CHEMISTRY LETTERS, pp. 1863-1866, 1982. © The Chemical Society of Japan 1982

NOVEL RHODIUM DIOXYGEN COMPLEXES. REACTION OF THE DIOXYGEN LIGAND WITH THE COORDINATED OLEFIN

Ryuichi SUGIMOTO, Hiroharu SUZUKI,*
Yoshihiko MORO-OKA,* and Tsuneo IKAWA
Research Laboratory of Resources Utilization, Tokyo Institute
of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

Novel dinuclear rhodium dioxygen complexes having olefinic ligand are prepared by the reaction of cationic rhodium diene complexes, $[(1,5\text{-cyclooctadiene})_2Rh]^+Y^-$ or $[(\text{norbornadiene})_2Rh]^+Y^-$ ($Y^- = BF_4^-, ClO_4^-$), with potassium superoxide in dichloromethane. Transfer of the dioxygen ligand to the coordinated olefin is confirmed by pyrolysis of the complex under an atmosphere of $^{18}O_2$.

Homogeneous oxidation of olefins catalyzed by rhodium complexes have recently been studied intensively, and in many cases rhodium dioxygen complexes have been considered to play an important role as potential oxidizing agents.[1] James, et al. showed that cyclooctene complex of rhodium, $[(C_8H_{14})_2RhCl]_2$, absorbed one mole of oxygen and oxidized the cyclooctene by way of rhodium dioxygen complex.[1n] Mimoun, et al. also reported direct oxygen transfer from peroxo complexes to olefins.[1i, k, m] However, it is unclear whether the olefin remains attached throughout in these experiments. Previously, we reported that the μ-peroxo complexes of palladium, platinum, and rhodium having olefinic ligands were prepared by the anion exchange reaction of μ,μ'-dihalo complexes with potassium superoxide.[2] We describe herein the preparation of novel dinuclear rhodium dioxygen complexes by treatment of mononuclear cationic rhodium complexes with potassium superoxide and the reaction of dioxygen ligand with the coordinated olefin.

Dinuclear rhodium dioxygen complexes were prepared using cationic rhodium complexes 1 as the starting material in a similar manner with dinuclear μ-peroxo complexes of palladium reported previously.[2] To a stirred dichloromethane solution of bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (1a) (811 mg, 2 mmol) excess of finely powdered potassium superoxide (711 mg, 10 mmol) was added at ambient temperature under an atmosphere of dry nitrogen and the reaction mixture was stirred at room temperature. The resulting yellowish orange suspension gradually turned red. After stirring for 40-60 h, KBF_4 formed in the reaction and excess KO_2 were removed by filtration through a sintered glass disk. Concentration of the filtrate and addition of 2 ml of dry diethyl ether gave brownish yellow powder of crude 2a. Crystallization from a mixed solvent of chloroform and diethyl ether gave yellow microprisms of 2a (277 mg, 57%). 2a: Mp (dec) 195°C; IR (KBr; cm^{-1}) 2920, 2870, 1472, 1435, 1114, 910. Anal. Calcd for $C_8H_{12}O_2Rh$; C, 39.53; H, 4.98. Found; C, 38.92; H, 5.50.

$$\underset{\underline{1}}{[(\text{diene})_2\text{Rh}]^+\text{Y}^-} + \text{KO}_2 \longrightarrow \underset{\underline{2}}{[(\text{diene})\text{RhO}_2]_2} + \text{diene} + \text{KY} \qquad (1)$$

a; diene = 1,5-cyclooctadiene
b; diene = norbornadiene
$\text{Y}^- = \text{BF}_4^-, \text{ClO}_4^-$

Elemental analysis was well consistent with the composition of (1,5-COD)RhO_2. Molecular weight measured by means of vapor pressure osmometry in chloroform indicated 2a was a dinuclear complex (Mw: Calcd 486.1; Found 535). Gradual oligomerization of 2a in chloroform solution was also observed. The ionic structure $[(1,5\text{-cyclooctadiene})\text{Rh}^+\text{O}_2^-]_2$ for 2a would be excluded since the electric conductivity of 2a measured in CH_2Cl_2 at 20°C was much smaller (1/400) than that of the corresponding cationic complex, $[(1,5\text{-cyclooctadiene})\text{Rh}]^+\text{ClO}_4^-$. The complex 2a showed an ESR signal with $g = 2.00$ at 297 K in dichloromethane solution, however, the spin concentration was extraordinarily low ($1.21 \times 10^{19}\ \text{mol}^{-1}$). Although the structure of 2a is still ambiguous, coordination of 1,5-cyclooctadiene and incorporation of dioxygen ligand in 2a are confirmed through the following experiments.

