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Iron-catalyzed intramolecular cyclotrimerization of triynes to annulated benzenes

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Abstract

An iron species derived from $FeCl_2$ or $FeCl_3$ by in situ reduction with zinc powder in the presence of imidazol-2-ylidene or bidentate nitrogen ligand could effectively catalyze intramolecular cycloisomerization of triynes to annulated benzenes. With a 2-iminomethylpyridine ligand, hydrates of $FeCl_2$ and $FeCl_3$ as well as their anhydrous ones could be used.

Keywords: *N*-heterocyclic carbene; Iron catalyzed reaction; Intramolecular cyclotrimerization; 2-Iminomethylpyridine

1. Introduction

After the first discovery by Reppe and Schweckendiek [1], complexes of many transition metals have been developed as an active catalyst for cyclotrimerization reaction of alkynes [2]. However, the iron-catalyzed reaction of this transformation has been less explored [3,4]. The methods reported so far involve iron-arene, -cyclooctadiene, -cycloheptatriene and -tetramethylcyclopentadienyl complexes as a catalyst. Interestingly, Carbonaro et al. reported that $FeCl_3$ could be activated by in situ reduction with *i*-PrMgCl to catalyze cyclotrimerization of internal alkynes, albeit with low conversion of alkynes [3e]. It has also been reported by tom Dieck that a (1,2-diimine)Fe(0) complex derived in situ from (1,2-diimine)$FeCl_2$ and an organometallic reducing agent could cyclotrimerize 4,4,7,7-tetramethylcyclooctyne to the corresponding benzene derivative [3g]. The instant protocol of these types which is allowed to be activated in situ starting from a stable inorganic salt or complex in the presence of substrate(s) is intrinsically advantageous due to easiness of handling, inexpensiveness and non-requirement of preparation and isolation of unstable low valent metal complexes. In addition, it requires a weak and minimal amount of stabilizing ligand(s), and therefore the catalyst can be initiated under milder conditions and can be expected to exhibit high reactivity. In this context, we have recently reported that an iron species derived from $FeCl_2$ or $FeCl_3$ by treatment with zinc powder in the presence of imidazol-2-ylidene (**3**) can effectively catalyze intramolecular cycloisomerization of triynes to annulated benzenes [5]. Further investigation revealed that bidentate or tridentate nitrogen-donor compounds such as 1,2-diimines (**4**), 2-iminomethypyridines (**5**) and 2,6-di(iminomethyl)pyridines (**6**) are effective for an $FeCl_n$/Zn catalytic system as a ligand (see Scheme 1). Herein we describe details of these reactions including their scope and limitation.

2. Results and discussion

2.1. $FeCl_2$ or $FeCl_3$-based reaction with a variety of ligands

Using a catalytic amount of anhydrous $FeCl_2$ or $FeCl_3$, we investigated the ability of a variety of compounds as a ligand for the cyclotrimerization of 1,4-bis-prop-2-ynyloxy-but-2-yne (**1a**) (see Table 1): Thus, to a mixture of zinc powder (10 mol%) and **1a** in THF was added a mixture of anhydrous $FeCl_n$ ($n = 2$ or 3, 2–5 mol%) and a ligand, [2,2′]bipyridinyl, dppe (bis-diphenylphosphinoethane),

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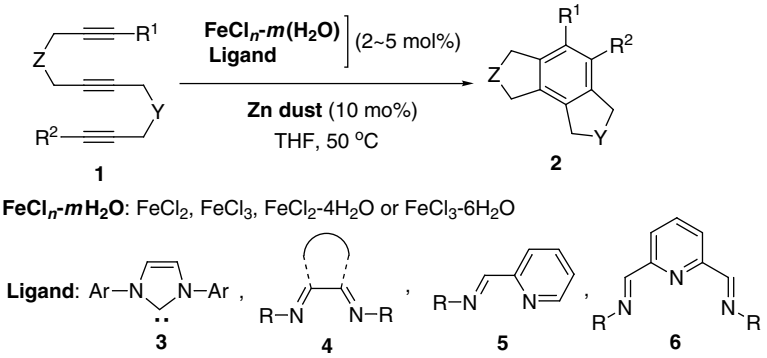


Scheme 1.

