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Shape Selective Oxygen Transfer to Olefins Catalyzed by Sterically Hindered Iron Porphyrins

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Epoxidation of olefins catalyzed by iron-tetraarylporphyrins were studied to see the shape selectivity in the competing reaction between *cis*- and *trans*- or internal and external olefins. *Cis*-olefins were more reactive than *trans*-olefins in the competing reaction between *cis*- and *trans*-olefins. Interestingly, in the epoxidation of *cis*-β-methystyrene by αβαβ atropisomer of Fe(III)TNPPPCl and iodosylbenzene, 27% of total product was phenylacetone. The unusually large amount of phenylacetone may be produced by hydride rearrangement of carbocationic intermediate. Regioselectivity of the reaction was also studied by using the most sterically hindered Fe(III)TTPPPCl. In the epoxidation of limonene with Fe(III)TTPPPCl, the disubstituted double bond was more reactive than trisubstituted double bond. This is in contrast to the results obtained with other iron-tetraarylporphyrins. Similar trend was also observed in the competing reaction between mono- and di-substituted olefins.

Introduction

Epoxidation of olefins catalyzed by metal complex has been extensively studied recently because of the versatility of epoxides as useful intermediates in the organic synthesis.[1] Stereo- and regioselective transformation of olefins by discriminating the substrates based on size and shape typical of enzymatic reaction are one of the main objects in the reaction. For example, a chiral epoxide can be obtained by optimizing the steric and electronic effect of a metal ligand.[2] The substrates for high enantioselectivities in the epoxidations are, however, limited to only olefins with certain functinal groups such as allylic alcohol.
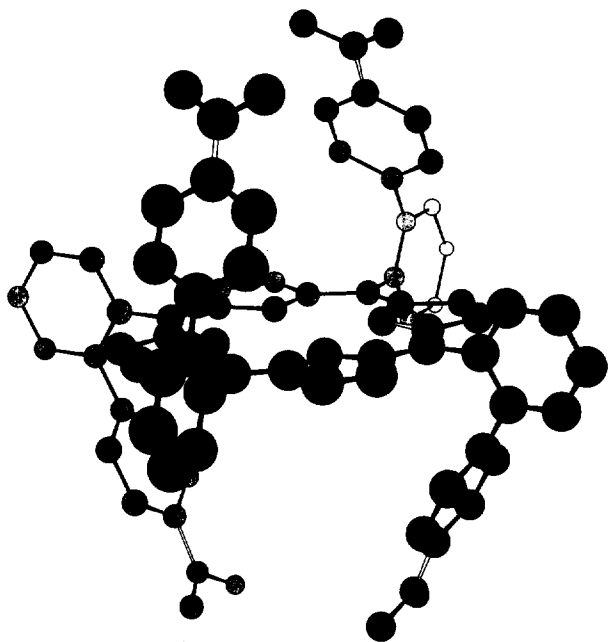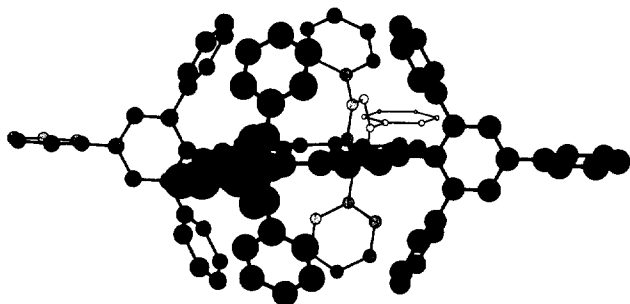
Metalloporphyrins have been used as effective catalysts for the oxidation of hydrocarbons with various oxidants in analogy to cytochrome P-450 catalyzed epoxidation reactions.[3] Shape selective oxygenations of hydrocarbons were attempted in some cases to mimic the enzyme.[4] High valent metal-oxo complexes have been usually proposed as an active oxidant in the reaction.

Iron porphyrins catalyze the oxygen transfer from iodosyl-benzene to olefins.[5] Epoxides are produced as a major product in the reaction along with some other compounds such

as allylic alcohols, aldehydes and ketones. The active oxidant is believed to be an oxo-iron(IV) porphyrin cation radical complex analogous to compound I of horse radish peroxidase.[6] A great deal of work has been reported regarding the mechanism of the oxygen atom transfer from the oxo-iron complex to olefins.[7] Substrate selectivities observed in the epoxidation reaction often contribute to the elucidation of the mechanism.

