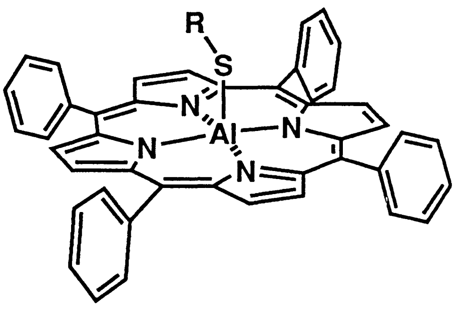
CHEMISTRY LETTERS, pp. 551-554, 1990.

Reaction of Carbon Dioxide with (Porphyrinato)aluminum Thiolates

Toru ARAI, Yoshihiro SATO, and Shohei INOUE*
Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

Reaction of (tetraphenylporphyrinato)aluminum thiolate ((TPP)AlSR) with CO_2 under atmospheric pressure at room temperature afforded (TPP)Al alkylthiocarbonate when R is alkyl or benzyl. Aluminum thiolate complex of capped porphyrin failed to undergo the same reaction, suggesting the importance of the sixth coordination site of the aluminum metal.



1 (TPP)AlSR

The chemical fixation of carbon dioxide (CO_2) has been of much interest in recent years, intending the circular utilization of carbon resources.[1)] We have been studying the reaction of (porphyrinato)aluminum complexes with CO_2. The examples are the insertion reactions of CO_2 under atmospheric pressure in the Al-X bond of the (tetraphenylporphyrinato)aluminum complexes (TPP)AlX where X is alkyl,[2a)] alkoxy,[2b)] or enolate[2c)] group in the presence of 1-methylimidazole. Aluminum porphyrins can bring about the catalytic formations of cyclic carbonate[2b)] or polycarbonate[2d)] from CO_2 and epoxide, and of carbamic ester from CO_2, amine, and epoxide,[2e)] via the intermediates bearing Al-O-C(=O)-X groups as the axial ligands. We report here a novel insertion reaction of CO_2 with (porphyrinato)aluminum thiolates, which proceeds easily even in the absence of added base under mild conditions such as atmospheric pressure of CO_2 at room temperature, and is influenced remarkably by the structure of the porphyrin ligand.

When CO_2 was bubbled to the solution of (tetraphenylporphyrinato)aluminum ethanethiolate ((TPP)AlSEt (**1a**)) (0.1 mmol) in CH_2Cl_2 (4 cm^3) at room temperature,[3)] a new absorption band appeared immediately at 1650 cm^{-1} in the IR spectrum of the reaction mixture, which is assignable to the absorption of an aluminum carbonate. In the ^{13}C NMR spectroscopy, when CO_2 enriched in ^{13}C was introduced to the $CDCl_3$ solution of **1a**, an enhanced signal assigned to the carbonyl carbon appeared at δ 163.4, while the dissolved CO_2 showed its signal at δ 124.9 (Fig. 1). ^1H NMR spectrum of the reaction mixture of **1a** and CO_2 showed the signals due to the ethylthio group at δ 0.96 (**A'**, q, 2H, CH_2) and at δ -0.02 (**B'**, t, 3H, CH_3) in $CDCl_3$, which were shifted downfield from the signals of the ethylthio group of **1a** at δ -2.02 (A, CH_2) and

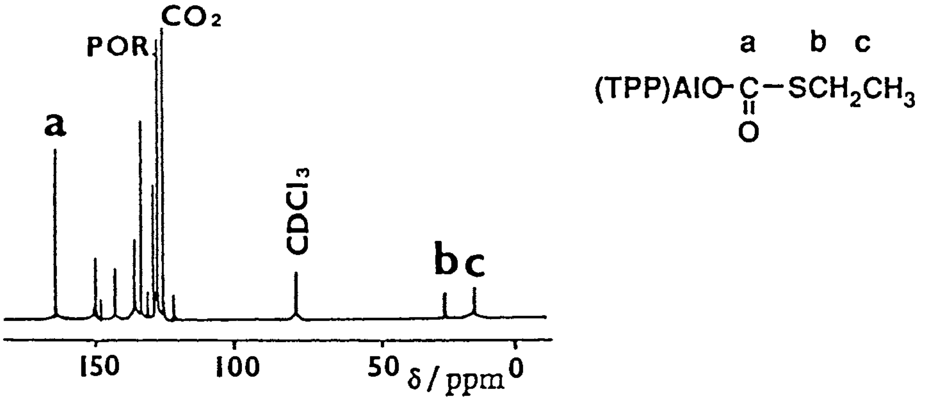


Fig 1. ^{13}C NMR spectrum of the reaction mixture of (TPP)AlSEt **1a** with $^{13}CO_2$ in $CDCl_3$.

