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Stereoselective Formation of Aluminum Enolate on Capped Porphyrin

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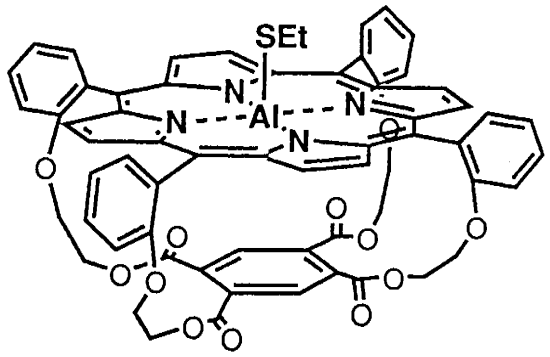
Addition of aluminum ethanethiolate complex of a capped porphyrin to α,β-unsaturated ketone affords the complexes with Z-enolate as the axial ligand stereoselectively. The aluminum ethanethiolate complex also reacts with enolizable ketone under irradiation with visible light to yield corresponding Z-enolate.

The reactions of metalloporphyrins have been paid much attention in view of their biological roles including the particularly high stereospecificity and their possible synthetic applications. We have found that (tetraphenylporphyrinato)aluminum enolates are formed stereoselectively by the reaction of (tetraphenylporphyrinato)aluminum ethanethiolate ((TPP)AlSEt) with α,β- unsaturated ketone, or by the reaction of (TPP)$AlNEt_2$ with enolizable ketone. The axial enolate groups formed in these reactions are exclusively the Z-isomer.[1] On the other hand, the side opposite to the axial ligand has been considered to play an important role in some reactions of aluminum porphyrin. For example, the reaction of carboxylic acid with (porphyrinato)aluminum carboxylate or the insertion of CO_2 to (porphyrinato)aluminum thiolate is suppressed when the sixth-coordinating site is protected as in the case of aluminum complexes of capped porphyrin (CapP)AlX.[2] In this communication are reported the reactions of aluminum ethanethiolate complex of a capped porphyrin



1 (CapP)AlSEt

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(CapP)AlSEt (**1**) with α,β-unsaturated ketone and enolizable ketone to produce Z-enolates selectively. It is interesting that the backside of the aluminum with respect to the axial ligand is not essential in the stereoselective formation of (porphyrinato)aluminum enolate.

$$(P)AlSEt + R^1COCH{=}CH_2 \longrightarrow (P)AlOCR^1{=}CHCH_2SEt \quad (1)$$

$$(P)AlSEt + PhCOCH_2R^2 \longrightarrow (P)AlOCPh{=}CHR^2 + HSEt \quad (2)$$

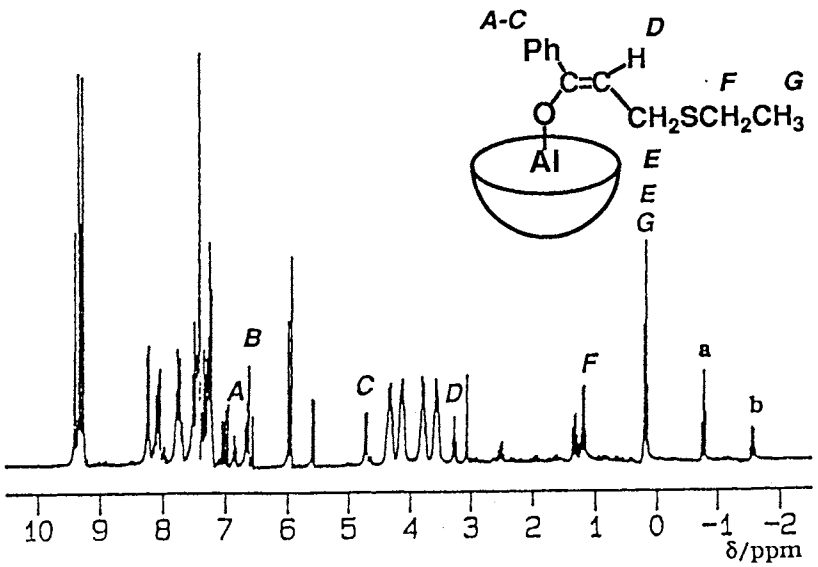
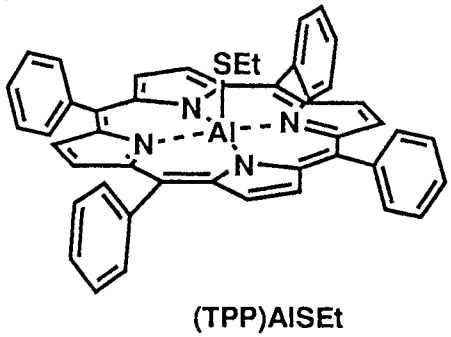


Fig.1 ^{1}H NMR spectrum of the reaction mixture (CapP)AlSEt **1** / phenyl vinyl ketone (1:2) after 3 h at room temperature in C_6D_6. **a** and **b** indicate the signals for **1**.