TMEDA (tetramethylethylenediamine), **3**, **4**, **5** or **6** (2–10 mol%), in THF at ambient temperature. The resulting mixture was stirred at 50 °C for 24–72 h. After work-up, the crude mixture was analyzed by 500 or 600 MHz ^{1}H NMR to determine the yield of annulated benzene **2a**. In all entries of Table 1, no other compound than **2a** and **1a** was produced. As revealed from Table 1, with no ligand the reaction did not afford **2a** (entry 1). Although with use of [2,2′]bipyridinyl, dppe or TMEDA as a ligand the reaction afforded trace of **2a** (entries 2–4), imidazol-2-ylidenes (**3**), 1,2-diimines (**4**), 2-iminomethylpyridines (**5**) and 2,6-di(iminomethyl)pyridines (**6**) were found to be effective as a ligand for the $FeCl_2$ or $FeCl_3$/Zn system (entries 5–22).

The results of the reactions with imidazol-2-ylidenes (**3**) reveal the following: $FeCl_2$ as well as $FeCl_3$ could be used (entries 5 and 6), which suggests that an active species may be Fe(I) or Fe(0). A 1:1 mixture of $FeCl_3$ and **3a** as well as a 1:2 mixture of them exhibited almost the same reactivity (entries 6 and 7). Use of imidazol-2-ylidene having sterically demanding substituents (**3a**) was better than a less bulky one (**3b**) (entries 6 and 8). The reaction with use of other metals powder as a reductant such as Mn, Al and Mg, instead of Zn did not yield **2a** (data not shown).

A series of 1,2-diimines **4** could act as a good ligand in a nearly stoichiometric amount to $FeCl_3$, where it was again observed that **4** with bulky *N*-substituents was a preferable ligand (entries 9–14). 4,5,4′,5′-Tetrahydro-[2,2′]bioxazolyl (**4f**) was also a good ligand (entry 15).

Regarding 2-iminomethylpyridines **5** and 2,6-di(iminomethyl)pyridines **6**, they with sterically demanding *N*-substituents such as **5a** and **6a** enabled effective catalysis but use of less bulky ones resulted in no reaction or low yield (entries 16–22). Among them, a $FeCl_3$/Zn reagent with 2-(2,6-diisopropylphenyl)iminomethylpyridine **5a** showed the highest catalytic activity (entry 17).

2.2. Reactions catalyzed by an imidazol-2-ylidene (*3a*)-$FeCl_3$/Zn reagent [5]

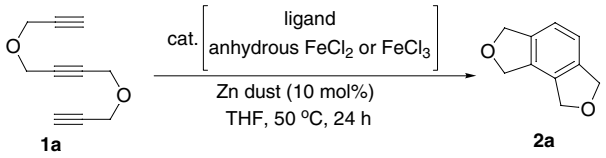
With the results mentioned above we first chose an imidazol-2-ylidene **3a** as a ligand and carried out **3a**-$FeCl_3$/Zn-catalyzed reaction with other substrates than **1a** (see Scheme 2). Using the combination reagent, cyclotrimerization of 1,6,11-triynes **1b**–**1f** could effectively proceed to give the corresponding annulated benzenes. Triynes having at least one terminal alkyne moiety, **1a**–**1c** afforded **2a**–**2c**, respectively, in good to excellent yield. Similarly, aryl substituted triyne **1d** provided **2d** in nearly quantitative yield. However, the reaction of dialkyl and bis-trimethylsilyl triynes, **1e** and **1f**, proceeded slowly to yield **2e** and **2f**, respectively, in moderate yield under identical conditions. Increase of reaction temperature from 50 °C to THF-reflux temperature improved the yields.

Closely related reaction conditions were subsequently utilized for the cyclotrimerization of a series of representative triynes **1g**–**1i** (see Scheme 3). The results feature the following characteristics: The reaction was compatible with functional groups such as ester, hydroxyl, and benzyloxy moieties. The formation of carbocyclic as well as *O*-heterocyclic compounds was possible. Double cyclotrimerization of hexaynes to biaryl compounds could effectively be carried out.

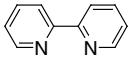
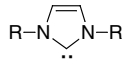
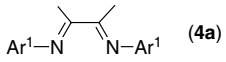
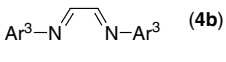
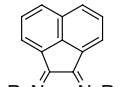
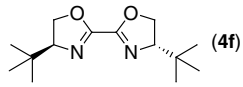
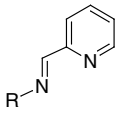
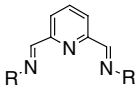
2.3. Reactions catalyzed by a 2-(iminomethyl)pyridine-$FeCl_3$/Zn reagent