To the stirred dichloromethane solution (8 ml) of 2a (61 mg, 0.126 mmol) was introduced HCl gas through gas-inlet tube for 10 min at room temperature. Filtration of resulting mixture and concentration of the filtrate under reduced pressure followed by the addition of n-pentane afforded di-μ-chlorobis(1,5-cyclooctadiene)-dirhodium (3a) as yellow crystals (44 mg, 71%) (eq. 2).

$$\underset{\underline{2a}}{[(1,5\text{-COD})\text{RhO}_2]_2} \xrightarrow[\text{C}_6\text{H}_6,\ \text{rt},\ 10\ \text{min}]{\text{HCl}} \underset{\underline{3a}}{[(1,5\text{-COD})\text{RhCl}]_2} \qquad (2)$$

71%

The dioxygen complex 2a also reacted with acetylacetone in benzene solution at room temperature to give acetylacetonato(1,5-cyclooctadiene)rhodium in 31% yield. These results evidently indicate that the superoxide anion radical does not attack the coordinated 1,5-cyclooctadiene in the reaction of 1a with potassium superoxide, and that 1,5-cyclooctadiene ligand remains attached in the dioxygen complex 2a.

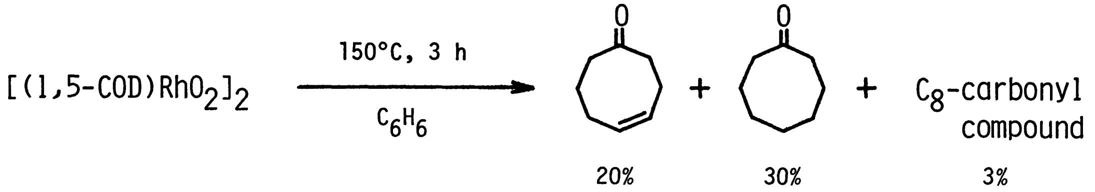
The coordinated dioxygen in the complex 2a was quantitatively determined as triphenylphosphine oxide in the pyrolysis of 2a at 120°C in degassed dry benzene (eq. 3).

$$\underset{\underline{2a}}{[(1,5\text{-COD})\text{RhO}_2]_2} + \underset{(\text{excess})}{\text{PPh}_3} \xrightarrow[\text{C}_6\text{H}_6]{120^\circ\text{C}} \underset{97\%}{\text{Ph}_3\text{PO}} \qquad (3)$$

Dioxygen complex 2b, $[(\text{norbornadiene})RhO_2]_2$, was also prepared from the corresponding cationic complex 1b, $[(\text{norbornadiene})Rh]^+BF_4^-$, in a 66% yield.

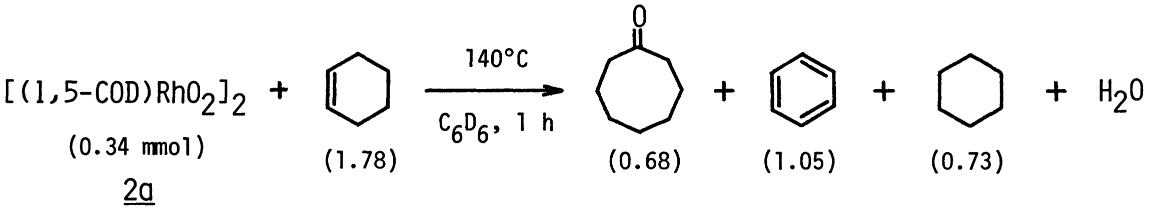
Participation of the coordinated dioxygen in the rhodium-catalyzed oxidation of olefins has been proposed by several authors.[1] In the oxidation of terminal olefins to methyl ketones, peroxometallocyclopentane resulting from the transfer of the coordinated dioxygen to the olefin has also been proposed as the reaction intermediate,[1h, i, k, l] and such a peroxometallocyclic complexes were isolated in the reaction of $(Ph_3P)_2PdO_2$ or $[(Ph_3P)_4RhO_2]^+ClO_4^-$ with tetracyanoethylene.[1i, 3] However, it is not so clear whether the coordinated dioxygen transfers directly to the coordinated olefin. Therefore, pyrolysis of 2a was examined in order to elucidate the reaction mechanism of oxygenation of olefins.

When 2a was pyrolyzed at 150°C in benzene in a sealed tube under dry nitrogen atmosphere, the formation of 4-cyclooctenone (20%), cyclooctanone (30%), and unidentified C_8-carbonyl compound was confirmed by means of GLC and ^1H-NMR (eq. 4).