To a solution of (CapP)AlSEt **1** (0.015 mmol) in C_6D_6 (0.7 cm^3), a solution of phenyl vinyl ketone (0.025 mmol) in C_6D_6 (0.5 cm^3) was added under nitrogen atmosphere.[3] In the ^{1}H NMR spectrum of the reaction mixture measured after 3 h (Fig.1), the signals of the axial SEt group of **1** (**a**, δ -0.78, t, $SCH_2\underline{CH_3}$, **b**, δ -1.56, q, $S\underline{CH_2}CH_3$) were decreased in intensities, and a set of new signals (**A-G**) was observed. The signals at δ 6.84 (**A**, t, para), 6.64(**B**, t, meta), and 4.71 (**C**, d, ortho) are due to the phenyl protons of the axial ligand which interact with the porphyrin ring current and shift to the higher magnetic fields than in phenyl vinyl ketone (δ 8.1 and 7.3 for phenyl group). Other signals (**D**, δ 3.26, t, $CPh{=}C\underline{H}CH_2$, **E**, δ 0.19, d, $CPh{=}CH\underline{CH_2}$, **F**, δ 1.17, q, $C\underline{H_2}CH_3$, **G**, δ 0.18, t, $CH_2C\underline{H_3}$) are also assigned to the protons of the axial enolate group of (CapP)AlOCPh=$CHCH_2$SEt (**2a**) on the basis of their chemical shifts, modes of splitting, and relative intensities (**A/B/C/D/(E** plus **G)/F** = 1/2/2/1/5/2). The signal intensities of (CapP)AlSEt **1** and (CapP)Al enolate **2a** relative to the porphyrin ligand (9.4 and 9.5, pyrrole protons) indicated that the conversion of (CapP)AlSEt **1** to the enolate **2a** was ca. 70% (Eq.3).[4]

$$(CapP)AlSEt + R^1COCH{=}CH_2 \longrightarrow (CapP)AlOCR^1{=}CHCH_2SEt \quad (3)$$
1 **2a:** R^1=Ph, **2b:** R^1=^{t}Bu

The vinyl proton of **2a** is considered to be located in the trans position to the (P)AlO- moiety from the observed chemical shift at δ 3.26 in C_6D_6, while the proton placed cis to AlO- would appear in higher magnetic field about δ 0[5] owing to the strong shielding effect of the porphyrin ring current. Hence (CapP)Al enolate **2a**, the reaction product of (CapP)AlSEt **1** with phenyl vinyl ketone is the Z-isomer. When tert-butyl vinyl ketone (2 equiv.) was reacted with (CapP)AlSEt **1** in $CDCl_3$, the addition reaction was much slower than in the case of phenyl vinyl ketone (ca. 40% consumption of **1** after 70 h), and Z-isomer of (CapP)AlOC^{t}Bu=CHCH$_2$SEt (**2b**) was formed almost quantitatively to the amount of **1** reacted.[6]



(TPP)AlSEt

(CapP)Al enolate is also formed when a $CDCl_3$ solution of (CapP)AlSEt **1** was irradiated with visible light in the presence of an enolizable ketone. Fig.2 shows the ^{1}H NMR spectrum of the reaction mixture between (CapP)AlSEt **1** (0.025 mmol) and propiophenone (0.20 mmol) in $CDCl_3$ (0.7 cm^3) after 24h irradiation with visible light (Xe lamp, 300 W). No signal of (CapP)AlSEt **1** (δ -1.33 and -2.35) was observed, but instead signals of EtSH (δ 2.58, quintet, $CH_3C\underline{H}_2SH$) was detected. The most remarkable signal in Fig.2 is the doublet **E** observed at δ -1.52, which can be assigned to the methyl protons of the axial enolate group, (CapP)AlOCPh=CH<u>Me</u> (**3**)(Eq.4). The relative intensities of the enolate ligand of **3** (**A**, δ 6.62, t, p-Ph, **B**, δ 6.34, t, m-Ph, **C**,δ 4.13, d, o-Ph, and **E**) revealed that the conversion of **1** to enolate **3** was ca. 40%. It is concluded that the reaction product of (CapP)AlSEt **1** and propiophenone (Fig.2) is the