In has been reported that olefins under different steric and electronic environments give different reactivities in the iron porphyrin catalyzed epoxidation.[5b] The reactivity difference of olefins under given conditions are known to be dependent upon the structure of iron porphyrins.

We report here the shape selective epoxidation of olefins catalyzed by sterically hindered iron porphyrins such as αβαβ isomer of chloro[5,10,15,20-tetra[o-(p-nitrophenyl)phenyl]porphyrinato] iron(III) [Fe(III)TNPPPCl] (Figure 1) and chloro[5,10,15,20-tetra[2,4,6-triphenylphenyl]porphyrinato] iron(III) [Fe(III)TTPPPCl] (Figure 2). We have found that a large amount of phenylacetone was unexpectedly produced in the epoxidation of *cis*-β-methylstyrene catalyzed by αβαβ Fe(III)TNPPPCl, which might give a clue for the mechanism of iron-porphyrin catalyzed epoxidation.

Figure 1. αβαβ H₂TNPPP ligand.

Figure 2. H₂TTPPP ligand.

Table 1. Epoxidation of Cyclododecene

Iron porphyrin[a]	*cis/trans* epoxide	% Yield
FeTPPCl[b]	1.55	33
FeTPPPCl[b]	1.52	55
FeTMPCl[b]	8.92	51
FeTNPPPCl	5.18	47
mCPBA[b]	0.59	—

[a]TPP: tetraphenylporphyrin, TMP: tetramesitylporphyrin. [b]ref 5 b.

Figure 3. H₂TMP ligand.

Table 2. Epoxidation of *Cis*- and *Trans*-β-methylstyrene Mixture

Porphyrin	Yield (%)			Cis/trans ratio
	Cis[a]	trans[b]	Ketone[c]	
FeTPPCl	41	21	4	1.9
FeTNPPPCl	49	15	16	3.3
FeToTPCl	65	15	6	4.3
FeTMPCl	46	2	0.8	23
FeTTPPPCl	53	6	0	9.0

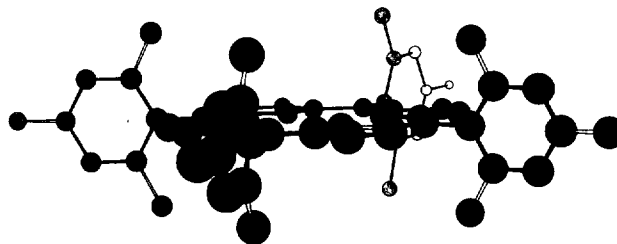[a]*cis*-β-methylstyrene oxide. [b]*trans*-β-methylstyrene oxide. [c]phenylacetone.

Results and Discussion

Epoxidation of *cis*- and *trans*-alkenes. The epoxidation of cyclododecene by sterically hindered αβαβ atropisomer of Fe(III)TNPPPCl indicated that the *cis*- cyclododecene was 5.18 times more reactive than trans alkene. This result confirms the steric effect of porphyrin ligand in the olefin epoxidation (Table 1).[5b] The *cis-trans* selectivity observed with Fe(III)TNPPPCl was better than those with any other catalysts except chloro-(5,10,15,20-tetramesitylporphyrinato) iron(III) [Fe(III)TMPCl]. Interestingly, the epoxidation with αβαβ Fe(III)TNPPPCl is 3.41 times more selective than with a mixture of rotational isomers of chloro[5,10,15,20-tetra [o-phenylphenyl]porphyrinato] iron(III) [Fe(III)TPPPCl]. These results indicate that steric hindrance around the metal center is important to achieve a high selectivity. In the case of Fe(III)TPPPCl, the catalyst is expected to exist as a statistical mixture of four rotational isomers such as αααα, αααβ, ααββ and αβαβ atropisomers. Accordingly, most of the epoxidation would occur at the sterically unhindered beta face of the major αααβ-atropisomer to give low selectivity. Fe(III)TNPPPCl was, however, shown to be less selective than Fe(III)TMPCl. CPK model of TNPPP ligand shows that the two o-(p-nitrophenyl)phenyl group covers the top

of the metal center enough to give a steric repulsion to the incoming olefin. However, olefins can approach the metal center from two unhindered sides. Further, the o-(p-nitrophenyl)phenyl group can rotate to allow space for the approaching olefin from side. By contrast, the TMP ligand (Figure 3) only has steric crowding at the side of porphyrin. The top of metal is open to the incoming olefin. Approach of the olefin from the side of the TMP ligand might have more nonbonded interaction with porphyrin periphery than the TNPPP ligand. Collectively, the better selectivity for *cis* olefin with Fe(III)TMPCl when compared to Fe(III)TNPPPCl led us to believe that an olefin approaches the activated metal center from the side.

