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SYNTHESES AND REACTIONS OF ALUMINUM COMPLEXES OF CAPPED PORPHYRIN

Toru Arai and Shohei Inoue*
Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan

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Al complexes of a capped porphyrin were newly synthesized with methyl, carboxylate, and phenoxide groups as axial ligands on the opposite side of the cap. (CapP)Al complexes undergo the exchange of the carboxylate or phenoxide group with carboxylic acid or phenol, respectively, much more slowly than the corresponding (TPP)Al complexes.

The reactions and coordination properties of metalloporphyrins have attracted much attention in relation to their biological role such as hemoglobin, cytochrome P-450, and chlorophyll[1]. In this connection, most studies have been carried out on iron, manganese, magnesium, and zinc porphyrins. On the other hand, aluminum porphyrins have not been paid much attention until recently. Buchler and coworkers prepared some aluminum complexes of octaethylporphyrin[2], but the reactions examined were rather limited. More recently, we have developed a number of novel, interesting reactions of aluminum complexes of tetraphenylporphyrin and some other porphyrins. Examples are the stereoselective formation of (porphyrinato)aluminum enolates from ketones[3], carbon dioxide fixation with aluminum porphyrins[4)5)6)7], and ring-opening reactions of epoxides and lactones[8]. These reactions take place at the fifth, axial ligand-aluminum (X-Al) bond, but in some cases the coordination of the substrate or another ligand to the vacant, sixth coordination site has been indicated to play an important role.

Such a *trans* effect has been observed, for example, in the coordination of dioxygen molecule on iron porphyrin[9]. On the other hand, in the reactions of aluminum porphyrins as cited above, the reacting group (X-Al) is not coordinating but is bound to the metal by a valence bond, and the dissociation as observed for coordinating ligand is not likely to occur in nonpolar media. Thus the effect of the additional coordinating ligand on the reaction of metalloporphyrins is expected to be understood more clearly for aluminum porphyrins

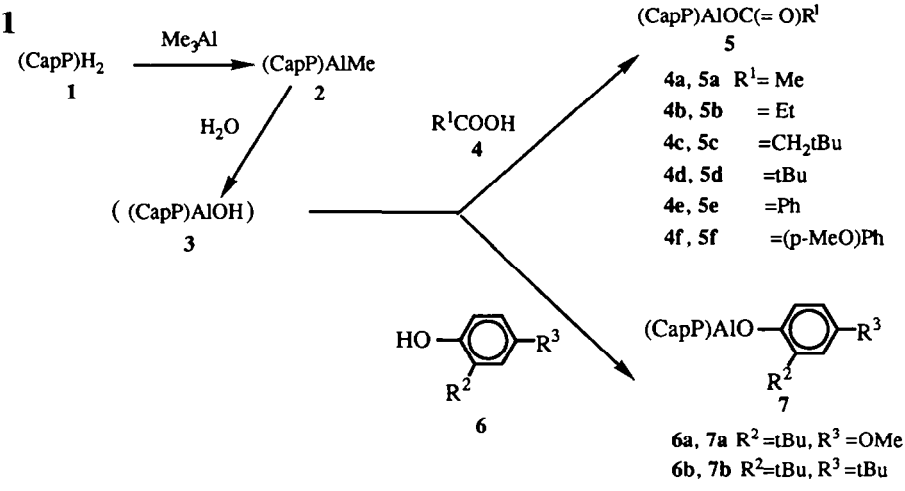
In the present study, aluminum complexes of a 'capped' porphyrin[10] were synthesized to prevent the sixth coordination, with methyl, carboxylate, and phenoxide axial groups. The coordination behavior of the complexes with 1-methylimidazole, and the exchange reactions of the axial groups with carboxylic acids or phenols were investigated. The reactivity was compared with that of the complex of tetraphenylporphyrin without cap[11].

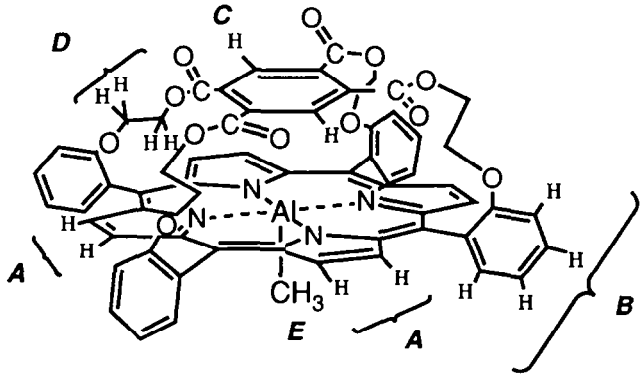
Results and Discussions

1. Formation of aluminum complexes of capped porphyrin

Quantitative formation of the aluminum complex of a capped porphyrin with axial methyl group, (CapP)AlMe **2** was found to take place when an excess amount of Me_3Al was added to (CapP)H_2 **1** in CH_2Cl_2[12]. (CapP)AlMe **2** could be obtained by removing the excess Me_3Al in vacuum. In ^1H NMR spectrum (Fig.1), the protons of (CapP)Al<u>Me</u> are strongly