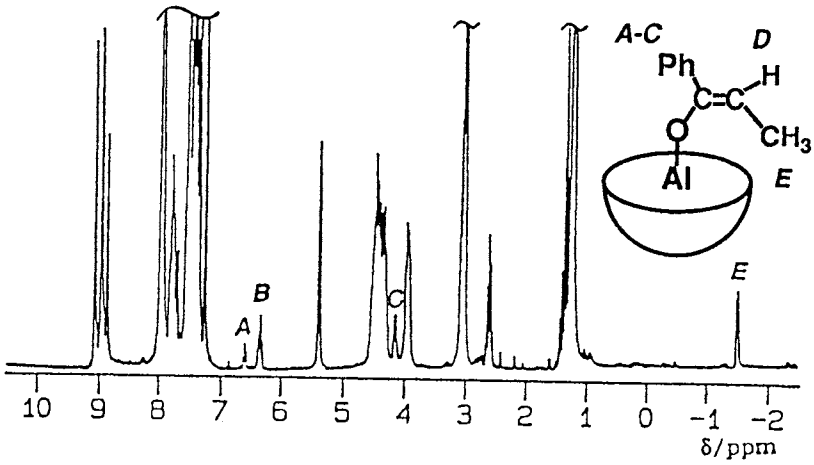


Fig.2 ^{1}H NMR spectrum of the reaction mixture (CapP)AlSEt **1** / propiophenone (1:8) after 24 h irradiation with visible light at room temperature in $CDCl_3$.

Z-isomer of the enolate, since the methyl signal of (TPP)AlOCPh=CHMe (Z-isomer) is observed at δ -1.12 in $CDCl_3$ indicating that the geometry as to the methyl and (P)AlO groups is all the same between (CapP)Al and (TPP)Al enolates.[7)]

$$\underset{\mathbf{1}}{\text{(CapP)AlSEt}} + \text{PhCOEt} \longrightarrow \underset{\mathbf{3}}{\text{(CapP)AlOCPh=CHMe}} + \text{HSEt} \quad (4)$$

It is interesting that both in the conjugated addition and proton abstraction, stereoselective formations of Z-enolates on capped porphyrin were observed. To investigate the possible mechanism which accounts for the stereoselection, that must proceed on one face of the porphyrin plane, is a further subject.

References

1) T. Arai, H. Murayama, and S. Inoue, J. Org. Chem., 54, 414 (1989).
2) T. Arai and S. Inoue, Tetrahedron, 46, 749 (1990); T. Arai, Y. Sato, and S. Inoue, Chem. Lett., 1990, 551.
3) (CapP)AlSEt 1 was synthesized by the reaction of (CapP)AlMe[2)] with excess amount (50 equiv.) of EtSH in benzene for 5 days. Unreacted thiol was removed from the reaction mixture by evacuation.
4) (CapP)AlOCPh=CHCH$_2$SEt **2a**: ^{13}C NMR (C_6D_6), δ 97.9 (CPh=$\underline{C}$HCH$_2$), 23.5 ($\underline{C}$H$_2$), 22.7 ($\underline{C}$H$_2$), 13.7 ($\underline{C}$H$_3$).
5) For (TPP)AlOCPh=CH$_2$, signals of the vinyl protons were observed at 2.36 (trans to Al), and δ -0.04 (cis to Al) in $CDCl_3$. For (TPP)AlOCPh=CHCH$_2$SEt, the vinyl proton was observed at δ 3.39 in C_6D_6. See Ref. 1).
6) (CapP)AlOC^{t}Bu=CHCH$_2$SEt **2b**: ^{1}H NMR ($CDCl_3$), δ 1.83 (t, C^{t}Bu=C$\underline{H}$CH$_2$), 0.69 (q, C$\underline{H}_2$CH$_3$), 0.08 (t, CH$_2$C$\underline{H}_3$), -0.91 (d, C^{t}Bu=CHC$\underline{H}_2$), -1.65 (s, $^t\underline{Bu}$). (TPP)AlOC^{t}Bu=CHCH$_2$SEt: ^{1}H NMR ($CDCl_3$), δ 2.10 (vinyl-H), 0.81, 0.02, -0.67, -1.43.
7) The reaction of propiophenone (3 equiv.) with (TPP)AlSEt in $CDCl_3$ affords Z-isomer of (TPP)AlOCPh=CHCH$_3$ quantitatively after 12 h irradiation with visible light. ^{1}H NMR ($CDCl_3$), δ 6.81, 6.53, 4.42, 2.84, -1.12

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