The epoxidation of *cis*- and *trans*-β-methylstyrene catalyzed by various iron porphyrins also gave similar results (Table 2). Again, Fe(III)TMPCl gave the highest *cis/trans* epoxide ratio. It is interesting that the epoxidation of β-methylstyrene showed more *cis-trans* selectivity than the epoxidation of cyclododecene. In the reaction with Fe(III)TMPCl, the selectivity for β-methylstyrene was 2.6 times higher than for cyclododecene. This enhanced selectivity can be explained based on the conformational analysis of the *cis*- and *trans*-olefins. For medium sized cycloalkenes, *trans*-olefins are

Table 3. Epoxidation Reaction of *Cis*-β-methylstyrene

Porphyrin	Yield (%)			
	Cis-oxide[a]	Ketone[b]	Oxide/ketone	Ketone/total
FeTPPCl	73	7	10	8.7
FeTNPPPCl	58	21	2.8	27
FeTMPCl	66	1.3	51	1.9

[a] *cis*-β-methylstyrene oxide. [b] phenylacetone

Table 4. Epoxidation Reaction of *Trans*-β-methylstyrene

Porphyrin	*Trans*-oxide (%)	Ketone (%)	Oxide/ketone
FeTNPPPCl	76	1.5	51
FeTPPCl	57	0.7	81
FeTMPCl	8	—	—

known to be more reactive toward the oxidants than *cis*-olefins to reduce the ring strain of *trans*-cycloalkenes. Thus, the relative reactivity of *cis*- and *trans*-cyclododecene toward mCPBA is shown to be 0.59 to 1. However, in the case of β-methylstyrene, the *cis*-compound was 1.5 times more reactive toward mCPBA than the *trans*-compound because of the steric repulsion between the methyl and phenyl groups. Thus, it is conceivable to see the better *cis-trans* selectivity for β-methylstyrene than for cyclododecene.

It has been assumed that the more sterically hindered catalyst might give the higher *cis-trans* selectivity because of increasing nonbonded repulsion with the *trans*-olefin. However, in contrast to the high selectivity observed with Fe(III)TMPCl, the most sterically hindered Fe(III)TTPPPCl unexpectedly showed a moderate selectivity. This result might be due to the large steric repulsion of Fe(III)TTPPPCl to both *cis*- and *trans*-β-methylstyrene. The approach of *cis*- and *trans*-β-methylstyrene to the metal center of Fe(III)TTPPPCl are expected to greatly hindered by four phenyl groups of the porphyrin. However, the *cis*-olefin was still more reactive than the *trans*-olefin.

As a control experiment, the epoxidations of *cis*- and *trans*-β-methylstyrene were performed with iron porphyrins and iodosylbenzene, respectively (Table 3, 4). As has been uniformly observed for iron and chromium porphyrins,[8] the epoxidation was stereospecific: *cis*-olefin was oxidized to *cis*-epoxide and *trans*-olefin to *trans*-epoxide. There were no indications of crossed products such as the formation of *trans*-epoxide from *cis*-olefin. Thus, the *cis-trans* selectivities observed in the competition reactions reveal the relative rate of epoxidation of each olefin isomers under the catalytic condition.

Particulaly noteworthy is the phenylacetone which might result from the hydride rearrangement during the epoxidation of β-methylstyrene. The amount of phenylacetone can be related to both the structure of olefins and porphyrins. In the epoxidation of *cis*-β-methylstyrene, significant amounts of phenylacetone was produced, whereas only a negligible amount of phenylacetone was obtained in the epoxidation of *trans*-β-methylstyrene. Further, while with sterically hindered Fe(III)TMPCl only 1.9% of the total products were

Table 5. Iron-porphyrin Catalyzed Epoxidation of Diene and Mixture of Olefins

| Porphyrin	Epoxide ratio		
	Limonene I/II (% yield)	Clyclooctene/ 1-octene	Norbornene/ 1-octene
FeTPPCl	—	>51 (33.9)	31.6(35.3)
FeTTPCl	19.6(78)	—	—
FeTMPCl	6.9(70)	51.2(42.8)	>31 (38.2)
FeTTPPPCl	0.325(14)	2.37(13.7)	1.62(26.6)
MnTTPPP(OAc)[a]	ca. 1.8	—	—
mCPBA	10.2(−)	—	—

[a] ref 4C.

rearranged, 8.7% were rearranged with Fe(III)TPPPCl. In particular, with αβαβ atropisomer of Fe(III)TNPPPCl 27% of the total product was the phenylacetone.

