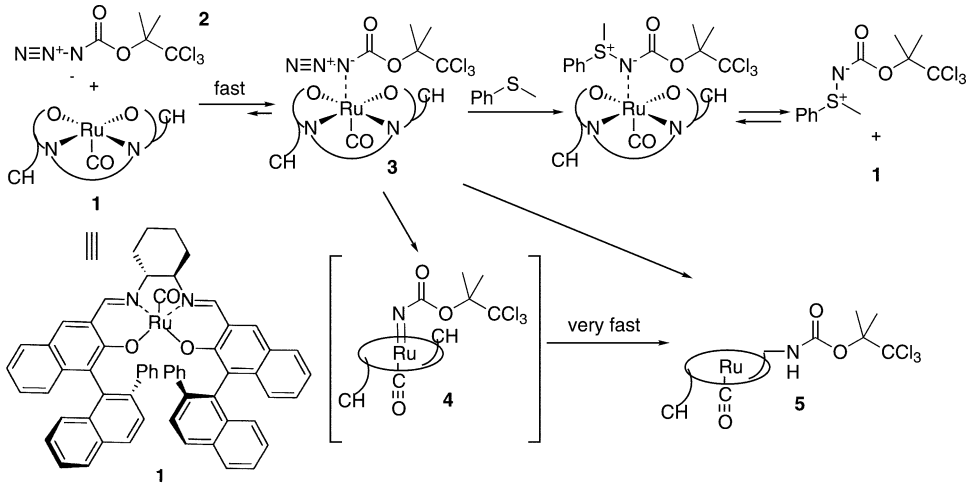


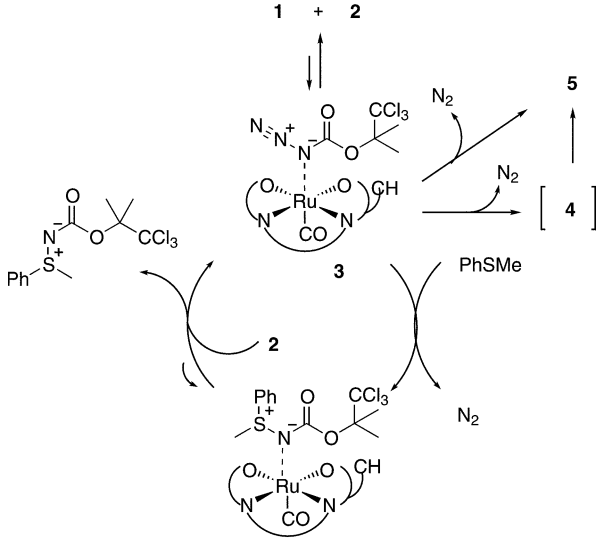
Figure 1. A, line **a**: visible spectrum of Ru(CO)-salen **1**; line **b**: visible spectrum of a mixture of **1** and **2**, immediately after the mixing; line **c**: visible spectrum of complex **5**. B, spectral change of the reaction of **1** and **2** (for 24 h). C, spectral change of the reaction of **1**, **2**, and PhSMe (for 24 h).



Scheme 2.

midation occurred. It is noteworthy that no intramolecular C–H amination was observed, when the sulfide existed in the reaction mixture. When the mixture was treated with 0.5 equiv. of methyl phenyl sulfide, the isosbestic transformation did not occur until the sulfide was consumed. In the catalytic sulfimidation of methyl phenyl sulfide using 2 mol% of **1** in the presence of 1 equiv. of azide **2**, 98% of the sulfide was consumed after 24 h but the formation of **5** was not detected. These results suggested that the above-described isosbestic transformation was hampered by the presence of the sulfide.

Finally, based on the isosbestic spectral change, two mechanisms are proposed for the conversion of **3** to **5**: i) complex **3** is directly transformed to **5**, and ii) complex **3** is slowly converted to a short-lived but active species such as nitrene–Ru species **4** and undergoes the intramolecluar amination. At present, we could not rule out either mechanism, though any short-lived species could not be detected.