Scheme 1





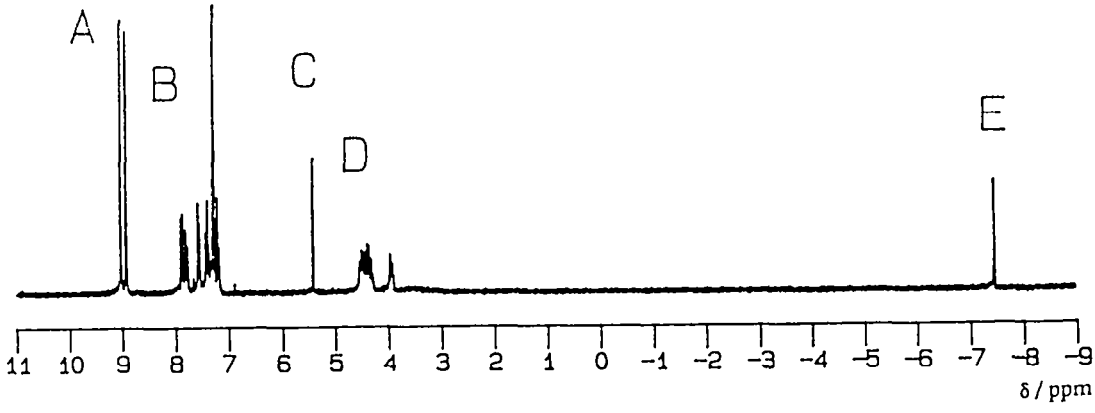
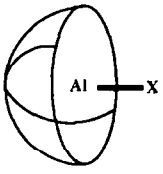


Figure 1. ^{1}H NMR spectrum of the reaction mixture between (CapP)H_2 **1** and Me_3Al (1:5), after evaporating the volatile materials and dissolved in $CDCl_3$.

Table 1. Selected ^{1}H NMR Data of (CapP)AlX and corresponding (TPP)AlX in C_6D_6 (in ppm)

	porphyrin ligand	X	ß-pyrrole	capping benzene	axial ligands
2	(CapP)	CH_3-	9.37, 9.24	6.03	-6.27
5a	(CapP)	CH_3COO-	9.40, 9.32	6.00	-0.66
5f	(CapP)	(p-MeO)PhCOO-	9.40, 9.33	6.01	6.00, 5.63, 2 97
7a	(CapP)	(2-tBu-4-MeO)PhO-	9.38, 9.32	6.00	3.13, -0.49
	(TPP)	CH_3-	9.36	-	-5.78
8a	(TPP)	CH_3COO-	9.35	-	-0.47
8f	(TPP)	(p-MeO)PhCOO-	9.35	-	5.99, 5.88, 2.93
9a	(TPP)	(2-tBu-4-MeO)PhO-	9.34	-	3 17, -0.40



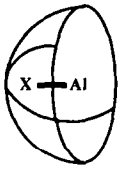
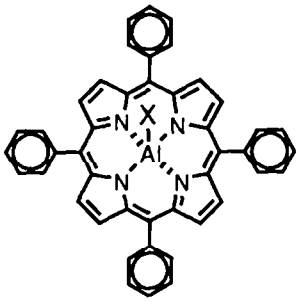


Figure 2. Possible structures for (CapP)AlX



X- = CH_3COO- **8a**
$tBuCH_2COO$- **8c**
PhCOO- **8e**
(p-MeO)PhCOO- **8f**
(2-tBu-4-MeO)PhO- **9a**
(2,4-di-tBu)PhO- **9b**

shielded by the porphyrin ring current and show their signal in a higher magnetic field, at δ -7.45 (E). The relative signal intensity of (CapP)AlMe to ß-pyrrole (A) is 3/8, showing the quantitative formation of (CapP)AlMe **2**.The signals of ß-pyrrole protons (A) are two singlets of which the signal intensities corresponding to 4H, respectively, and the signal due to 'capping' benzene (C) is a singlet with intensity corresponding to 2H. Thus, no side reaction such as cleavage or reduction of the ester linkage of the ligand was confirmed to occur, which would have resulted in a more complicated spectrum.

(CapP)Al carboxylates **5a** – **5f** and phenoxides **7a**, **7b** were formed by the treatment of (CapP)AlMe **2** with water followed by the corresponding carboxylic acids or phenols (Scheme 1). ^{1}H NMR data of the (CapP)Al complexes and the corresponding tetraphenylporphynato(TPP) aluminum complexes are summarized in Table 1.

As for (CapP)Al complexes, the axial ligands are expected to exist on the opposite side of the capped face of the porphyrin. In fact, only one set of signals were observed for every (CapP)Al complex in ^{1}H NMR spectra, even in the case of **2** (Fig.1) of which the axial ligand is methyl group, suggesting that the ligands exist in one side of the porphyrin plane. (pMeO-)PhCOO- or (2-tBu-4-MeO)PhO- group is too bulky to be in the cavity of the cap, so these axial ligands of **5f** and **7a** should exist in *trans* to the cap. The chemical shifts of the ß-pyrrole protons of (CapP)Al complexes with different axial ligands **2**, **5**, and **7** resemble each other, and the signals of the capping benzene protons are also observed to be almost the same. These facts suggest that the axial ligands of **2**, **5**, **7** are on the same side of the porphyrin plane, *trans* to the cap (Fig. 2).

The chemical shifts of the axial ligands in (CapP)Al carboxylates **5** and (CapP)Al phenoxides **7** are very similar to

those for the signals of the corresponding (tetraphenylporphirinato)Al complexes ((TPP)Al complexes) **8** and **9**, respectively; for instance, δ -0.66 for (CapP)AlOC(=O)CH_3 **5a** and δ -0.47 for (TPP)AlOC(=O)CH_3 **8a**; δ -0.49 for (CapP)AlO(2-tBu-4-MeO)Ph **7a** and d -0.40 for (TPP)AlO(2-tBu-4-MeO)Ph **9a**. The capping structure of the ligand with ester groups is considered to have no essential effect on the Al atom of the (CapP)Al complexes.