We next chose 2-iminomethylpyridine (**5a**) as an alternative ligand effective to an iron-catalyzed instant protocol for alkyne-cyclotrimerization since **5a** can be readily prepared from commercially available, inexpensive pyridine 2-carboxaldehyde and 2,6-diisopropylaniline by simple mixing in EtOH. Using **5a** as a ligand in essentially one equivalent amount to an iron salt, several salts of Fe(II) and Fe(III) were subjected as an iron source to the reaction of **1a** in the presence of catalytic amount of reductant (see Table 2). As revealed from entries 1 to 6, Zn powder was found to be more effective than other metal powder such as Mg and Mn, and organometallic reducing agents such as EtMgBr could also activate the catalysis. Hydrates of $FeCl_2$ and $FeCl_3$ as well as their anhydrous form could be utilized equally but Fe(acac)$_3$ was less effective. The amount of **5a**/$FeCl_3$-6H$_2$O could be reduced to 2 mol% (entry 7).

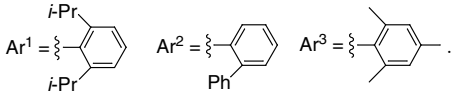
Table 1
Ligand effects on iron-catalyzed intramolecular cyclotrimerization



1a **2a**

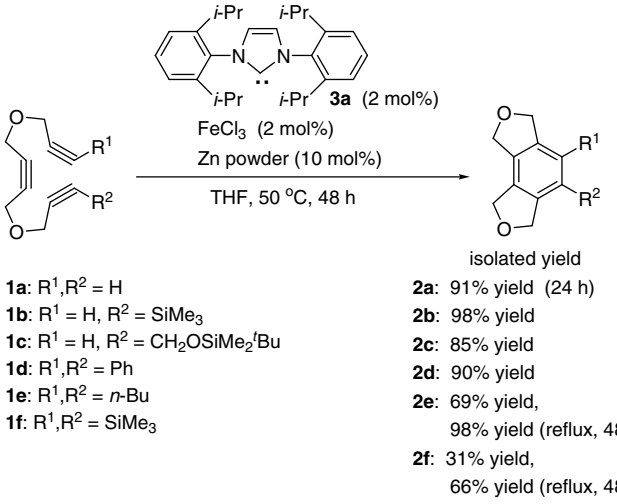
Entry	Ligand (mol%)[a]		$FeCl_n$ *n* (mol%)	Yield of **2a** (%)[b]
1	–		3 (5)	Trace
2		(2)	3 (2)	Trace
3	$Ph_2P(CH_2)_2PPh_2$[dppe]	(5)	3 (5)	4
4	$Me_2NCH_2CH_2NMe_2$[TMEDA]	(5)	3 (2)	Trace
5	 R = Ar^1 (**3a**)	(10)	2 (5)	49
6		(4)	3 (2)	~100 (48 h)
7		(2)	3 (2)	91
8	R = Ar^3 (**3b**)	(10)	3 (5)	58
9	 (**4a**)	(6)	3 (5)	~100
10	 (**4b**)	(2.4)	3 (2)	8
11	 R = Ar^1 (**4c**)	(2.4)	3 (2)	64
12		(2.4)	3 (2)	92 (72 h)
13	R = Ar^2 (**4d**)	(2.4)	3 (2)	~100 (48 h)
14	R = Ar^3 (**4e**)	(2.4)	3 (2)	54
15	 (**4f**)	(2.4)	3 (2)	71
16	 R = Ar^1 (**5a**)	(6)	2 (5)	~100
17	R = Ar^1 (**5a**)	(6)	3 (5)	~100
18	R = Ph (**5b**)	(6)	3 (5)	Trace
19	R = *t*-Bu (**5c**)	(6)	3 (5)	Trace
20	 R = Ar^1 (**6a**)	(2.4)	3 (2)	62
21	R = Ph (**6b**)	(2.4)	3 (2)	15
22	R = *t*-Bu (**6c**)	(3.6)	3 (3)	18

[a] Substituents $Ar^1 \sim Ar^3$ on an N atom are as follows:



[b] Yield was determined by ^1H NMR analysis of the crude mixture using an internal standard.