Scheme 3.

Based on the above-described results, we propose a catalytic cycle via the addition compound **3**, for asymmetric sulfimidation using **1** as the catalyst (Scheme 3). Although the ^{13}C NMR analysis of **5** only indicated that this C–H amination occurred at its aromatic ring, the X-ray analyses of the metallosalen complexes bearing the same salen ligand as **1** showed that the phenyl group on naphthalene ring is located close to the metal centers.[17] Thus, it seems reasonable to speculate that C–H amination occurred at the phenyl group.[18]

References

1. (a) Faul, M. M.; Evans, D. A. In *Asymmetric Oxidation Reaction, Practical Approach in Chemistry*; Katsuki, T., Ed.; Oxford University Press: Oxford, 2001; Chapter 2.7; (b) Jacobsen, E. N. In *Comprehensive Asymmetric Catalysis II*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds.; Springer: Berlin, 1999; Chapter 17.
2. (a) Kohmura, Y.; Katsuki, T. *Tetrahedron Lett*. **2001**, *42*, 3339–3342; (b) Liang, J.-L.; Yu, X.-Q.; Che, C.-M. *Chem. Commun*. **2002**, 124–125; (c) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S. *J. Chem. Soc., Chem. Commun*. **1996**, 931–932; (d) Takada, H.; Nishibayashi, Y.; Ohe, K.; Uemura, S.; Baird, C. P.; Sporey, T. J.; Taylor, P. C. *J. Org. Chem*. **1997**, *62*, 6512–6518; (e) Baird, C. P.; Clark, A. J.; Rooke, S. M.; Sparey, T. J.; Taylor, P. C. *Phosphorus Sulfur Silicone Relat. Elem*. **1997**, *120–121*, 365–366; (f) Miyake, Y.; Takada, H.; Ohe, K.; Uemura, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2373–2376; (g) Nishikori, H.; Ohta, C.; Oberlin, E.; Irie, R.; Katsuki, T. *Tetrahedron* **1999**, *55*, 13937–13946.
3. (a) Lai, T.-S.; Kwong, H.-L.; Che, C.-M.; Peng, S.-M. *Chem. Commun*. **1997**, 2373–2374; (b) Ohta, C.; Katsuki, T. *Tetrahedron Lett*. **2001**, *42*, 3885–3888.
4. Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc*. **1995**, *117*, 5889–5890.