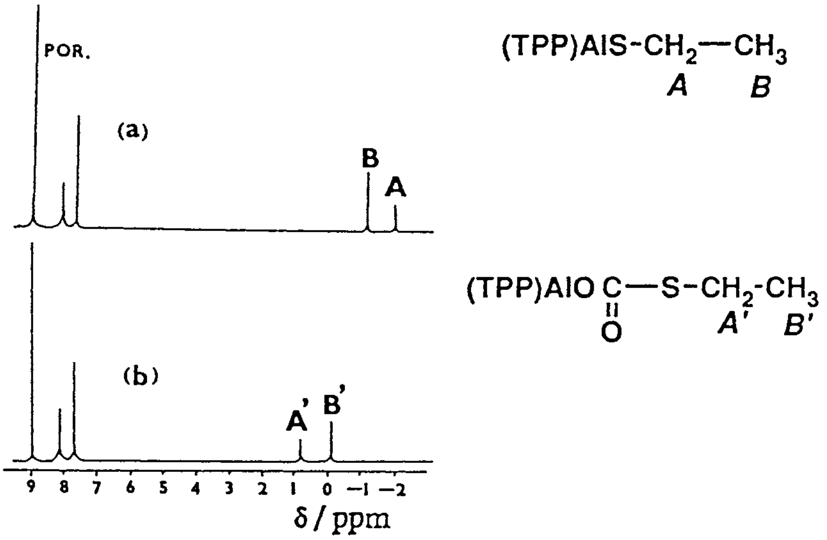
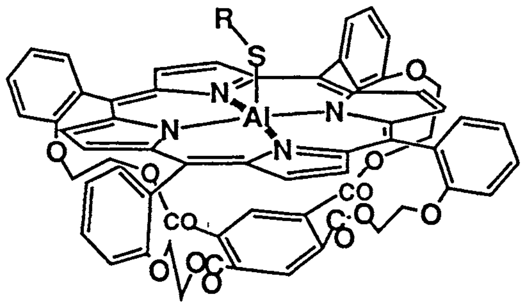


Fig. 2. ^{1}H NMR spectra of (TPP)AlSEt **1a** (a) and the reaction mixure of **1a** with CO_2 (b) in $CDCl_3$.

δ -1.14 (**B**, CH_3), respectively (Fig. 2). The downfield shifts of the signals of the ethylthio group in ^{1}H NMR correspond to the insertion of CO_2 between Al and SEt group to form ethylthiocarbonate complex (TPP)AlOC(=O)SEt (**2a**), resulting in a longer distance between porphyrin plane and SEt group, and decrease in the shielding effect of the porphyrin ring current (Eq.1).

$$\underset{\mathbf{1}}{\text{(TPP)AlSR}} + CO_2 \longrightarrow \underset{\mathbf{2}}{\text{(TPP)AlOC(=O)SR}} \qquad (1)$$

1a, 2a : R = Et
1b, 2b : = ^{n}Pr
1c, 2c : = ^{t}Bu
1d, 2d : = CH_2Ph



3 (CapP)AlSR
3a : R = Et
3b : R = ^{n}Pr
3d : R = CH2Ph

Similarly, CO$_2$ was found to react with various (TPP)AlSR **1** (-R=-^{n}Pr, -^{t}Bu, -CH$_2$Ph), to form the corresponding (TPP)AlOC(=O)SR complex **2** quantitatively in CDCl$_3$, but (TPP)AlSPh or (TPP)AlSC(=O)Me did not trap CO$_2$. The reaction of (TPP)AlSR (R=alkyl, benzyl) with CO$_2$ proceeded in CH$_2$Cl$_2$, CHCl$_3$, and THF. The reaction was reversible in CH$_2$Cl$_2$ and CHCl$_3$. When N$_2$ gas was bubbled to the reaction mixture of **1a-d** and CO$_2$ in CDCl$_3$ to purge CO$_2$ unreacted, **2a-d** was decarboxylated quickly, and quantitative recovery of **1a-d** was confirmed by ^{1}H NMR.

The most interesting finding observed in the study of this CO$_2$ insertion reaction is that the aluminum thiolate complex of capped porphyrin ((CapP)AlSR (3)$^{4)}$) did not react with CO$_2$ under the same conditions. Figure 3a shows the high magnetic field region of the ^{1}H NMR spectrum of the mixture of (TPP)AlSCH$_2$Ph **1d** (13 μmol) and (CapP)AlSCH$_2$Ph 3d (13 μmol) in CDCl$_3$ (0.61 cm^3). The signals at δ -0.91 (C) and at δ -1.31 (D) are due to the benzyl methylene protons of the axial ligands of **1d** and 3d, respectively. To this mixture was introduced CO$_2$ for a minute, followed by