2. ^{27}Al NMR spectroscopic study

It has been known that the signals of ^{27}Al NMR are observed in different regions of chemical shifts depending on the coordination number of the Al atom[13]. Benn *et al.* studied the ^{27}Al NMR of 50 aluminum compounds and their adducts with base, and found an experimental rule that 4-coordinated Al shows its signal between 180 and 125 ppm (relative to $Al(NO_3)_3$ in D_2O); for instance δ 153 for $(Me_3Al)_2$ and δ 182 for Me_3Al·THF. On the other hand, Al of 6-coordination such as $Al(acac)_3$ shows the signal at δ 0. Five compounds such as $(Me_2AlO(CH_2)_2OMe)_2$ and $(Et_2AlOCH_2$-2-$H_4C_5N)_2$ are observed to show their signals in a range of δ 105-121 in toluene-d8[13b)-13d)]. On the other hand, $AlCl_3$·$(THF)_2$ shows its signal at δ 63.0 in CH_2Cl_2/THF[13a)]. Koester *et al.* reported another example, $Cl_2AlOXOAl(Cl)OXOAlCl_2$ (X=B(Ph)OB(Ph)), in which central Al atom is 5-coordinated by four O atoms and one Cl atom, showing its ^{27}Al NMR signal at δ 43 in toluene-d8[14]. Koester's complex is unique in the respect that the central Al atom is tetragonal pyramidal in the structure determined by the X-ray diffraction analysis. These examples show that the chemical shifts in ^{27}Al NMR do not always correspond to the coordination number of the aluminum atom, but aluminum complexes of similar structures show their signals in a similar region.

In Fig. 3 and in Fig. 4 are shown ^{27}Al NMR spectra of (CapP)AlOC(=O)(p-MeO)Ph **5f** and (CapP)AlO(2-tBu-4-MeO)Ph **7a**, and the spectra of the corresponding (TPP)Al complexes **8f** and **9a**, respectively. The two carboxylate complexes, **5f** (δ 13) and **8f** (δ 14) show similar spectra independent of the porphyrin ligand. A similar observation is

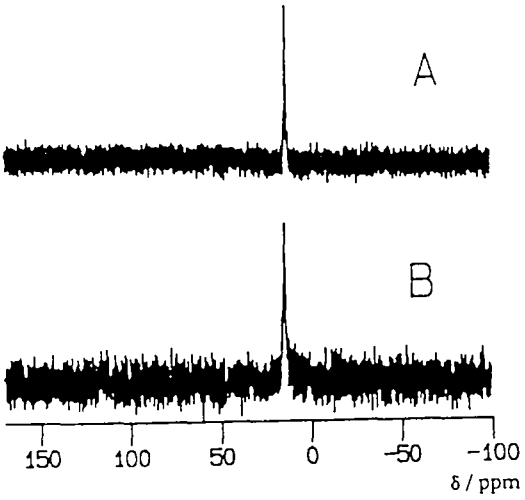


Figure 3. ^{27}Al NMR spectra of (CapP)AlOC(=O)(p-MeO)Ph **5f** (**A**) and (TPP)AlOC(=O)(p-MeO)Ph **8f** (**B**) in C_6D_6/toluene (104.05 MHz).

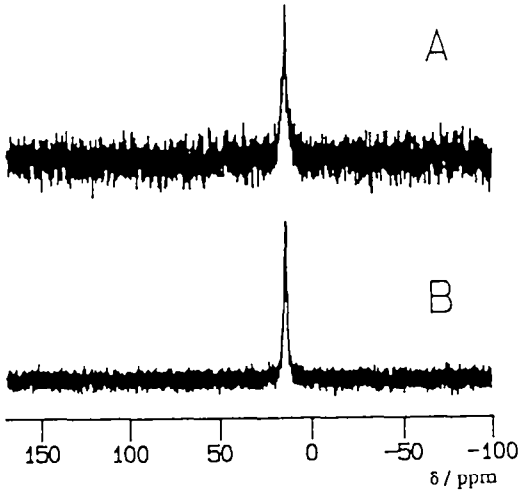


Figure 4. ^{27}Al NMR spectra of (CapP)AlO(2-tBu-4-MeO)Ph **7a** (**A**) and (TPP)AlO(2-tBu-4-MeO)Ph **9a** (**B**) in C_6D_6/toluene (77 26 MHz).

made for the spectra of the two phenoxides, **7a** (δ 14) and **9a** (δ 14). It is strongly suggested that between (CapP)Al complexes and (TPP)Al complexes, no great difference in their mode of ligand coordination may exist. (TPP)AlOMe has been reported to show its signal at δ 20 ppm in $CDCl_3$[15].

Fig. 5 shows ^{27}Al NMR spectra of (CapP)AlO(2-tBu-4-MeO)Ph **7a** and the corresponding TPP complexes **9a**, in C_6D_6 containing 5% 1-methylimidazole (1-MeIm). (TPP) complex **9a** shows the signal at δ -14 ppm and apparently forms 6-coordination complexes with the ligation of 1-MeIm. In contrast, essentially no change was observed upon addition of 1-MeIm in the case of (CapP) complex **7a**. ^1H NMR and UV-Vis spectra also exhibited no changes when 1-MeIm was added to the solution of **7a** in C_6D_6. In the case of (TPP) complex **9a**, ^1H NMR spectra show distinct shift for the tBu proton from δ -0.40 to δ -0.51 with the addition of 1-MeIm to the solution in C_6D_6. (TPP)AlOMe added by 1-MeIm in $CDCl_3$ has been reported to show the signal in ^{27}Al NMR at δ -11 ppm[15][16]. Coordination of 1-MeIm to (TPP)AlOMe has been also indicated by our earlier study of ^1H NMR and UV-VIS spectroscopy[4]. From the results mentioned above, the coordination of 1-MeIm to the Al atom of (CapP) complex **7a** was not detected, in contrast to TPP complex[17]. Similar observations were made in the mixing of 1-MeIm to (CapP)AlOC(=O)CH_3 **5a** or (TPP)AlOC(=O)CH_3 **8a**, respectively. ^1H and ^{27}Al NMR showed the coordination of 1-MeIm to **8a** in $CDCl_3$, but in the case of **5a** no coordination. These facts also indicate that the axial ligands of (CapP)Al carboxylate or phenoxide exist on the opposite side of the cap.