5. (a) Bach, T.; Körber, C. *Eur. J. Org. Chem.* **1999**, 1033–1039; (b) Bach, T.; Körber, C. *J. Org. Chem.* **2000**, *65*, 2358–2367.
6. Cenini, S.; Tollari, S.; Penoni, A.; Cereda, C. *J. Mol. Catal. A: Chem.* **1999**, *137*, 135–146.
7. (a) Cenini, S.; Gallo, E.; Penoni, A.; Ragaini, F.; Tollari, S. *Chem. Commun.* **2000**, 2265–2266; (b) Ragaini, F.; Penoni, A.; Gallo, E.; Tollari, S.; Gotti, C. L.; Lapadula, M.; Mangioni, E.; Cenini, S. *Chem. Eur. J.* **2003**, *9*, 249–259.
8. (a) Murakami, M.; Uchida, T.; Katsuki, T. *Tetrahedron Lett.* **2001**, *42*, 7071–7074; (b) Murakami, M.; Uchida, T.; Saito, B.; Katsuki, T. *Chirality* **2003**, *15*, 116–123.
9. Tamura, Y.; Uchida, T.; Katsuki, T. *Tetrahedron Lett.* **2003**, *44*, 3301–3303.
10. Tamura, Y.; Uchida, T.; Katsuki, T., unpublished results.
11. Omura, K.; Murakami, M.; Uchida, T.; Irie, R.; Katsuki, T. *Chem. Lett.* **2003**, *32*, 354–355.
12. (a) Au, S.-M.; Fung, W.-H.; Cheng, M.-C.; Che, C.-M.; Peng, S.-M. *Chem. Commun.* **1997**, 1655–1656; (b) Au, S.-M.; Huang, j.-S.; Yu, W.-Y.; Fung, W.-H.; Che, C.-M. *J. Am. Chem. Soc.* **1999**, *121*, 9120–9132.
13. (a) Du Bois, J.; Hong, J.; Carreira, E. M.; Day, M. W. *J. Am. Chem. Soc.* **1996**, *118*, 915–916; (b) Minakata, S.; Ando, T.; Nishimura, M.; Ryu, I.; Komatsu, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3392–3394.
14. Intramolecular C–H hydroxylation has been observed, when $M^{III}(Tp^{R})$ complexes [Tp = tris(pyrazolyl)borate, M = Ni, Co, R = *i*-Pr] are treated with H_2O_2. See: Hikichi, S.; Yoshizawa, M.; Sasakura, Y.; Komatsuzaki, H.; Moro-oka, Y.; Akita, M. *Chem. Eur. J.* **2001**, *7*, 5012–5028.
15. Spectroscopic analyses of the isolated complex **5** gave satisfactory data; ^{1}H NMR (400 MHz): δ 8.35 (s, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.65 (s, 1H) 7.64 (d, J = 7.3 Hz, 1H), 7.59 (dd, J = 7.8, 7.1 Hz, 1H), 7.53–7.45 (m, 5H), 7.38–7.29 (m, 5H), 7.21–7.14 (m, 4H), 7.09–6.96 (m, 5H), 6.93–6.87 (m, 2H), 6.78–6.69 (m, 2H), 6.43 (d, J = 7.8 Hz, 1H), 6.29 (d, J = 8.5 Hz, 1H), 5.79 (s, 1H), 5.55 (dd, J = 7.4, 7.1 Hz, 1H), 3.48 (br t, J = 10.8 Hz, 1H), 2.79 (br d, J = 9.3 Hz, 1H), 2.66 (br t, J = 10.8 Hz, 1H), 2.04 (br d, J = 12.2 Hz, 1H), 1.95 (br d, J = 10.8 Hz, 2H), 1.67–1.25 (m, 2H), 1.13 (s, 3H), 1.16–1.10 (m, 2H), 0.30 (s, 3H). IR ($CHCl_3$): 3425, 1934, 1614, 1587, 1556, 1383, 1329, 1288 cm^{-1}. HRFABMS datum is given in text. We examined sulfimidation using complex **5**, instead of **1**, under the otherwise same conditions, but no reaction occurred under the conditions.
16. The reaction was also traced by IR spectroscopy, but no observable change in the absorption (1934 cm^{-1}) of the apical CO group was detected during the reaction. This suggests that the CO group is not dissociated during the reaction. IR spectra (in $CHCl_3$) of complexes **1**, and a mixture of **1** and **2**; **1**: 1934 cm^{-1}, **1** and **2** (immediately after the mixing): 2139, 1934, 1733 cm^{-1}. Besides the absorption of the CO group, IR spectrum of **5** shows a broad absorption band for N–H stretch at 3425 cm^{-1} (see Ref. 15).
17. Hashihayata, T.; Punniyamurthy, T.; Irie, R.; Katsuki, T.; Akita, M.; Moro-oka, Y. *Tetrahedron* **1999**, *55*, 14599–14610.
18. A diastereomer of complex **1** was prepared from (*S*,*S*)-1,2-diaminocyclohexane, and the reaction of the diastereomeric complex and azide **2** was examined. The reaction also showed isosbestic spectral change and gave an intramolecular C–H insertion product [ESI-MS m/z, calcd for $C_{66}H_{50}Cl_3N_3O_5Ru+H^+$: 1172.3. Found: 1172.3.]