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Zirconium Porphyrins as Novel Active Catalysts for Highly Regio- and Stereo-selective Ethylalumination of Alkynes

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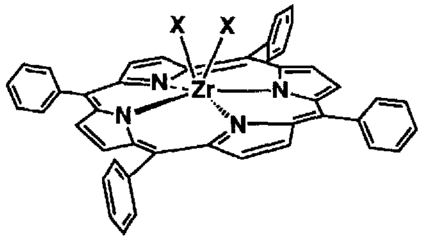
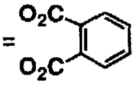
Abstract : Zirconium(IV) complexes of 5, 10, 15, 20-tetraphenylporphyrin ((TPP)ZrX_2) catalyze highly regio- and stereo-selective ethylalumination of terminal alkynes with satisfactorily high turnover numbers.



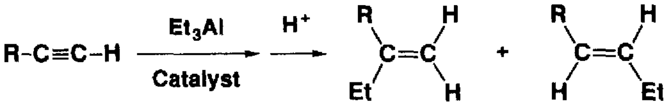
1a X = O_2CCH_3
1b X = $O_2CC(CH_3)_3$ (O_2C^tBu)
1c X_2 =



1d X = Cl

Carbometallation of alkynes is of high potential utility to synthesize regio- and stereo-defined polysubstituted alkenes. However, to date, only limited success has been reported for controlled carbometallation reactions.[1] Negishi *et. al.* has exploited an elegant methodology for controlled carboalumination of alkynes by using the system composed of trimethylaluminum (Me_3Al) and zirconocene dichloride (Cp_2ZrCl_2), which proceeds with high regio- and stereo-selectivities.[2] The reaction proceeds catalytically with respect to Cp_2ZrCl_2, but the turnover number is rather low, and the regioselectivities using higher alkylaluminums such as Et_3Al are far from satisfaction.

We wish to report here metalloporphyrins of zirconium(IV) ((TPP)ZrX_2 (**1**), TPP: 5,10,15,20-tetraphenylporphinato)[3] as novel, highly active catalysts for regio- and stereo-controlled ethylalumination of terminal alkynes with Et_3Al (**Scheme I**).



2 **3** **4**

Scheme I

A typical example is as follows: To a 10 mL round-bottomed flask fitted with a three-way stopcock containing a toluene suspension (0.5 mL) of (TPP)Zr(O_2C^tBu)$_2$ (**1b**) (0.022 g, 0.025 mmol) under dry nitrogen were added 100 molar equiv. of Et_3Al at room temperature, where **1b** was immediately dissolved to give a clear reddish brown solution. To this system was added 1-heptyne (1.25 mmol, 50 equiv.) at 0 °C, and the mixture was stirred magnetically, where the conversion of 1-heptyne, as determined by GC after quenching the reaction mixture with methanol, reached 26 and 71 % in 24 and 60 h, respectively, to give virtually a single regioisomer, 2-ethyl-1-heptene (**3**, R = $^nC_5H_{11}$)[4] (selectivity > 99 %) (**runs 9** and **10**, **Table 1**). The yield of another regioisomer, 3-nonene (**4**, R = $^nC_5H_{11}$), was negligibly low throughout the reaction. For comparison, when Cp_2ZrCl_2 was used as catalyst under similar conditions, 1-heptyne was ethylaluminated in only 9 % yield with a poor regioselectivity ([**3**]/[**4**] = 70:30) (**run 14**).

Other zirconium porphyrins, **1a**, **c** and **d**, also exhibited high catalytic activities and regioselectivities for the ethylalumination of 1-heptyne (**runs 7**, **11**, **12**), while other metalloporphyrins such as (TPP)$TiCl_2$, (TPP)TiO, (TPP)VO, [(TPP)NbO]$_2$O, (TPP)FeO_2CCH_3

Table 1. Catalytic Ethylalumination of Alkynes with the Et_3Al/(TPP)ZrX_2 (**1**) System.[a]

run	**2** (R =)	catalyst	temp. in °C	time in h	conv. in %[c,d]	**3**:**4**[c]
1	$^nC_3H_7$	**1b**	0	55	26	>99:<1
2	$^nC_3H_7$	Cp_2ZrCl_2	0	55	8	71:29
3	$^iC_4H_9$	**1b**	0	72	17	97: 3
4	$^iC_4H_9$	Cp_2ZrCl_2	0	72	15	62:38
5	$^tC_4H_9$	**1b**	35	6	48	<1:>99
6	$^tC_4H_9$	Cp_2ZrCl_2	35	6	31	15:85
7	$^nC_5H_{11}$	**1a**	20	20	40	94: 6
8	$^nC_5H_{11}$	**1b**	20	13	52	96: 4
9[b]	$^nC_5H_{11}$	**1b**	0	24	26	>99:<1
10[b]	$^nC_5H_{11}$	**1b**	0	60	71	>99:<1
11	$^nC_5H_{11}$	**1c**	20	24	33	80:20
12	$^nC_5H_{11}$	**1d**	20	24	52	88:12
13	$^nC_5H_{11}$	Cp_2ZrCl_2	20	24	31	61:39
14[b]	$^nC_5H_{11}$	Cp_2ZrCl_2	0	72	9	70:30
15[b]	Ph	**1b**	0	72	52	90:10
16[b]	Ph	Cp_2ZrCl_2	0	72	11	21:79