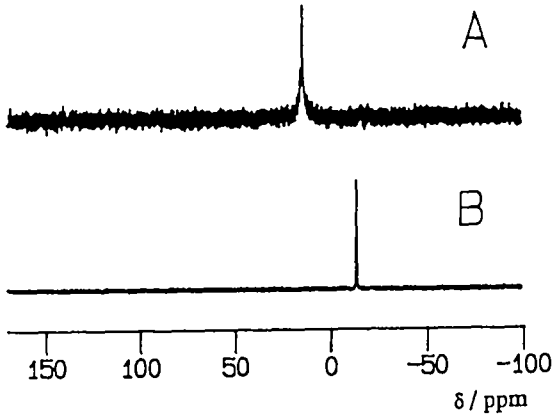


Figure 5. ^{27}Al NMR spectra of (CapP)AlO(2-tBu-4-MeO)Ph **7a** ((**A**), 104.05MHz) and (TPP)AlO(2-tBu-4-MeO)Ph **9a** ((**B**), 77.26MHz) in C_6D_6/toluene containing 5% 1-methylimidazole.

3. Exchange of axial ligands of (CapP)Al complexes

When a carboxylic acid was added to the solution of (CapP)AlOC(= O)CH_3 **5a**, a slow reaction was observed to form another carboxylate **5b-5f**, and resulted in an equilibrium mixture (eq. 1).

$$\text{(CapP)Al-X} + \text{YH} \rightleftharpoons \text{(CapP)Al-Y} + \text{XH} \qquad (1)$$

^1H NMR spectra of the reaction mixture showed the decrease of (CapP)AlOC(=O)CH_3 **5a** (δ -0.66) and propionic acid **4b** (δ 2.15 for CH_2), and corresponding formation of (CapP)AlOC(=O)CH_2CH_3 **5b** (δ -0.41 for CH_2) and acetic acid **4a** (δ 1.75 for CH_3). The total amount of **5a** and **5b** was quantitative with respect to the initial amount of **5a**, and no side reaction was observed by ^1H NMR during the reaction. As seen in Fig.6, the reaction of **5a** with **4b** with the initial molar ratio of **5a**/**4b** = 3.0 or 0.33 attained to the equilibrium within about 2 hours. The observed equilibrium constant K, $[\mathbf{5b}]_\infty[\mathbf{4a}]_\infty/[\mathbf{5a}]_\infty[\mathbf{4b}]_\infty$, where $[\mathbf{5b}]_\infty$ is the concentration of **5b** at the equilibrium, etc., was calculated to be 0.71 under these conditions.

In Table 2 are listed the equilibrium constants of axial ligand exchange observed for (CapP)Al carboxylate and phenoxide complexes. Large K valueis in the reaction of benzoic acid **4e** with (Cap)AlOC(=O)CH_3 **5a** may be due to the

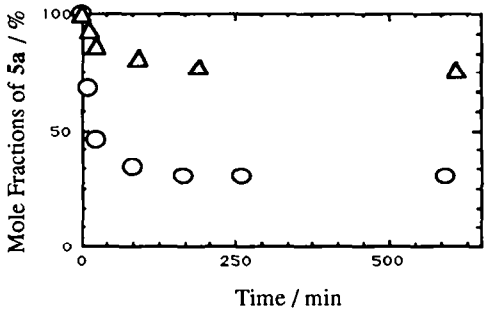


Figure 6. Reaction of (CapP)AlOC(=O)CH_3 **5a** with propionic acid **4b** at room temperature in C_6D_6. Mole fractions of **5a**. The initial ratio of **5a** / **4b** was 3.0 (O) and 0.33 (Δ), respectively. The initial concentration of **5a** was 4.0 x 10^{-3} mol·dm^{-3}. The molar fractions of **5a** and **5b** were determined based on their ^{1}H NMR signals at δ -0.66 (CH_3 of **5a**) and δ -0.41 (CH_2 of **5b**), respectively.

large difference of the acidity between benzoic acid and acetic acid.

In the reaction of benzoic acid **4e** with (CapP)AlOC(=O)CH_3 **5a**, the reverse reaction in their equilibrium may be neglected in the initial stage. The reaction (**5a**+**4e** ⟶ **5e**+**4a**) was observed to be a second-order process (eq. 2)

$$R_1 = k_1 [\mathbf{5a}][\mathbf{4e}] \qquad (2)$$

where R_1 is the reaction rate, and the rate constant k_1 was determined to be 1.9 x 10^{-1} mol^{-1}·dm^3·sec^{-1} at 25°C.

The rate of the reaction between (CapP)AlO(2-tBu-4-MeO)Ph **7a** and 2,4-di-t-butylphenol **6b** was determined in a reaction carried out at 60°C. 16 equivalents of **6b** was added to the mixture of **7a** (initial concentration was 8.2 x 10^{-4} mol·dm^{-3}) and 2-t-butyl-4-methoxyphenol **6a** (4.4 eq. to **7a**) in C_6D_6 at 60°C. The mixture attained to their equilibrium in the molar ratio of **7a**/**6b**/**7b**/**6a** = 0.3/15.3/0 7/5.1. In such an exchange reaction in which the reverse reaction may not be neglected from its initial stage (K≈1), the rate of the reaction R_2 is given by Mckay's equation [18] (eq. 3),

$$R_2 = - \ln (1-F)/t \cdot [\, A \cdot B/(A+B)] \qquad (3)$$

where F is $[\mathbf{7a}]_t/[\mathbf{7a}]_\infty$, $[\mathbf{7a}]_t$ is the concentration of **7a** at time t, $[\mathbf{7a}]_\infty$ is that at the equilibrium, A is [**7a**] + [**6a**], and B is [**7b**] + [**6b**]. In the equilibrium the rate of the reaction **7a** + **6b** ⟶ **7b** + **6a** is defined by eq.4.

$$R_2 = k_2[\mathbf{7a}]_\infty[\mathbf{6b}]_\infty \qquad (4)$$

and k_2 was determined from (eq.3) and (eq. 4) to be 0.2 mol^{-1}·dm^3·sec^{-1}.