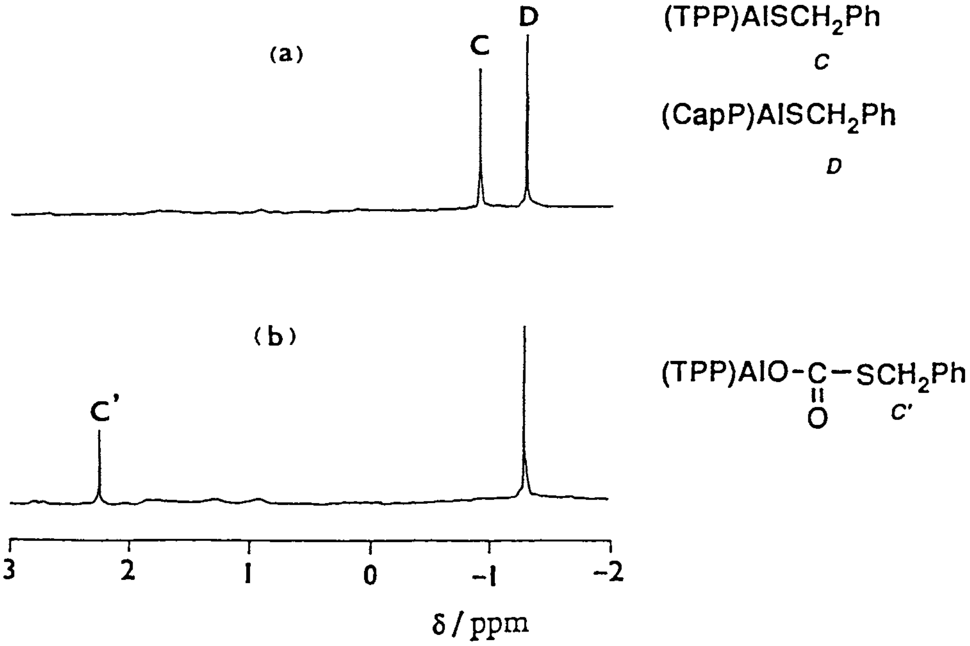


Fig.3. ^{1}H NMR spectra of the mixture of (TPP)AlSCH$_2$Ph **1d** and (CapP)AlSCH $_2$Ph **3d** in CDCl$_3$ before (a) and after (b) the addition of CO$_2$.

^{1}H NMR analysis (Fig. 3b). It is clearly shown that **1d** reacted with CO_2 to form benzylthiocarbonate complex **2d**. Signal **C** due to **1d** disappeared completely, while the proton of the benzyl group of **2d** was observed at δ 2.24 (**C'**). In clear contrast, under exactly the same conditions, **3d** remained unreacted (signal **D**). A similar observation was made when CO_2 was bubbled to the mixture of (TPP)AlSEt **1a** and (CapP)AlSEt **3a**.

The difference in the reactivities between (TPP)AlSR and (CapP)AlSR in the insertion reaction of CO_2 suggests the importance of the sixth coordination site of the aluminum. It is considered that the solvent or possibly CO_2 molecule coordinating to this site enhances the reactivity of the aluminum-axial ligand bond. There is also the possibility that CO_2 coordinated to this site is activated for the attack by (TPP)AlSR. In the case of (CapP)Al complexes backside to the axial ligand of the aluminum is entirely protected by the 'cap', and the participation of the sixth coordination site in the reaction is unlikely. Detailed study of the reaction mechanism is in progress.

We thank Dr. Hideki Murayama for preliminary experiments.

References

1) Recent reviews : S. Inoue and H. Koinuma, *Rev. Inorg. Chem.*, **6**, 291 (1984); "Carbon Dioxide as a Source of Carbon," ed by M. Aresta, and G. Forti, D. Reidel Publishing Company, Dordrecht (1987).
2) a) S. Inoue and N. Takeda, *Bull. Chem. Soc. Jpn.*, **50**, 984 (1977); b) T. Aida and S. Inoue, *J. Am. Chem. Soc.*, **105**, 1304 (1983); c) Y. Hirai, T. Aida, and S. Inoue, ibid., **111**, 3062 (1989); d) T. Aida, M. Ishikawa, and S. Inoue, *Macromolecules*, **19**, 8 (1986); e) F. Kojima, T. Aida, and S. Inoue, *J. Am. Chem. Soc.*, **108**, 391 (1986).
3) (TPP)AlSR was synthesized from (TPP)AlEt and the corresponding thiol, see : T. Arai, H. Murayama, and S. Inoue, *J. Org. Chem.*, **54**, 414 (1989).
4) (CapP)AlSR was synthesized from (CapP)AlMe and thiol. For the syntheses of (CapP)AlX and the substitution reaction of Al-X group with protic compounds, see : T. Arai and S. Inoue, *Tetrahedron*, in press.

(Received January 11, 1990)