

Concurrently Observed Activation of Aryl–oxygen and Alkyl–oxygen Bonds in The Formation of Rhodium(III) Complexes

Tatsuya Kawamoto,* Yuki Fujimura, and Takumi Konno

Department of Chemistry, Graduate School of Science, Osaka University, 1-16 Machikaneyama, Toyonaka, Osaka 560-0043

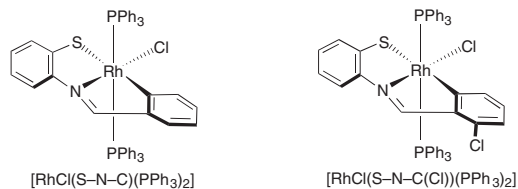
(Received July 16, 2003; CL-030641)

The reaction of 2-(2,6-dimethoxyphenyl)benzothiazoline with $[\text{RhCl}(\text{PPh}_3)_3]$ led to two rhodium(III) complexes, $[\text{RhCl}(\text{S}-\text{N}-\text{C}(\text{OMe}))(\text{PPh}_3)_2]$ (**1**) and $[\text{Rh}(\text{S}-\text{N}-\text{O}(\text{OMe}))(\text{S}-\text{NH}(\text{OMe})_2)(\text{PPh}_3)]$ (**2**), accompanied by C(aryl)–O and C(alkyl)–O bond cleavage, respectively.

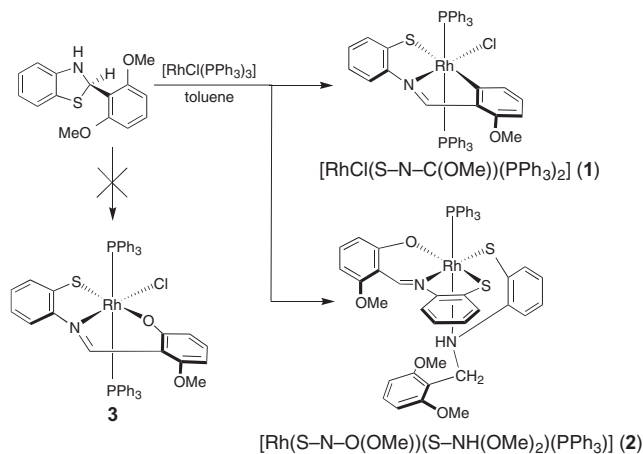
Activation of C–O bonds by metal complexes as well as that of C–H or C–Cl bonds is a field of much interest because of the useful applications, for example in organic synthesis or in mechanistic insights into catalytic reactions. However, contrary to the vast chemistry on activation of C–H or C–Cl bonds,^{1,2} activation of C–O bonds is rare.³ In fact, our previous attempts to cleavage of C–O bonds of methoxyphenyl group by nickel(II) complex were unsuccessful, while an attractive interaction between the nickel center and the methoxy oxygen atom was observed.⁴ As a continuation of our investigations, the reactions of 2-(2,6-dimethoxyphenyl)benzothiazoline with $[\text{RhCl}(\text{PPh}_3)_3]$ were carried out to probe the possibility of activating methoxy group. Consequently, we found the cleavage of C(aryl)–O and C(alkyl)–O bonds which results in the formation of **1** and **2**, respectively (Scheme 1). To the best of our knowledge, concurrent C(aryl)–O and C(alkyl)–O bond activation followed by the formation of rhodium(III) complexes is unprecedented. In addition, these are very rare examples of cleavage of C(aryl)–O^{3f} and C(alkyl)–O^{3b} bonds of methoxyphenyl group induced by low valent transition metal complex.