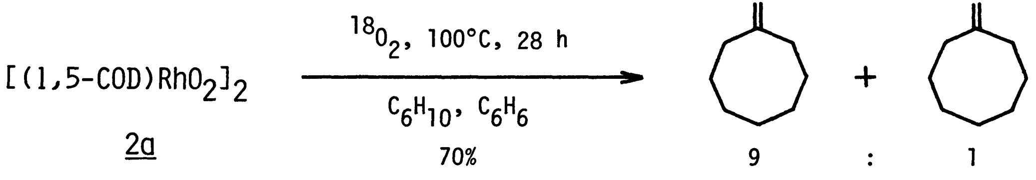
(4)

Decomposition of 2a at 140°C in C_6D_6 in the presence of cyclohexene resulted in a quantitative conversion of coordinated cyclooctadiene to cyclooctanone (eq. 5). Benzene, cyclohexane, and water were also formed but any formation of the oxygenated product of cyclohexene, such as cyclohexenol or cyclohexanone, was not observed. This result suggests the uncoordinated olefin is not oxygenated,[4] and that cyclohexene served as only hydrogen donor.



(5)

Pyrolysis of 2a under an atmosphere of $^{18}O_2$ was conducted as follows. Into a cooled (-78°C) and evacuated pyrex tube containing the benzene solution (2 ml) of 2a (0.206 mmol) and cyclohexene (2.06 mmol) was introduced $^{18}O_2$ gas (0.413 mmol, 99.5% $^{18}O_2$) through a vacuum line, and the tube was sealed. After heating of the reaction mixture at 100°C for 28 h, the products were identified and quantified by means of GLC and GC-MS. Cyclooctanone formed in 70% yield was composed of 90% of cyclooctanone-^{16}O and 10% of cyclooctanone-^{18}O (eq. 6).



(6)

The result suggests that the liberation of the coordinated dioxygen in 2a did not occur prior to the oxygen-transfer to the coordinated cyclooctadiene and supports strongly the oxygen-transfer reaction between two coordinated species. A detailed reaction mechanism will be reported in due course.

References

1. (a) J. P. Collman, K. Kubota, and J. W. Hosking, J. Am. Chem. Soc., 89, 4908 (1967).
   (b) V. P. Kurzov, J. Z. Pasky, and J. B. Lavigne, J. Am. Chem. Soc., 90, 4743 (1968).
   (c) J. E. Baldwin and J. C. Swallow, Angew. Chem. Int. Ed. Engl., 8, 601 (1969).
   (d) K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka, and S. Teranishi, Bull. Chem. Soc. Jpn., 43, 3898 (1970).
   (e) C. W. Dudley and G. Read, Tetrahedron Lett., 1972, 5273.
   (f) K. Kaneda, T. Itoh, Y. Fujiwara, and S. Teranishi, Bull. Chem. Soc. Jpn., 46, 3810 (1973).
   (g) C. W. Dudley, G. Read, and P. J. C. Walker, J. Chem. Soc. Dalton, 1974, 1926.
   (h) G. Read and P. J. C. Walker, J. Chem. Soc. Dalton, 1977, 883.
   (i) F. Igersheim and H. Mimoun, J. Chem. Soc. Chem. Commun., 1978, 559).
   (j) F. Mares and R. Tang, J. Org. Chem., 43, 4631 (1978).
   (k) H. Mimoun, M. M. P. Machirant, and I. S. de Roch, J. Am. Chem. Soc., 100, 5473 (1978).
   (l) R. Tang, F. Mares, N. Neary, and D. E. Smith, J. Chem. Soc. Chem. Commun., 274 (1979).
   (m) H. Mimoun, J. Mol. Cat., 7, 1 (1980).
   (n) B. R. James and E. Ochiai, Can. J. Chem., 49, 975 (1971).
2. (a) H. Suzuki, K. Mizutani, Y. Moro-oka, and T. Ikawa, J. Am. Chem. Soc., 101, 748 (1979).
   (b) P. J. Chung, H. Suzuki, Y. Moro-oka, and T. Ikawa, Chem. Lett., 1980, 63.
   (c) F. Sakurai, H. Suzuki, Y. Moro-oka, and T. Ikawa, J. Am. Chem. Soc., 102, 1749 (1980).
3. R. A. Sheldon and J. A. Van Doorn, J. Organometal. Chem., 94, 115 (1975).
4. 1,5-Cyclooctadiene is coordinated more strongly than cyclohexene and Shurig reported cyclohexene did not form any complex with rhodium(I) [Chem. Ztg., 101, 173 (1977)].

(Received August 28, 1982)