It has been proposed that rearrangement products result from a carbocationic intermediate in the epoxidation.[7] The carbocationic intermediate may be formed from a dissymmetrical approach of two olefinic carbons of an olefin to the oxo-iron oxidant. The dissymmetrical approach may be pronounced in the epoxidation by αβαβ Fe(III)TNPPPCl because of steric repulsion between the phenyl group of *cis*-β-methylstyrene and the nitrophenyl group of αβαβ TNPPP ligand. Thus, a large amount of phenylacetone was observed in the epoxidation with Fe(III)TNPPPCl. However, the carbocationic intermediate may not be the intermediate for the epoxide because the *cis*-olefin was convertd to *cis*-epoxide without isomerization to *trans*-epoxide even with Fe(III)TNPPPCl. Otherwise, the carbocationic intermediate would have to give a mixture of *cis*- and *trans*-epoxide as well as phenylacetone as shown in the Ru(II) porphyrin catalyzed epoxide isomerization.[9]
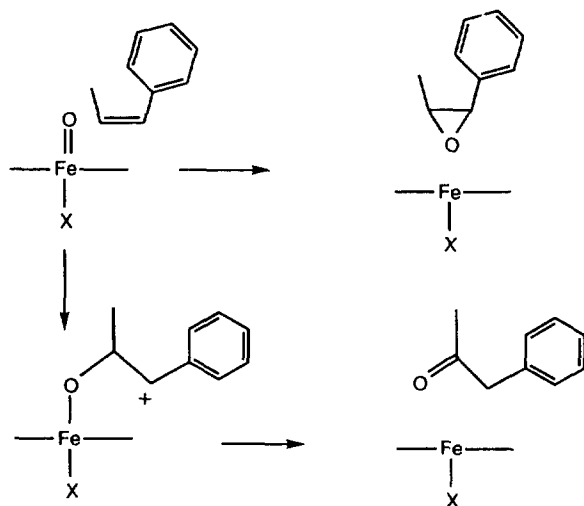
Shape Selective Epoxidation. We have also tested the steric effect of porphyrin ligand in the competing epoxidation of terminal and internal double bonds (Table 5). Limonene has two double bonds under different steric and electronic environments. Since the double bond with trisubstituents is more reactive toward electrophilic oxidants than

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double bond with disubstituents, the epoxidation of limonene by mCPBA gave mostly the ring epoxide. This was still the case even in the epoxidation with Fe(III)TTPCl and Fe(III) TMPCl.[4a] However, Fe(III)TTPPPCl, the most sterically hindered porphyrin remarkably enhanced the epoxidation of the external double bond of limonene. Surprisingly, the external double bond was even 3 times more reactive than the internal double bond. In contrast to the hydroxylation of hydrocarbons showing the superior shape-selectivities[4b] by manganese porphyrins when compared to iron porphyrins, the selectivity obtained with Fe(III)TTPPPCl was twice better than Mn(III)TTPPP(OAc) system.[4c]

I   II
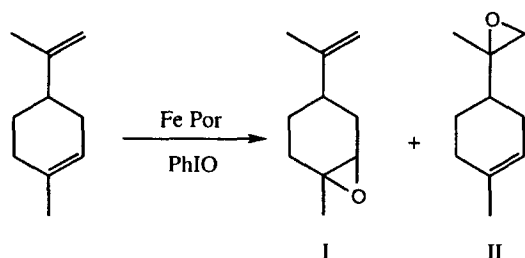
The enhanced selectivity for external double bond was also seen in the competing reaction between 1-octene and cyclooctene. Cyclooctene oxide was exclusively produced in the reaction with Fe(III)TPPCl or Fe(III)TMPCl. Less than 2% of the total products was 1-octene oxide. However, Fe(III) TTPPPCl remarkably enhanced the production of 1-octene oxide. About 30% of epoxides was 1-octene oxide. The space for the incoming olefin to the TTPPP ligand seems to be so limited that disubstituted olefins may feel much more steric repulsion than mono-substituted olefin. The enhancement of terminal epoxide by Fe(III)TTPPPCl was once again shown in the competition reaction between 1-octene and norbornene. Similar shape selectivity for terminal olefin was also reported with complex manganese picknic basket porphyrins.[10] Collectively, the epoxidation occurred at the porphyrin metal center, and substituents on the porphyrin periphery are thus important in obtaining high shape-selectivity in the epoxidation of olefins.