The 2:1 reaction of 2-(2,6-dimethoxyphenyl)benzothiazoline (0.19 g) with $[\text{RhCl}(\text{PPh}_3)_3]$ (0.31 g) in toluene (20 cm³) under reflux for 20 min gave reddish brown solution, from which **1** (violet) and **2** (yellow) were isolated in a ca. 1:5 ratio after chromatographic purification.⁵ In the electronic absorption spectrum, **1** shows an intense visible band at $16.6 \times 10^3 \text{ cm}^{-1}$

($\epsilon = 2,070 \text{ M}^{-1} \text{ cm}^{-1}$) with a shoulder at higher energy ($17.5 \times 10^3 \text{ cm}^{-1}$, $\epsilon = 1,930 \text{ M}^{-1} \text{ cm}^{-1}$), which are responsible for the violet color. This spectral feature is the same as those observed for $[\text{RhCl}(\text{S}-\text{N}-\text{C}(\text{PPh}_3)_2)]$ and $[\text{RhCl}(\text{S}-\text{N}-\text{C}(\text{Cl}))(\text{PPh}_3)_2]$ having Rh–C bonds.^{2,6b} On the other hand, **2** displays an absorption spectrum quite different from that of **1**, giving an intense band at $21.9 \times 10^3 \text{ cm}^{-1}$ ($\epsilon = 5,060 \text{ M}^{-1} \text{ cm}^{-1}$) with a shoulder at lower energy ($20.2 \times 10^3 \text{ cm}^{-1}$, $\epsilon = 3,872 \text{ M}^{-1} \text{ cm}^{-1}$). The ¹H NMR spectrum of **1** shows one singlet at δ 3.80 with relative integration of 3H for the methoxy hydrogen atoms, while that of **2** contains two singlets at δ 3.16 and 3.76 with relative integrations of 6H:3H. In light of the solid-state structure (vide infra), the NMR spectra can be interpreted as the presence of one methoxy group in **1** and three methoxy groups, two of which are equivalent, in **2**. The IR spectra of **1** and **2** (KBr pellets) show characteristic bands corresponding to the $\nu(\text{N}=\text{C})$ at 1603 and 1578 cm⁻¹, respectively. In addition, **2** has a medium intensity band assigned to $\nu(\text{N}-\text{H})$ at 3058 cm⁻¹.



The structures of **1** and **2** were determined by X-ray diffraction study.⁷ As shown in Figure 1, **1** is a distorted octahedral complex with two triphenylphosphine moieties at the apical po-



Scheme 1.

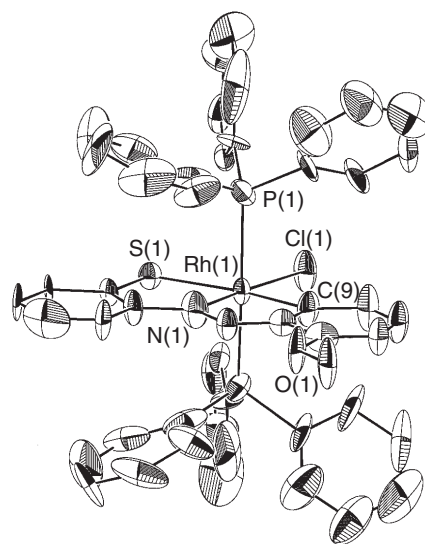


Figure 1. Molecular structure of complex **1**. Selected bond lengths (Å): Rh(1)–S(1) 2.44(3), Rh(1)–Cl(1) 2.41(4), Rh(1)–P(1) 2.360(15), Rh(1)–N(1) 2.01(9), Rh(1)–C(9) 2.13(10).