We have already reported the reactions of (TPP)Al alkoxide with alcohol, (TPP)Al carboxylate with carboxylic

Table 2. Equilibrium constants K in the exchange reaction of (CapP)Al X with YH (eq.1)[a]

(CapP)Al X	**5a**	**5a**	**5a**	**5a**	**5f**	**7a**
X	CH_3COO-	CH_3COO-	CH_3COO-	CH_3COO-	(p-MeO)PhCOO-	(2-tBu-4-MeO)PhO-
YH	**4b**	**4c**	**4d**	**4e**	**4c**	**6a**
Y	CH_3CH_2COO-	$tBuCH_2COO$-	tBuCOO-	PhCOO-	$tBuCH_2COO$-	(2-4-di-tBu)PhO-
K	0.71	1.79	0.94	6.16	0.98	0 89

a) The reactions were carried out in C_6D_6 at room temperature (*ca.* 23°C). The initial concentration of (CapP)AlX was 4.0 x 10^{-3} mol·dm^{-3}.

acid[8], and (TPP)Al enolate with ketone[3]. In the case of (CapP)Al complexes, the sixth coordination site of the Al metal (*trans* position to the axial ligand) is protected by the capping structure. Therefore, in the substitution reactions of the axial ligands, carboxylic acids or phenols are considered to attack the Al atom from the opposite side of the 'cap', or the same side of the axial ligands.

4. Relative reactivity of aluminum complexes of capped porphyrin and tetraphenylporphyrin

Further information about the exchange reaction of the axial ligands of Al porphyrins was obtained from the study of the relative reactivity between (CapP)Al complexes and (TPP)Al complexes. (eq.5)

To a mixture of (CapP)AlOC(= O)CH_3 **5a** and (TPP)AlOC(= O)CH_3 **8a** in C_6D_6 was added a C_6D_6 solution of benzoic acid **4e** (**5a** : **8a** : **4e** = 1: 1: 7) at room temperature, and this mixture was subjected to the ^{1}H NMR analysis. Fig. 7 shows the mole fraction of **5a** (d -0.66 for -C<u>H</u>$_3$) in all of the (CapP)Al complexes, and the mole fraction of **8a** (d -0.47 for -C<u>H</u>$_3$) in all of the (TPP)Al complexes in the reaction mixture. As shown in Fig. 7, **8a** decreases rapidly to form (TPP)AlOC(= O)Ph **8e**, but (CapP)AlOC(=O)CH_3 **5a** and (CapP)AlOC(=O)Ph **5e** attained to their equilibrium after about 2 hours. The reaction of t-butylacetic acid **4c** with the mixture of (CapP)AlOC(=O)(p-MeO)Ph **5f** and (TPP)AlOC(=O)(p-MeO)Ph **8f** proceeded in a similar fashion. The reaction of 2,4-di-t-butyl-phenol **6b** with the mixture of (CapP)AlO(2-tBu-4-MeO)Ph **7a** and the corresponding (TPP)Al complex **9a** gave similar results. (TPP)Al complexes attained to equilibrium within 5 minutes in each reaction. On the other hand, the (CapP)Al complexes came to their equilibrium in about 2 hours.

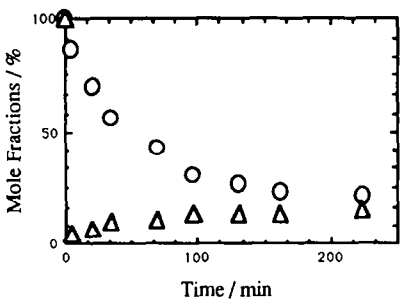
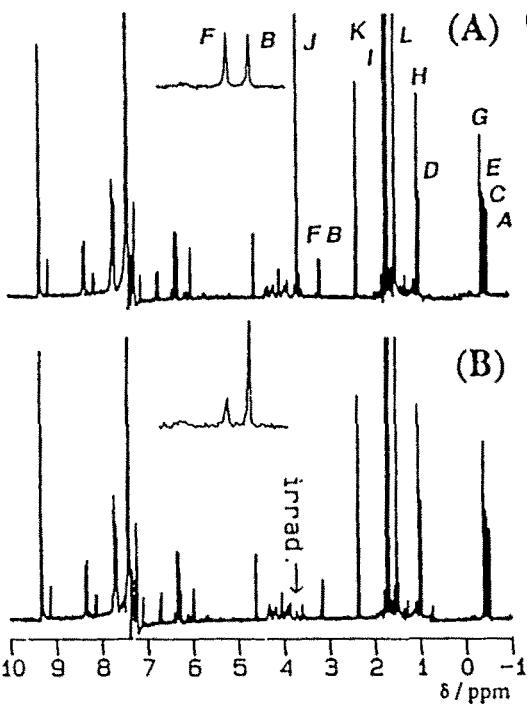


Figure 7. Reaction of the mixture of (CapP)AlOC(=O)CH_3 **5a** (O) and (TPP)AlOC(=O)CH_3 **8a** (Δ) with benzoic acid **4e** at room temperature in C_6D_6. The ratio of **5a/8a/4e** was 1/1/7, and the initial concentration of **5a** was 4.0 x 10^{-3} mol·dm^{-3}. The molar fractions of **5a** and **5b** were determined based on their ^{1}H NMR signals at δ -0.66 (C<u>H</u>$_3$ of **5a**) and δ -0.47 (C<u>H</u>$_3$ of **8a**), respectively.