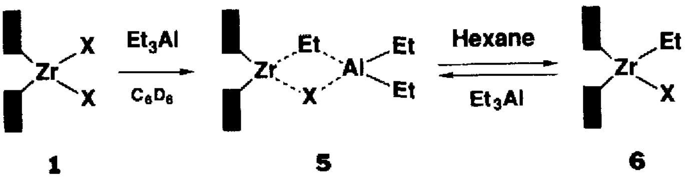
[a] [Alkyne]$_0$/[Et_3Al]$_0$/[catalyst]$_0$ = 1.25/2.5/0.025 (in mmol) in benzene (0.5 mL).
[b] In toluene. [c] By GC. [d] Conv./2 = turnover number.

and (TPP)MnO_2CCH_3 exhibited little or no catalytic activities.

1b also catalyzed regioselective ethylalumination of other terminal alkynes (**runs 1, 3, 5** and **15**), where the regioselectivities and turnover numbers are higher than those obtained with Cp_2ZrCl_2 as catalyst (**runs 2, 4, 6** and **16**). In the ethylaluminations of 1-pentyne (**run 1**) and 4-methyl-1-pentyne (**run 3**) using **1b** as catalyst, terminal alkenes (**3**) were obtained as major products, while the reaction of 3,3-dimethyl-1-butyne gave internal alkene (**4**) predominantly (**run 5**). *In these cases, the isomers preferentially formed are the same as those obtained* using Cp_2ZrCl_2 as catalyst. On the other hand, this is not the case for the ethylalumination of phenylacetylene, where the catalyst **1b** preferred the formation of terminal alkene (**run 15**), while internal alkene was favorably formed when Cp_2ZrCl_2 was used as catalyst (**run 16**).

2,2-Dimethyl-3-hexene obtained in **run 5** was exclusively the *trans* isomer ($^3J_{HH}$ = 15.63 Hz), indicating *cis* addition of the aluminum - ethyl group onto the carbon - carbon triple bond. Furthermore, (E)-1-deuterio-2-phenyl-1-butene was obtained when the reaction mixture in **run 15** was quenched with D_2O,[5] again indicating *cis* addition. Thus, the high stereoselectivity of the reaction should be noted.

In the ^1H NMR spectrum of the mixture of **1b** ($^tBuCO_2$-Zr(TPP): δ0.26) and Et_3Al (1/3) in C_6D_6, characteristic signals were observed in the upfield region at δ-2.68 (t, CH_3), -3.37 (q, CH_2) and -0.03 (s, $C(CH_3)_3$), which are assignable to *Et*-Zr(TPP) and $^tBuCO_2$-Zr(TPP), respectively, considering a strong shielding effect of the porphyrin ring. Integration of these signals indicated the presence of the Et, $^tBuCO_2$ and (TPP)Zr moieties in 1:1:1 ratio. When hexane was added to the above mixture, a rather unstable, crystalline compound, presumably (TPP)Zr(Et)O_2C^tBu (**6**) (**Scheme II**), was obtained, which showed in the ^1H NMR spectrum the absence of any signals assignable to *Et*-Al species together with downfield shifts for the signals of *Et*-Zr(TPP) (δ-0.80 (t, CH_3) and -3.21 (q, CH_2)) and $^tBuCO_2$-Zr(TPP) (δ0.39) from those of the **1b**/Et_3Al system. However, when Et_3Al was supplied to this system, the chemical shift values of these signals reverted to those before adding hexane. Judging from these NMR profiles, the (TPP)Zr($O_2C^tBu)_2$ (**1b**)/Et_3Al system is likely to involve a bridged structure such as **5**.



Scheme II

The present work demonstrated a potential utility of rigid, bulky porphyrin macrocycle for sterically controlled organic syntheses.[6] Further studies are in progress.

References and Notes

[1] Reviews: for example, E. Negishi and T. Takahashi, *Aldrichimica Acta* 1985, **18**, 31; Idem, *Synthesis* **1988**, 1.

[2] D. E. Van Horn and E. Negishi, *J. Am. Chem. Soc.* 1978, **100**, 2252; T. Yoshida and E. Negishi, *ibid.* 1981, **103**, 4985; E, Negishi, D. E. Van Horn and T. Yoshida, *ibid.* 1985, **107**, 6639.