sitions, while C,N,S donor atoms of the dianionic S–N–C(OMe) ligand and a chlorine atom constitute the basal square plane. The coordination of the dianionic S–N–C(OMe) ligand in **1** indicates the activation of the C(aryl)–O bond. The Rh–S distance of 2.44(3) Å is considerably longer than those observed for other Rh(III)–S(thiolate),⁸ as expected, because of the strong *trans* influence of the Rh–C bond.² The Rh–C distance of 2.13(10) Å is slightly longer than the values obtained for related complexes.^{2,6} On the other hand, the Rh center in **2** is coordinated by N,O,S donor atoms of the dianionic S–N–O(OMe) ligand, besides N,S donor atoms of the monoanionic S–NH(OMe)₂ ligand and one triphenylphosphine (Figure 2). The formation of Rh–O bond means the activation of the C(alkyl)–O bond. The Rh–S distances (av 2.313(2) Å) *trans* to Rh–N and Rh–O bonds are shorter than the Rh–S distance in **1** and are rather short when compared to other related complexes.⁸ It is noted that the Rh–N(2) distance of 2.191(4) Å is distinctly longer compared to normal Rh–N(imine) bond distance found in Rh–N(1) distance of 2.042(4) Å.^{2,6} In addition, the N(2)–C(21) distance of 1.500(7) Å and N(2)–C(21)–C(22) angle of 115.9(5)° indicate the N–C single bond, whereas the N(1)–C(7) distance of 1.300(6) Å is in agreement with the N=C bond distance. These imply that the N(2) atom has a secondary amine form.

In this study, it was evidenced that the reaction of a dimethoxyphenylbenzothiazoline derivative with [RhCl(PPh₃)₃] is accompanied by two kinds of bond cleavage modes of C(aryl)–O and C(alkyl)–O. The C(aryl)–O bond cleavage afforded the diphosphine rhodium(III) complex with a tridentate-C,N,S ligand (**1**), which is analogous to [RhCl(S–N–C)(PPh₃)₂] and [RhCl(S–N–C(Cl))(PPh₃)₂] obtained by cleavage of C–H and C–Cl bonds in unsubstituted and dichloro-substituted phenyl

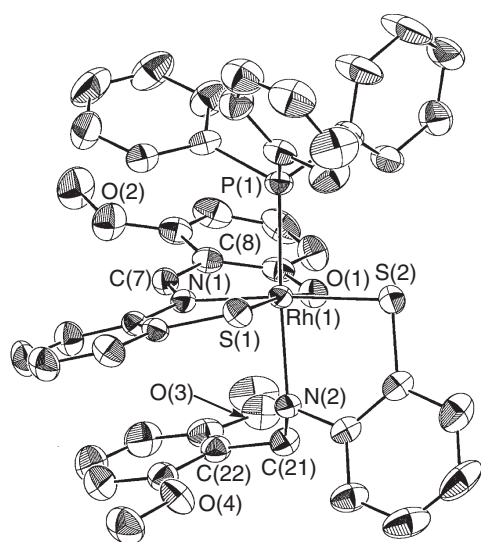


Figure 2. Molecular structure of complex **2**. Selected bond lengths (Å): Rh(1)–S(1) 2.298(2), Rh(1)–S(2) 2.328(2), Rh(1)–P(1) 2.301(2), Rh(1)–O(1) 2.056(4), Rh(1)–N(1) 2.042(4), Rh(1)–N(2) 2.191(4), N(1)–C(7) 1.300(6), N(2)–C(21) 1.500(7). Selected bond angles (°): N(1)–C(7)–C(8) 127.6(5), N(2)–C(21)–C(22) 115.9(5).

groups, respectively.² However, the C(alkyl)–O bond cleavage did not give the corresponding complex **3** under the present experimental conditions, but produced **2** having a reduced bidentate-N,S ligand, together with a tridentate-N,O,S one (Scheme 1).