Relative reactivity of (CapP)Al complexes and (TPP)Al complexes in such exchange reactions of axial ligands was determined by the combination of NMR saturation transfer method[19] and the reaction kinetics. Figure 8 shows the ^{1}H NMR spectra of the reaction mixture in which 2,4-di-t-butylphenol **6b** (5.7μmol) was added to the mixture of (CapP)AlO(2-tBu-4-MeO)Ph **7a** (initial amount was 0.8 μmol), (TPP)AlO(2-tBu-4-MeO)Ph **9a** (0 9μmol) and 2-t-butyl-4-methoxyphenol **6a** (4.4μmol) in C_6D_6 (0.6 ml) at 60°C. The equilibrium mixture of **7a**, (CapP)AlO(2,4-di-t-butyl)Ph **7b**, **9a**, (TPP)AlO(2,4-di-tBu)Ph **9b**, **6a**, and **6b** in a molar ratio of **7a/7b/9a/9b/6a/6b** = 47/53/48/65/450/593 was obtained after 24

$$\left\{\begin{array}{c}\text{(CapP)AlX}\\ +\\ \text{(TPP)AlX}\end{array}\right\} + 2\text{YH} \rightleftharpoons 2\text{XH} + \left\{\begin{array}{c}\text{(CapP)AlY}\\ +\\ \text{(TPP)AlY}\end{array}\right\} \qquad (5)$$



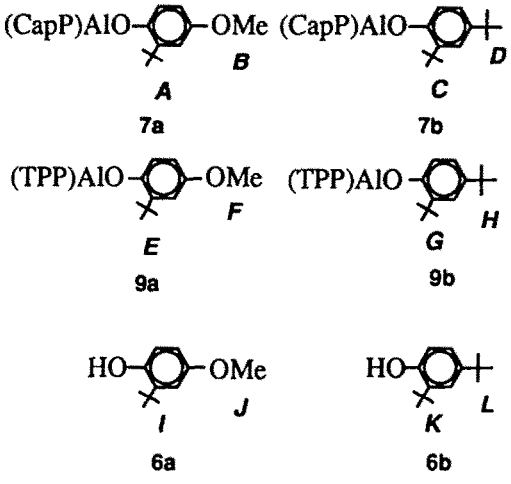


Figure 8. ^{1}H NMR spectra of the equilibrium mixture of **7a**, **7b**, **9a**, **9b**, **6a**, and **6b** in a ratio of 47/53/48/65 /450/593 in C_6D_6 at 60°C, without irradiation (*A*), with irradiation to saturate the signal (J) at d 3.67 (*B*). Concentration of the total (CapP)Al complexes was 1.3 x 10^{-3} mol·dm^{-3}.

hours . When the protons of the MeO - group of the 2-t-butyl-4-methoxy-phenol **6a** at δ 3.67 ppm (J) was saturated with irradiation at 60 °C, the signal of the MeO- protons of (TPP)complex **9a** (F) decreased in intensity to 28% (Fig. 8*B*) compared with the intensity without irradiation (Fig. 8*A*). In contrast, the signal of MeO- group of (CapP)complex **7a** (B) remained without any change. These results mean that the reaction between (TPP)Al phenoxide **9a** and phenol **6a** in the equilibrium system occurs in a time scale comparable to the spin lattice relaxation time T_1 of the protons of MeO- group of **9a**.

The apparent rate constant kobs of the exchange reaction is given by eq. 6,

$$I' / I = 1 / (1 + kobs \cdot T_1) \qquad (6)$$

where I' and I are signal intensities with and without saturation transfer, respectively. The T_1 for the protons of MeO-group of **9a** in this system at 60 °C was observed to be 3.1sec, so kobs was calculated to be 0.8 sec^{-1}. The rate constant k_3 of the second order reaction between **9a** and **6a** can be obtained from eq. 7,

$$R_3 = kobs\ [\mathbf{9a}] = k_3\ [\mathbf{9a}]\ [\mathbf{6a}] \qquad (7)$$

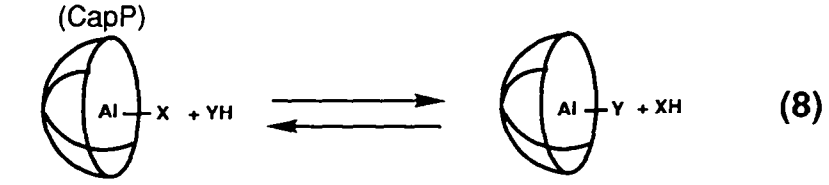
where R_3 is the rate of this reaction. Since [**6a**] at the equilibrium was 6.0 x 10^{-3} mol·dm^{-3}, k_3 was determined to be *ca* . 1 x 10^2 mol^{-1}·dm^3· sec^{-1}.

On the other hand, T_1 for the MeO- protons (B) of (CapP)Al phenoxide **7a** was 2.5 sec. being not much different

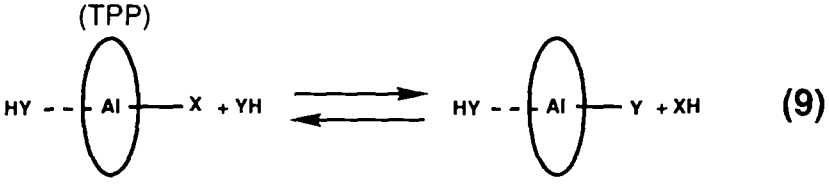
from that for **9a**. Therefore, the exchange between **7a** and phenol **6a** is considered to be so slow ($k_{obs} \cdot T_1 \ll 1$) that effective saturation transfer was not observed, in contrast to the TPP complex.

Thus, the rate constant for (CapP)Al complex was about 1 / 500 fold compared with that for (TPP)Al complex in the exchange of the axial phenoxide ligand.

The approach of the phenol, for instance, to the central metal of the (CapP)AlX is considered to proceed from the same direction of the axial ligand on the porphyrin plane. The exchange of the axial ligand of the (TPP)Al complex is considered to take place on one face of the porphyrin plane similarly to the (CapP)Al complex. Carboxylic acid or phenol approaches to the Al metal from the same direction of the axial ligand to form another carboxylate or phenoxide.



