Synthesis of RuCl(amino acido)$(PPh_3)_2$, a Catalyst for Oxidative Dehydrogenation of Glycerin

SUMIO SHINODA, NAOKI INOUE, KEIJI TAKITA and YASUKAZU SAITO*

Institute of Industrial Science, University of Tokyo, 22-1, Roppongi 7 Chome, Minoa-ku, Tokyo 106, Japan

Received February 4, 1982

While various kinds of transition-metal complexes of amino acids are known [1], soft-acid metal complexes involving phosphine as other ligands are rare. This type of complex may have potential utility to homogeneous catalysis using amino acids as chiral educts [2, 3] for asymmetric products [4]. We now find that $RuCl_2(PPh_3)_3$ reacts readily with amino-acid anions with substitution of one chloride and one phosphine ligand to form a chelate amino-acid complex. This substitution was found to occur in a highly regioselective manner as confirmed by $^{31}P\{^1H\}$ NMR spectroscopy (Jeol JNM-FX60, 24.21 MHz). Exploratory experiments have also been done for the oxidation of glycerin, a prochiral substrate, with the synthesized Ru(II)-amino acid complex and N-methylmorpholine [5] used as homogeneous catalyst and oxidant, respectively (eqn. 1).

$$CH_2(OH)CH(OH)CH_2OH + \text{N-methylmorpholine-N-oxide} \xrightarrow{\text{Ru complex cat.}} HCOCH(OH)CH_2OH + \\ + CH_2(OH)COCH_2OH + \text{N-methylmorpholine} + H_2O \quad (1)$$

$[RuCl_2(PPh_3)_3]$ was prepared by the literature method [6]. Introduction of amino-acid anion was performed, referring to the reaction of $RuCl_2(PPh_3)_3$ with pyridine, sodium acetate, *etc.* [7, 8]. Typical example: To the acetone solution (200 ml) of $RuCl_2(PPh_3)_3$ (0.96 g, 1 mmol), L-serine (0.42 g, 4 mmol) and $NaHCO_3$ (0.34 g, 4 mmol) were added. When the mixture was refluxed for 4 h with stirring, the color of the solution changed from dark brown to orange-yellow. Cooling of the hot filtrate gave yellow needles, which were recrystallized from chloroform-ether ([RuCl(L-serinato)$(PPh_3)_2$], *Analysis*, Found (Calcd.): C, 61.2 (61.2), H, 5.0 (4.7), N, 1.9 (1.8)%; $\nu_{C=O}$ = 1630 cm^{-1}; 70% yield for $RuCl_2(PPh_3)_3$). All the procedures were made under an inert atmosphere.

*Author to whom correspondence should be addressed.

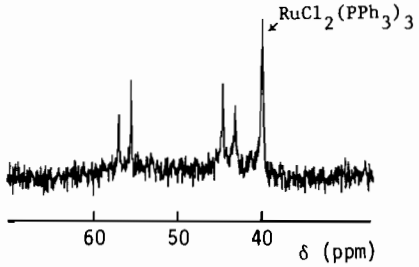
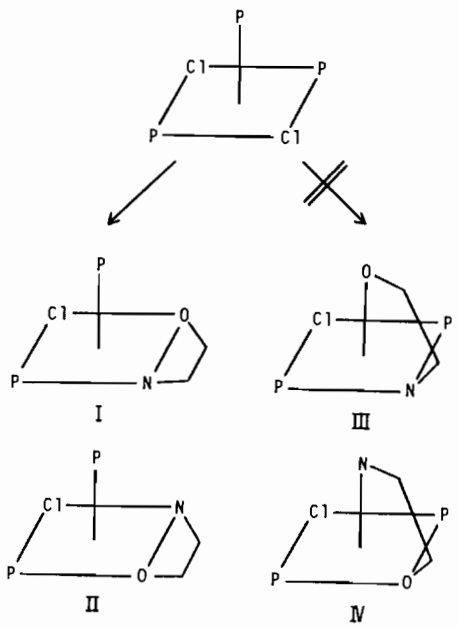


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of RuCl(glycinato)$(PPh_3)_2$ (24.21 MHz, $CDCl_3$ solution, ambient temperature, external 85% H_3PO_4 standard).

Figure 1 shows the $^{31}P\{^1H\}$ NMR spectrum of a crystalline precipitate obtained for glycine before the completion of the substitution reaction.