Experimental

General Data. Analytical gas chromatography was done on Varian instrument Model 3700 equipped with flame ionization detectors. Peak areas were measured by electronic integration using a Hewlett-Packard 3380 A or Spectra Physics SP4100 reporter-integrator. The Mass spectra were taken on a Finnigan 4021 gas chromatograph/mass spectrometer. NMR-spectra were taken on a Varian T-60A or Bruker WM 360 NMR spectrometer. Chemical shift values are reported relative to Me$_4$Si. Infrared spectra were taken on a Beckman IR 4240. Visible spectra were measured on a Varian Carey 219 spectrometer. Cyclododecene and *trans*-β-methylstyrene were purchased from Aldrich Chemical Co.; *cis*-β-methylstyrene from ICN Biomedicals, INC. Alkenes were purified by passing through alumina column. Iodosylbenzene was prepared by the hydrolysis of the iodobenzene diacetate (Aldrich Chemical Co.) with aqueous sodium hydroxide.[11]

Porphyrins. Porphyrins and porphyrin complexes were prepared according to known procedures.[5b,12]

Reaction of Iodosylbenzene with Cis- and Trans-cyclododecene Catalyzed by Fe(III) TNPPPCl. In the three neck flask, 1.15 mg (9.68×10^{-7} mol) of porphyrin and 0.05 m*l* (43.2 mg, 2.60×10^{-4} mol) of purified cyclododecene (*trans/cis* = 2.27) was added. The reaction vessel was purged with nitrogen for 10 minutes. After the addition of 2 m*l* of CH$_2$Cl$_2$, the solution was purged with nitrogen for 10 min. Iodosylbenzene (11.92 mg, 5.42×10^{-5} mol) was added slowly over 30 minutes and the mixture was stirred for 1.5 hours. 1.21 mg (8.05×10^{-6} mol) of adamantanone was added as an internal standard. The yields and ratios of epoxides formed were determined by glpc (Carbowax 20 M, initial 105 ℃, 2 min, 4 ℃/min, 190 ℃; adamantanone, 20.03 min; *cis*-cyclododecene oxide, 22.21 min, 33%; *trans*-cyclododecene oxide, 21.17 min, 14%; cyclododecanone, 28.17 min, 2% and cyclododecenol, 30.14 min, 14%). The yields were calculated based on iodobenzene.

Epoxidation Reactions of β-methylstyrene. Most reactions were carried out in a 25 m*l* three-neck-flask with an addition tube containing the preweighed iodosylbenzene, a bubbler, setum cap and stirring bar. All reactions were done under nitrogen and the reaction mixture was purged with nitrogen for approximately 10 min before the addition of iodosylbenzene. Iodosylbenzene (5×10^{-5} mol) was added to a solution of β-methylstyrene (4×10^{-4} mol) and ferric porphyrin chlorides (1.2×10^{-6} mol) in methylene chloride (2 m*l*). Products were analyzed after completion of reactions by glpc (Carbowax 20 M, Capillary, 150 ℃; iodobenzene, 6.85 min; *cis*-β-methylstyrene oxide, 8.27 min; *trans*-β-methylstyrene oxide, 9.84 min, and phenylacetone, 13.68 min). The yields were calculated based on iodobenzene produced. Control experiment showed that only negligible amount of epoxides (less than 0.5% of epoxides) rearranged to phenylacetone in glpc.

Reaction of Iodosylbenzene with Mixture of Cyclooctene and 1-Octene Catalyzed by Ferric Porphyrins. Iodosylbenzene (6.26×10^{-5} mol) was added to a solution of cyclooctene (2.2×10^{-4} mol), 1-octene (2.2×10^{-4} mol) and ferric porphyrin (1.7×10^{-6} mol) in methylene chloride (2 mL). Analysis with glpc (Carbowax 20 M, Carpillary, 50 ℃, 3 min, 10 ℃/min) showed three products which corresponded to 1-octene oxide, cyclooctene oxide and iodobenzene.