(8)



(9)

Carboxylic acid or phenol (YH) may coordinate to the Al of the TPP complex from the opposite side of the axial ligand to form a 6-coordinated complex. For example, when benzoic acid (10eq.) was added to the solution of (TPP)AlCl in $CDCl_3$, the signal of the ^{27}Al NMR shifted from δ 102.6 to δ 14, indicating the coordination of benzoic acid to (TPP)AlCl [20]. The higher reactivity of the (TPP) Al complex in the exchange of the axial ligand may be interpreted in terms of such 6-coordinated intermediate. 6-coordinated TPP complex is considered to undergo the ligand substitution reaction much faster than the 5-coordinated Al complex, since HY which coordinate to the backside of the axial ligand may enhance the reactivity of Al-X group of (TPP)AlX, which reacts with another HY molecule that approaches the metal from the same direction of Al-X. Higher reactivities of 6-coordinated (TPP)Al complexes in the reactions with CO_2 have been suggested in our earlier studies[4)6)]. In the case of (CapP)AlX, the enhancement of the reactivity by the coordination of HY from the back side of the axial ligand is not possible.

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Experimental

Materials Capped porphyrin ((CapP)H_2, **1**) was synthesized following the procedure of Baldwin *et al.*[10d)].

Tetraphenylporphyrin ((TPP)H_2) was synthesized by Adler's procedure[21]. Commercially available Me_3Al was purified by distillation under reduced pressure of N_2, and stored under a N_2 atmosphere as a toluene solution. CH_2Cl_2 and $CDCl_3$ were distilled over CaH_2. Toluene and C_6D_6 were distilled over Na benzophenone ketyl. 1-Methylimidazole (1-MeIm) was distilled over CaH_2 under reduced pressure, and stored under N_2 atmosphere. Phenols were recrystallized from hexane. Other organic materials were used as received.

Measurement ^1H NMR spectra were measured in 5mm tubes sealed in a N_2 atmosphere, with JEOL Type JNM GSX-270 spectrometer operating at 270.05 MHz at room temperature (*ca.* 23°C) or in the pre-heated probe set at the desired temperature. Chemical shifts were determined with respect to C_6H_6 (δ 7.40) or $CHCl_3$ (δ 7.28). Relaxation time T_1's were determined by the standard inversion-recovery sequence (180°-t -90° pulse). ^{27}Al NMR spectra were obtained by JEOL Type JNM GX-400 spectrometer or JNM GSX-270 spectrometer operating at 100.45MHz and 70.26MHz, respectively, with a multi-nuclei tunable probe for 10mm tubes, at room temperature. Samples were dissolved in 3ml of C_6D_6/toluene (1:2) in 10mm tubes, unless otherwise noted ([C] ≈ 1 x 10^{-2} mol·dm^{-3}). 1.5 M solution of $Al(NO_3)_3 \cdot 9H_2O$ in D_2O was used as an external standard for chemical shifts. Typical parameters for measurement were as follows (GSX-270): Frequency of measurement was 30000Hz, *i.e.*, δ200 ~ δ–230 in ppm, 45° pulse, dead time and delay time (before sampling free induction decay signal (FID)) were 100 μsec, respectively, and the relaxation delay between pulses was 0.2 sec. 1800 to 20000 FIDs were collected by 16K data points, one time zero filling was done to obtain 1.8 Hz resolution. Such prolonged dead time and delay time before sampling FIDs were chosen according to the kind advice at Tohoku university, to prevent the background signals without distorting the signal shapes[13c].

(CapP)AlMe **2**

To a solution of (CapP)H_2 **1** (42mg, 0.04mmol) in dry CH_2Cl_2 (4ml) was added a solution of Me_3Al (0.2mmol) in toluene (1ml) at room temperature in a N_2 atmosphere. The greenish purple solution was evaporated in vacuum after 3 hours, to obtain **2** as a red solid. ^1H NMR ($CDCl_3$): δ 9.02 (s, 4H, ß-pyrrole), 8.91 (s, 4H, ß-pyrrole), 7.88 (dd, J = 7 and 2 Hz, 4H, meso-Ph), 7.81 (dt, 2 and 8 Hz, 4H, meso-Ph), 7.56 (d, 8 Hz, 4H, meso-Ph), 7.40 (t, 7 Hz, 4H, meso-Ph), 5.41 (s, 2H, 'capping' benzene), 4.6-4.2 (m, 12H, CH_2CH_2), 4.0-3.9 (m, 4H, CH_2CH_2), – 7.45 (s, 3H, Al-CH_3).

(CapP)AlOC(= O)CH_3 **5a**

a) (CapP)H_2 **1** (9mg, 0.009mmol) was dissolved in dry CH_2Cl_2 (1ml) and a solution of Me_3Al (0.045mmol) in toluene (0.2ml) was added in a N_2 atmosphere . After 2 hours, acetic acid (1ml) was added, and the red solution thus obtained was washed with water four times. The organic phase was dried (Na_2SO_4), and evaporated to give a red solid, which was indicated to be a mixture of (CapP)AlOH **3** and (CapP)AlOC(= O)CH_3 **5a** by ^1H NMR. This solid was again dissolved in acetic acid (2ml), reacted at 50°C for 2 hours, and the reaction mixture was evaporated to dryness. Then dry toluene was added to dissolve the solid, and volatile materials were evaporated in vacuum. This procedure was repeated 3 times to exclude trace amount of acetic acid to give 7.7 mg of a red powder (0.007mmol, 76%). ^1H NMR (C_6D_6): δ 9.40 (s, 4H, ß-pyrrole), 9.32 (s, 4H, ß-pyrrole), 8.19 (d, 4H meso-phenyl), 7.7-7.2 (m, 12H meso-phenyl), 6.00 (s, 2H, 'capping' benzene), 4.32 (m, 4H, CH_2CH_2), 4.10 (m, 4H, CH_2CH_2), 3.81 (m, 4H, CH_2CH_2), 3.62 (m, 4H, CH_2CH_2), –0.66 (s, 3H, AlOC(= O)CH_3). ^{27}Al NMR ($CDCl_3$): δ 13.5. Anal. for the product obtained by recrystallization from CH_2Cl_2/AcOH: Found:

C, 65.87; H, 3.96; N 4.65: calcd. for (CapP)AlOC(= O)CH_3·2CH_3COOH: C, 65.81; H, 3.98; N 4.51 %.

b) (CapP)H_2 **1** (84mg, 0.08mmol) was reacted with Me_3Al (0.4mmol) in CH_2Cl_2 (8ml) at room temperature for 2 hours, and 10 ml of H_2O containing 10% methanol was added. After 1h of vigorous stirring of the mixture, CH_2Cl_2 and methanol was evaporated, and a pink solid was filtered from the water layer, and the solid thus obtained was dried and-washed by CH_2Cl_2 to give a red solution. The solution was evaporated to dryness, then the residual solid was dissolved in dry toluene, and the solution was evaporated in vacuum to exclude trace of water if any, to obtain a red solid which is considered to be (CapP)AlOH **3** by ^{1}H NMR in $CDCl_3$; signal at δ -1.81 assigned to Al-O<u>H</u> which diminished when D_2O was added[22]. To 3.8mg (0.0035mmol) of this solid was added 2.5ml of acetic acid, and the heterogeneous system was heated at 60°C. The mixture became homogeneous, and after 1 hour of reaction at that temperature the red solution was evaporated to dryness, and 2.5ml of acetic acid was again added to the residue, and reaction was continued at 60°C for additional 13 hours. Evaporation of the reaction mixture and subsequent azetropic distillation with toluene gave a red solid. ^{1}H NMR analysis showed that the product was identical with the product of method a).

<u>(CapP)AlOC(=O)(p-Me)Ph **5f**</u>

To the solution of the red solid obtained by the reaction of (CapP)AlMe **2** and water (15.3mg, corresponding to 0.014mmol of **3**) in dry CH_2Cl_2 (5ml) p-methoxybenzoic acid **4f** (0.014mmol) in toluene (0.95ml) was added at 35°C in a N_2 atmosphere. After 14 hours, volatile materials were evaporated in vacuum, then the solid was dissolved in the mixture of CH_2Cl_2 (5ml) and toluene (2ml). The mixture was heated at 45°C for 10 hours, then evaporated to dryness to obtain **5f** as a red solid. ^{1}H NMR (C_6D_6): δ 9 40 (s, 4H), 9.33 (s, 4H), 8.10(d, 4H), 7.73 (t, 4H), 7.3-7.1 (m, 8H), 6.01(s, 2H, 'capping' benzene), 6.00 (d, 9Hz, 2H, m-Ph of the benzoate), 5.62 (d, 9Hz, 2H, o-Ph of the benzoate), 4.51 (m, 4H), 4.30 (m, 4H), 3.82 (m, 4H), 3.61 (m, 4H), 2.97 (s, 3H, CH_3O-). ^{27}Al NMR (C_6D_6/toluene, 104.05 MHz): δ 13.3, the line width at the 1/2 height (w1/2): 60Hz.

<u>(CapP)AlO(2-tBu-4-MeO)Ph **7a**</u>

To a solution of the red solid obtained by the reaction of (CapP)AlMe **2** and water (3mg, 0.003mmol as **3**) in dry CH_2Cl_2 (1ml) was added a solution of 2-t-butyl-4-methoxyphenol **6a** (0.006mmol) in CH_2Cl_2 (1ml) at room temperature. After 2 hours the reaction mixture was evaporated to dryness, then 3ml of toluene was added to dissolve the solids, and again evaporated in vacuum to exclude trace amount of H_2O generated in the reaction, to leave a red solid, which was found to be a 1:1 mixture of **7a** and 2-t-butyl-4-methoxyphenol **6a** by ^{1}H NMR. This mixture was used for further reaction. ^{1}H NMR (C_6D_6) assigned to **7a**: δ 3.13 (s, 3H, OMe), –0 49 (s, 9H, tBu). ^{27}Al NMR (C_6D_6/toluene, 70.26 MHz): δ 14.2 (w1/2=100Hz)

<u>(TPP)AlOC(=O)(p-MeO)Ph **8f**</u>

To a stirred solution of (TPP)H_2 (64.3mg, 0.11mmol) in dry CH_2Cl_2 (7ml) was added Me_3Al (0.11mmol) in toluene (0.68ml) at room temperature. After 2 hours, p-methoxybenzoic acid **4f** (16.8mg, 0.11mmol) was added and stirring was continued overnight. Evaporation of the reaction mixture gave **8f** as a purple powder[23]. ^{1}H NMR (C_6D_6): δ 9.35 (s, 8H), 8.33 (d, 8H), 7.69, (m, 12H), 5.99 (d, 9Hz, 2H, o-Ph of benzoate), 5.88 (d, 9Hz, 2H, m-Ph of benzoate), 2.93 (s, 3H, OMe). ^{27}Al NMR (C_6D_6/toluene, 104.05MHz): δ 14 2 (w1/2=100Hz).

<u>(TPP)AlO(2-tBu-4-MeO)Ph **9a**</u>

To a stirred solution of (TPP)H_2 (62.4mg, 0.10mmol) in dry CH_2Cl_2 (2ml) was added Me_3Al (0.10mmol) in toluene

(0.62ml) at room temperature. After 2 hours, 2-tert-butyl-4-methoxyphenol **6a** (18.4mg, 0.10mmol) in toluene (0.6ml) was added and stirring was continued overnight. Evaporation of the reaction mixture gave **9a** as a purple powder[7]. ^{1}H NMR (C_6D_6): δ 3.17 (s, 3H, OMe), -0.40 (s, 9H, tBu). ^{27}Al NMR (C_6D_6/toluene, 70.26MHz): δ 14.3 (w1/2=100Hz).

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