It was confirmed that the distinct AB quartet in the spectrum was assigned to the glycinato complex [RuCl(glycinato)$(PPh_3)_2$], in which the two PPh_3 ligands should be magnetically unequivalent. Therefore, the spectrum indicates that the substitution proceeds regioselectively to give only one kind of complex dominantly. If the substitution occurs with retention of square-pyramidal configuration of $RuCl_2(PPh_3)_3$ [9], the observed magnitude of $^2J(PP)$ (35 Hz; Table I) strongly suggests the structure of either I or II for the complex formed [10, 11] (Scheme).

Scheme



0020-1693/82/0000-0000/$02.75

TABLE I ^{31}P NMR Spectral Parameters of [RuCl(amino acido)$(PPh_3)_2$].

Amino Acid	δ (ppm)[a]		$^2J(PP)$ (Hz)
Glycine	56.0	44.2	35
L-Serine	51.5	40.6	38
	62.4	49.7	39
L-Hydroxyproline	48.9	41.9	39
	60.4	45.6	38
L-Allohydroxyproline[b]	57.8	45.2	40

[a]Relative to external 85% H_3PO_4 standard (high frequencies being taken as positive). [b]Prepared by the method of ref. 14.

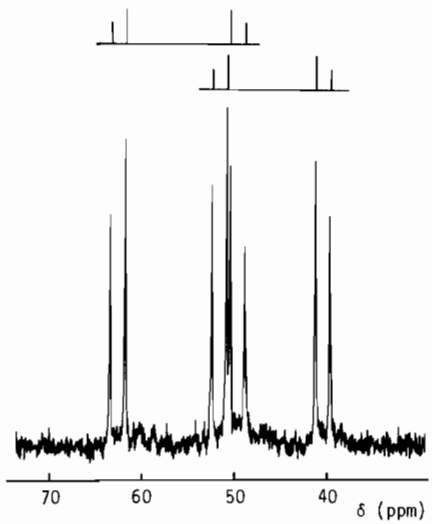


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of RuCl(L-serinato)$(PPh_3)_2$ (24.21 MHz, $CDCl_3$ solution, ambient temperature, external 85% H_3PO_4 standard).

The $^{31}P\{^1H\}$ NMR spectrum of the L-serinato complex, isolated and purified, is given in Fig. 2. As denoted in Fig. 2 the spectrum consists of the superposition of two kinds of AB quartet with almost equal intensity. Assuming the predominance of the same type of coordination structure as that in the glycinato complex, the observed two isomers may be derived from the chirality of L-serine, corresponding to either set of (Ia, Ib) or (IIa, IIb) in Fig. 3. Very small differences of $^2J(PP)$ between the two isomers (Table I) may support the identity of the configuration of ligating atoms [11].

While an analogous $^{31}P\{^1H\}$ NMR pattern was observed for the L-hydroxyprolinato complex, only one isomer was detected for the L-allohydroxyprolinato case.

Apparently this difference is brought about by the configuration of the hydroxyl group in the pyrrolidine ring. Since the hydroxyl group of the latter would project toward the coordination site of ruthenium(II) in the complexed state, the Ia- or IIa-type isomer may prevail as a result of inter-ligand steric interactions [12]. The ^{31}P NMR parameters of the synthesized complexes are listed in Table I.

TABLE II. Oxidative Dehydrogenation of Glycerin with Ru Complex Catalysts.

Catalyst	Turnover Number	GA selectivity (%)[a]
$RuCl_3 \cdot 3H_2O$	23	90
$RuCl_2(PPh_3)_3$	45	88
RuCl(glycinato)$(PPh_3)_2$	14	95
RuCl(L-serinato)$(PPh_3)_2$	41	97
RuCl(L-allo)$(PPh_3)_2$[b]	28	94

[a]GA = glyceraldehyde, within 3% error [b]L-allo = L-allohydroxyprolinato.

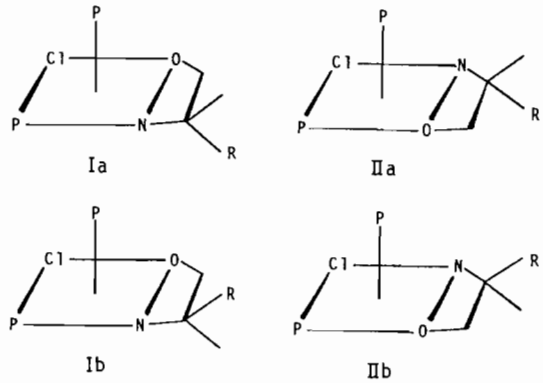


Fig. 3. Diastereomer sets of RuCl(amino acido)$(PPh_3)_2$ with *cis* disposition of PPh_3 ligands in square-pyramidal structure.