[3] **1a** was prepared similarly to (OEP)Zr$(O_2CCH_3)_2$ (OEP: octaethylporphinato) reported in J. W. Buchler, G. Eikelmann, L. Puppe, K. Rohbock, H. H. Schneehage and D. Weck, *Liebigs Ann. Chem.* 1971, **745**, 135. ^{1}H NMR (CDCl$_3$): δ9.03 (s, 8H, pyrrole-*β*), 8.41, 8.15 (br. d, 4H x 2, phenyl-*o*), 7.7 - 7.9 (m, 12H, phenyl-*m*, *p*), 0.30 (s, 6H, O_2CCH_3). ^{13}C NMR (CDCl$_3$) δ150.1 (pyrrole-*α*), 142.2 (phenyl-*ipso*), 134.9, 133.2 (phenyl-*o*), 131.3 (pyrrole-*β*), 128.0 (phenyl-*p*), 126.8 (phenyl-*m*), 125.4 (meso), 185.7 (C=O), 20.7 (CH$_3$). UV-vis (CH$_2$Cl$_2$): λ_{max} 396.0, 417.5, 540.5, 631.5. IR (KBr): 1560, 1470, 690 cm^{-1} (O_2CCH_3). **1b - d** were obtained as reddish purple crystals by refluxing **1a** in carboxylic acids/pyridine (**1b**, **c**) or HCl/CHCl$_3$ (**1d**). For **1b**, ^{1}H NMR (CDCl$_3$): δ8.96 (s, 8H, pyrrole-*β*), 8.53 (m), 7.94 (br. d) (4H x 2, phenyl-*o*), 7.80 - 7.82 (m, 8H, phenyl-*m*), 7.70 - 7.78 (m, 4H, phenyl-*p*), -0.03 (s, 18H, $O_2CC(CH_3)_3$). ^{1}H NMR (C$_6$D$_6$): δ9.26 (s, 8H, pyrrole-*β*), 8.86, 8.18 (br. d, 4H x 2, phenyl-*o*), 7.6 - 7.9 (m, 12H, phenyl-*m*, *p*), 0.26 (s, 18H, $O_2CC(CH_3)_3$). ^{13}C NMR (CDCl$_3$) δ150.3 (pyrrole-*α*), 142.4 (phenyl-*ipso*), 134.2, 133.7 (phenyl-*o*), 131.4 (pyrrole-*β*), 127.9 (phenyl-*p*), 126.8, 126.7 (phenyl-*m*), 125.3 (meso), 193.1 (C=O), 37.1 (*C*(CH$_3$)$_3$), 25.5 (CH$_3$). UV-Vis (CH$_2$Cl$_2$): λ_{max} 396.0, 416.5, 540.0, 632.5; for **1c**, ^{1}H NMR (CDCl$_3$): δ8.96 (s, 8H, pyrrole-*β*), 8.43, 8.01 (br. d, 4H x 2, phenyl-*o*), 7.7 - 7.9 (m, 12H, phenyl-*m*, *p*), 6.78 (br. d, 2H, phenylene-*o*), 5.98 (br. d, 2H, phenylene-*m*). ^{13}C NMR (CDCl$_3$): δ150.1 (pyrrole-*α*), 142.2 (phenyl-*ipso*), 135.4, 134.1 (phenyl-*o*), 131.1 (pyrrole-*β*), 127.8 (phenyl-*p*), 127.1, 126.7 (phenyl-*m*), 125.1 (meso), 175.7 (C=O); for **1d**, ^{1}H NMR (CDCl$_3$): δ9.18 (s, 8H, pyrrole-*β*), 8.54, 8.09 (br. d, 4H x 2, phenyl-*o*), 7.7 - 7.9 (m, 12H, phenyl-*m*, *p*). ^{13}C NMR (CDCl$_3$): δ150.2 (pyrrole-*α*), 141.0 (phenyl-*ipso*), 135.2, 133.5 (phenyl-*o*), 132.5 (pyrrole-*β*), 128.6 (phenyl-*p*), 127.4, 127.1 (phenyl-*m*), 126.4 (meso).

[4] Products were identified by GC-MS, ^{1}H and ^{13}C NMR.

[5] The product showed a signal due to the vinylic proton only at δ5.2 (d, 1H) characteristic of that at the *cis* position to the phenyl group, while no signal was observed at δ5.0 due to that at the *trans* position.

[6] Our related studies on stereo-controlled reactions with metalloporphyrins: (1) T. Arai, H. Murayama and S. Inoue, *J. Org. Chem.* 1989, **54**, 414. (2) K. Konishi, K. Makita, T. Aida and S. Inoue, *J. Chem. Soc., Chem. Commun.* **1988**, 643. (3) K. Konishi, T. Aida and S. Inoue, *J. Org. Chem.* 1990, **55**, 816.

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