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Aldol Condensation Catalyzed by Highly Electron Deficient Iron Porphyrin

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Abstract: *The perchlorate complex of 2,4,6,8-tetratrifluoromethyl-1,3,5,7-tetraethylporphyrin•Fe(III) shows the extraordinarily positive reduction potential, 0.81 V vs. Ag/AgCl (reversible). The complex catalyzes the aldol condensation of cyclohexanone.*

Recently, we found a highly electrophilic Rh(III) complex of octa-ethylporphyrin(OEP) catalyzed aldol condensation under a neutral condition *via* enolization of ketone.1) The catalytic activity is considered to be due to the high electrophilic nature of the central rhodium ion. Here, we report that such catalytic activity is not special characteristics of the complex of higher transition metals such as Rh but an iron porphyrin also shows similar catalytic activity for aldol condensation, if appropriately designed electron deficient porphyrin is used as the ligand (Fig. 1).

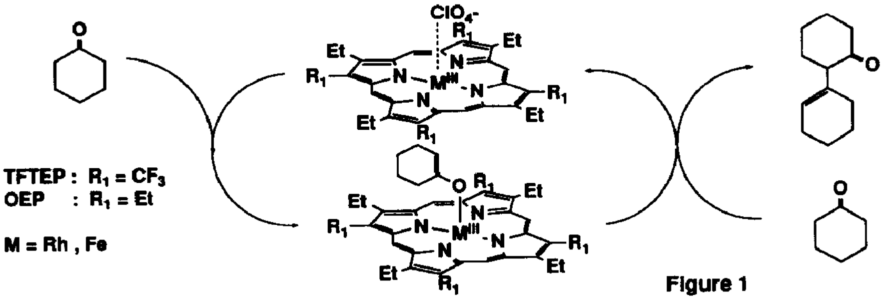

Figure 1

The iron complex of 2,4,6,8-tetratrifluoromethyl-1,3,5,7-tetraethyl-porphyrin (TFTEP•Fe(III)•Cl) shows highly positive reduction potential (-0.07 V vs. Ag/AgCl) compared with the corresponding octaethylporphyrin (OEP) complex (-0.37 V vs. Ag/AgCl).2) This electron deficient nature of TFTEP may be further enhanced by changing the chloride ligand for a noncoordinating perchlorate counterion.3) As expected, the cyclic voltammetory experiment for TFTEP•Fe(III)•ClO_4, which is prepared by addition of 1.5 eq. $AgClO_4$ into the solution (CH_2Cl_2) of TFTEP•Fe(III)•Cl, shows the extraordinarily positive reduction potential, 0.81 V vs. Ag/AgCl (reversible).4) Thus, this highly electrophilic TFTEP•Fe(III)•ClO_4 is tested as the catalyst for the aldol condensation. The reaction was carried out by using catalytic amount of the complex and $AgClO_4$ in neat cyclohexanone. The results and detailed conditions are summarized in Table 1.

Comparison of electronic spectra of the reaction mixture before and after the reaction indicates

Table 1. The aldol condensation of cyclohexanone catalyzed by TFTEP•Fe(III)•ClO$_4$. a)

Porphyrin (μmol)	[AgClO$_4$] (μmol)	Yield b) %)	Temp. (°C)	Turnover No. c)
TFTEP•Fe(III)•Cl (2.6)	26	13	50	1000
OEP•Fe(III)•Cl (2.6)	26	<0.1	50	—
TPP•Fe(III)•Cl d) (2.6)	26	<0.1	50	—
TFTEP•Fe(III)•Cl (2.6)	26	23	90	1770
TFTEP•Fe(III)•Cl (2.6)	26	69 e)	90	5300
TFTEP•Fe(III)•Cl (2.6)	0	<0.1	90	—
TPFPP•Fe(III)•Cl f) (2.6)	26	12	90	920
None	26	<0.1	90	—
[BF$_3$•Et$_2$O (13)	0	10	90	153] g)

a) All reactions are carried out in neat cyclohexanone (20 mmol) under N$_2$. b) Yields of 2-(1-cyclohexenyl)cyclohexanone based on used cyclohexanone. The yields are determined after 12 h. for the reactions at 50 °C and 2h. for that at 90 °C, respectively. c) The values of (amount of product) / (porphyrin used). d) TPP : Tetraphenylporphyrin. e) The yield is determined after 10 h. reaction. f) TPFPP : meso-tetrakis(pentafluorophenyl)porphyrin, g) The reaction using BF$_3$•Et$_2$O as usual Lewis acid catalyst without porphyrin.

that no appreciable decomposition of the catalyst is observed during the reaction. The results shown in Table 1 clearly indicate following characteristics of the present reaction ; a) both TFTEP•Fe complex and AgClO$_4$ are essential for the present catalysis, b) iron complexes of usual porphyrins such as OEP and TPP are catalytically inactive even in the present of AgClO$_4$, c) the significantly large turnover numbers indicate that TFTEP complex is the true catalyst for the present aldol condensation, and d) the TFTEP complex seems to be a more effective catalyst than typical Lewis acid catalyst such as BF$_3$•Et$_2$O. Importance of the high reduction potential nature of the ligand is also shown by the fact that another typical electron defficient porphyrin, TPFPP, also catalyzes the present reaction as shown in Table 1. Furthermore, the preliminary experiments suggest that the present system also catalyzes self condensations of other cyclic alkanones and their cross condensation with benzaldehyde.

Since the present results suggest that it is possible to develop new types of metal catalysts for aldol condensations by the *ligand design*, we are now investigating detailed mechanisms of these reactions.

References and Notes.

1) Aoyama, Y. ;Tanaka, Y. ;Yoshida, T. ;Toi, H.;Ogoshi, H.,*Organometallic Chem.*,**1987**,*329*, 251.
2) a) Homma, M. ;Aoyagi, K.;Aoyama, Y. ;Ogoshi, H.,*Tetrahedron Lett.*, **1983**, *24* , 4343. b) Honda, H. ;Toi, H. ;Aoyama, Y. ;Ogoshi, H.,*ibid.*, **1986**, *26*, 4221. c) Aoyagi, K. ;Toi, H. ;Aoyama, Y. ; Ogoshi, H., *Chem. Lett.*, **1988**, 1891. d) Ogoshi, H. ;Suzuki, Y. ;Kuroda, Y., *ibid.*, **1991**, 1547.
3) The reduction potentials of OEP•Fe(III)•ClO$_4$ and TPP•Fe(III)•ClO$_4$ are reported to be 0.15 and 0.27 V vs. Ag/AgCl, respectively, see Kadish, K. M. ; Bottomley, L. A. ; Kelly, S. ; Schaeper, D. ; Shiue, L. R., *Bioelectrochem. Bioenerg.*, **1981**, *8*, 213.
4) On addition of AgClO$_4$, the Soret band of TFTEP•Fe•Cl at λ_{max} 407 nm (log ε = 4.95) shows a significant blue shift to λ_{max} 395 nm (log ε = 5.14).

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