Oxidative dehydrogenation of glycerin was performed by mixing the Ru(II)–amino acid complex (0.25 mmol), glycerin (25 mmol), and N-methylmorpholine-N-oxide (50 mmol) in argon-blanketed acetone (250 ml), followed by stirring for 10 h at room temperature. Degree of conversion was determined from the relative abundance of N-methylmorpholine-N-oxide and N-methylmorpholine, using

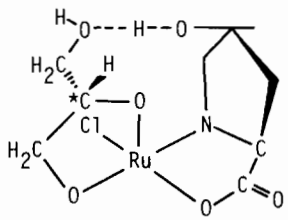


Fig. 4. Postulated hydrogen bonding between coordinated glycerin and L-allohydroxyprolinato ligand appropriate for asymmetric synthesis of glyceraldehyde.

quantitative ^{13}C NMR analysis (CH_3 carbons) of the reaction solution itself. Regioselectivity (glyceraldehyde *vs.* dihydroxyacetone) was determined by the ^1H NMR spectrum of 2,4-dinitrophenylhydrazone (NH protons, in $(CD_3)_2CO$), which was obtained from an oily residue after complete evaporation of the solvent acetone.

At the beginning of the reaction the solution was homogeneous and colored deep red, but a dark brown precipitate began to appear after *ca.* 4 h. The results for the reaction are summarized in Table II.

It should be emphasized that selectivities to glyceraldehyde are quite high, which may reflect the higher reactivity of ruthenium complex catalysts to n-alcohols than to sec-alcohols [5]. Since N-methylmorpholine is easily oxidized to N-methylmorpholine-N-oxide with H_2O_2 [13], a cycle may be composed to obtain glyceraldehyde by the H_2O_2 oxidation of glycerin with N-methylmorpholine working as a mediator.

With regard to the stereoselectivity in the glyceraldehyde formation, we have obtained a preliminary result of 3% excess of D-antipode with the L-allohydroxyprolinato complex catalyst. An attractive interaction would be utilized for the asymmetric conversion of glycerin-type substrates. On the basis of the observation that coordinated PPh_3 is oxidized by N-methylmorpholine-N-oxide and liberated as $O{=}PPh_3$ during the reaction, a possible mode of complexation with hydrogen bonding is illustrated in Fig. 4.

References

1 C. A. McAuliffe, *Inorg Biochem., 1,* 1 (1979), *2,* 1 (1981).
2 S. Shinoda, Y. Yamaguchi and Y. Saito, *Inorg. Chem., 18,* 673 (1979).
3 S. Shinoda, Y. Sudo, Y. Yamaguchi, T. Iwayanagi and Y. Saito, *J Organometal. Chem., 121,* 93 (1976).
4 T. F. Buckley III and H. Rapoport, *J. Am Chem. Soc., 103,* 6157 (1981).
5 K. B. Sharpless, K. Akashi and K. Oshima, *Tetrahedron Lett.,* 2503 (1976).
6 P. S. Hallman, T. A. Stephenson and G. Wilkinson, *Inorg. Synth., 12,* 237 (1970).
7 J. D. Gilbert and G. Wilkinson, *J. Chem. Soc A,* 1749 (1969).
8 A. R. Middleton, J. R. Thornback and G. Wilkinson, *J Chem. Soc. Dalton Trans.,* 174 (1980).
9 P. R. Hoffman and K. G. Caulton, *J Am. Chem. Soc., 97,* 4221 (1975).
10 Y. Koie, S. Shinoda and Y. Saito, *Inorg Nucl. Chem. Lett., 17,* 147 (1981).
11 P. S. Pregosin and R. W. Kunz, ^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes', Springer-Verlag, Berlin (1979).
12 S. R.Ebner and R. J. Angelici, *Inorg. Chem., 20,* 2971 (1981).
13 V. VanRheenen, R. C. Kelly and D. Y. Cha, *Tetrahedron Lett.,* 1973 (1976).
14 A. Neuberger, *J Chem. Soc ,* 429 (1945).