References and Notes

- a) G. R. Newkome, W. E. Puckett, V. K. Gupta, and G. E. Kiefer, *Chem. Rev.*, **86**, 451 (1986). b) I. Omae, *Coord. Chem. Rev.*, **83**, 137 (1988). c) A. D. Ryabov, *Chem. Rev.*, **90**, 403 (1990). d) J. K. Stille and K. S. Y. Lau, *Acc. Chem. Res.*, **10**, 434 (1977).
- T. Kawamoto, *Inorg. Chim. Acta*, **300–302**, 512 (2000).
- a) T. Yamamoto, J. Ishizu, T. Kohara, S. Komiya, and A. Yamamoto, *J. Am. Chem. Soc.*, **102**, 3758 (1980). b) H. D. Empsall, E. M. Hyde, C. E. Jones, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, **1974**, 1980. c) Y. Yamamoto, R. Sato, F. Matsuo, C. Sudoh, and T. Igoshi, *Inorg. Chem.*, **35**, 2329 (1996). d) J. Albert, J. Granell, R. Moragas, M. Font-Bardia, and X. Solans, *J. Organomet. Chem.*, **522**, 59 (1996). e) J.-S. Sun, C. E. Uzelmeier, D. L. Ward, and K. R. Dunbar, *Polyhedron*, **17**, 2049 (1998). f) M. E. van der Boom, S.-Y. Liou, Y. Ben-David, L. J. W. Shimon, and D. Milstein, *J. Am. Chem. Soc.*, **120**, 6531 (1998). g) X.-H. Han and Y. Yamamoto, *J. Organomet. Chem.*, **561**, 157 (1998). h) F. P. Pruchnik, R. Starosta, M. W. Kowalska, E. Galdecka, Z. Galdecki, and A. Kowalski, *J. Organomet. Chem.*, **597**, 20 (2000). i) Y. Yamamoto, K. Sugawara, and M. Kakeya, *Inorg. Chim. Acta*, **340**, 21 (2002).
- T. Kawamoto and T. Konno, *Bull. Chem. Soc. Jpn.*, **76**, 127 (2003).
- For the reaction in a 1:1 ratio, only **1** was isolated. Anal. Calcd for C₅₀H₄₁ClNOP₂RhS·0.5C₆H₅CH₃ of complex **1**: C; 67.62, H; 4.77, N; 1.47%. Found: C; 67.60, H; 5.05, N; 1.45%. Anal. Calcd for C₄₇H₄₂N₂O₄PRhS₂·0.75CH₂Cl₂ of complex **2**: C; 59.71, H; 4.56, N; 2.92%. Found: C; 59.69, H; 5.15, N; 2.83%.
- a) L.-Y. Huang, U. R. Aulwurm, F. W. Heinemann, F. Knoch, and H. Kisch, *Chem.—Eur. J.*, **4**, 1641 (1998). b) S. Dutta, S.-M. Peng, and S. Bhattacharya, *J. Chem. Soc., Dalton Trans.*, **2000**, 4623.
- Crystal data: Complex **1**: C₅₀H₄₁ClNOP₂RhS·(CH₃CH₂)₂O, *M_r* = 978.38, orthorhombic, space group *A2₁am*, *a* = 17.47(1), *b* = 18.160(7), *c* = 15.124(4) Å, *V* = 4798(4) Å³, *Z* = 4, *D_{calcd}* = 1.355 g cm⁻³, *μ*(Mo *Kα*) = 0.547 mm⁻¹. Of 2414 data collected, 2025 were independent (*R_{int}* = 0.155). *R* = 0.099 and *wR* = 0.118 for [*I* > 2σ(*I*)]. Complex **2**: C₄₇H₄₂N₂O₄PRhS₂·0.5CHCl₃, *M_r* = 956.56, triclinic, space group *P1̄*, *a* = 12.193(2), *b* = 16.200(2), *c* = 11.417(2) Å, *α* = 90.84(1), *β* = 97.95(1), *γ* = 71.220(9)°, *V* = 2113.4(5) Å³, *Z* = 2, *D_{calcd}* = 1.504 g cm⁻³, *μ*(Mo *Kα*) = 0.573 mm⁻¹. Of 10494 data collected, 8823 were independent (*R_{int}* = 0.029). *R* = 0.049 and *wR* = 0.052 for [*I* > 2σ(*I*)].
- a) D. Sellmann, G. H. Rackelmann, F. W. Heinemann, F. Knoch, and M. Moll, *Inorg. Chim. Acta*, **272**, 211 (1998). b) K. Sorasane, J. R. Galan-Mascaros, and K. R. Dunbar, *Inorg. Chem.*, **41**, 433 (2002).