Reaction of Iodosylbenzene with (+)-limonene Catalyzed by FeTTPPCl. Iodosylbenzene (13.64 mg, 6.2×10^{-5} mol) was added to a solution of (+)-limonene (28.5 mg, 2.09×10^{-4} mol) and FeTTPPCl (1.21 mg, 7.49×10^{-7} mol) in methylene chloride (2.5 m*l*). Analysis with glpc (Carbowax 20M, 110 ℃) showed that four epoxide were formed. Two fast moving bands (rt. 3.30 and 3.38 min) were 1,2-epoxides (ratio 2.13) and next bands (rt. 4.15, 4.22 min) were 7,8-oxides (ratio 0.831). The ratio between 1,2-epoxides and 7,8-epoxides were 0.325. The total yield of epoxides was 14% based on iodobenzene.

Reaction of Iodosylbenzene with Mixture of 1-Octene and Norbornene Catalyzed by Ferric Porphyrings. Iodosylbenzene (5.60×10^{-5} mol) was added to a solution of 1-octene (2.3×10^{-4} mol), norbornene (2.7×10^{-4} mol) and ferric porphyrins (1.7×10^{-6} mol) in methylene chloride (2 m*l*). Analysis of products with glpc (Carbowax 20 M, Capillary, 50 ℃, 3 min, 10 ℃/min), showed unknown compound (4.76 min), 1-octene oxide (4.91 min), norbornene oxide (5.31

min) and iodobenzene (8.32 min).

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Selective Dimerization and Cyclotrimerization of Phenylacetylene with Rhodium and Iridium Complexes

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Oligomerization of phenylacetylene is catalyzed by Rh(ClO₄)(CO)(PPh₃)₂ (**Rh-1**), [Rh(CO)(PPh₃)₃]ClO₄ (**Rh-2**), [Rh(COD)L₂]ClO₄ (L₂=(PPh₃)₂, **Rh-3**; (PPh₃)(PhCN), **Rh-4**; (PhCN)₂, **Rh-5**), [Rh(C₃H₅)(Cl)(CO)(SbPh₃)₂]ClO₄ (**Rh-6**), [Ir(COD)L₂]ClO₄(L₂=(PPh₃)₂, **Ir-1**; (PPh₃)(PhCN), **Ir-2**; (PhCN)₂, **Ir-3**; (AsPh₃)(PhCN), **Ir-4**; Ph₂PCH₂CH₂PPh₂, **Ir-5**; COD, **Ir-6** and 2,2′-dipyridyl, **Ir-7**), Ir(ClO₄)(CO)(PPh₃)₂, **Ir-8**, [Ir(PhCN)(CO)(PPh₃)₂]ClO₄, **Ir-9** to produce dimerization products, 1,3-diphenylbut-1-yn-3-ene, **1**, (E)-1,4-diphenylbut-1-yn-3-ene, **2** and (Z)-1,4-diphenylbut-1-yn-3-ene, **3**, and cyclotrimerization products, 1,3,5-triphenylbenzene, **4** and 1,2,4-triphenylbenzene, **5**. Product distribution of the oligomers varies depending on various factors such as the nature of catalysts, reaction temperature, counter anions and excess ligand present in the reaction mixtures. Increasing reaction temperature in general increases the yield of the cyclotrimerization products. Exclusive production of dimer **1** and trimer **4** can be obtained with **Ir-1** at 0 ℃ and with **Ir-2** in the presence of excess PhCN (or CH₃CN) at 50 ℃, respectively. Dimer **2** (up to 81%) and trimer **5** (up to 98%) are selectively produced with **Rh-1** at 50 and 100 ℃, respectively. Production of **3** is selectively increased up to 85% by using PF₆⁻ salt of [Ir(COD)(PPh₃)₂]⁺ at 25 ℃. Addition of CH₃I to **Rh-1** produces CH₃PPh₃⁺I⁻ and increases the rate of oligomerization(disappearance of phenylacetylene). Among the metal compounds investigated in this study, **Ir-1** catalyzes most rapidly the oligomerization where the catalytically active species seems to contain Ir(PPh₃)₂ moiety. The stoichiometric reaction of phenylacetylene wth **Ir-9** at 25 ℃ quantitatively produces hydridophenyl-ethynyl iridium (III) complex, [Ir(H)(C≡CPh)(PhCN)(CO)(PPh₃)₂]ClO₄ (**Ir-11**), which seems to be an intermediate for the oligomerization.

Introduction

Dimerization[1] and cyclotrimerization[1b,2] of terminal alkynes are known to be catalyzed by transition metal complexes for some time. While the head-to-tail dimerization product (type **1**) and both the E- (type **2**)[1b,c,e,f] and Z-isomer (type **3**)[1j,k] of the head-to-head dimerization products have been reported, both two isomers (type **4** and type **5**) have been