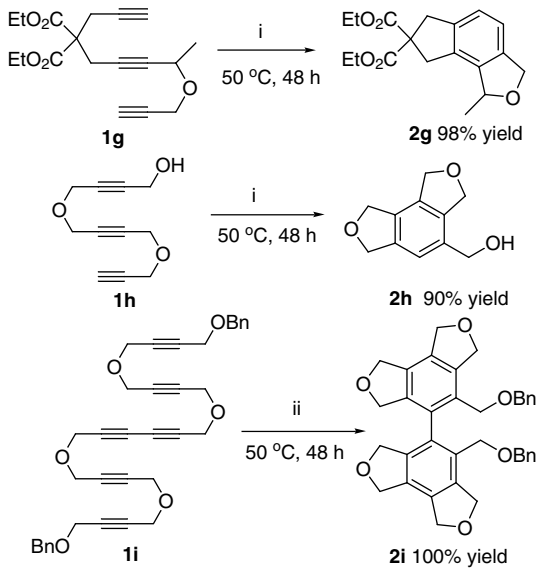
With these results, we chose a combination reagent **5a**/$FeCl_3$-$6H_2O$/Zn as a catalyst because of the stability and inexpensiveness of the iron salt and carried out the reactions of representative triynes. Scheme 4 indicates the isolated yields of the product. The cyclotrimerization of triynes **1a**, **1d**, **1e**, **1f**, **1h** and hexayne **1i** proceeded smoothly to provide the corresponding annulated benzenes and biaryl compound in moderate to good yield.



Scheme 2. Reagents: (i) **3a** (2 mol%), $FeCl_3$ (2 mol%), Zn powder (10 mol%) in THF (ii) **3a** (5 mol%), $FeCl_3$ (5 mol%), Zn powder (10 mol%) in THF.

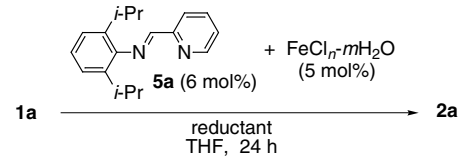
2.4. Chemoselective reaction

As mentioned above, both **3a**/$FeCl_3$/Zn and **5a**/$FeCl_3$/Zn reagents could effectively cyclotrimerize triynes intramolecularly but attempts to apply them to intermolecular reaction failed. For instance, a mixture of 1,6-diyne **7** and alkyne **8** was treated with a **5a**/$FeCl_3$-$6H_2O$/Zn reagent under identical reaction conditions to those for the intramolecular reaction but no reaction proceeded and the starting **7** and **8** were recovered quantitatively (see Fig. 1). Although application of the present catalytic system to an intermolecular reaction must await further investigation, this feature enabled chemoselective cyclization of polyyne: the reaction of pentayne **1j** with a **5a**/$FeCl_3$-$6H_2O$/Zn proceeded selectively at internal alkyne moieties in an intramolecular fashion to provide benzene derivative **2j** having terminal alkyne substituents (see Scheme 5). Similarly, diene–triyne **1k** with the catalyst afforded the corresponding annulated benzene **2k** with allyl substituents in good yield. It seems that such chemoselective reactions are not necessarily an easy task by the other methods reported [6].



Scheme 3. Reagents: (i) **3a** (2 mol%), $FeCl_3$ (2 mol%), Zn powder (10 mol%) in THF (ii) **3a** (5 mol%), $FeCl_3$ (5 mol%), Zn powder (10 mol%) in THF.

Table 2
Reactions with various iron salts and reductants in the presence of ligand **5a**

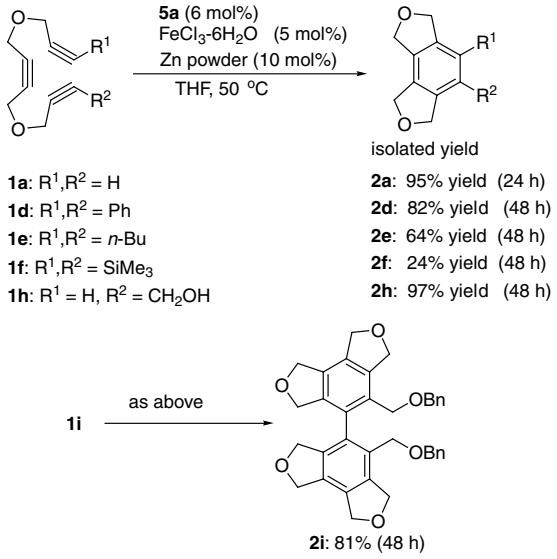


Entry	$FeCl_n$-mH_2O	Reductant (mol%)	Temperature (°C)	Yield of **2a**, %[a]
1[b]	$FeCl_3$	Zn (10)	50	~100 (entry 17, Table 1)
2[b]	$FeCl_3$	Zn (10)	Room temp.	~100
3[b]	$FeCl_3$	Mg (10)	50	~0
4[b]	$FeCl_3$	Mn (10)	Room temp.	13
5[b]	$FeCl_3$	EtMgBr (15)	Room temp.	~100
6[b]	$FeCl_3$	*n*-BuLi (15)	Room temp.	13
7	$FeCl_3$-$6H_2O$	Zn (10)	50	~100
8	$FeCl_3$-$6H_2O$ (2 mol%)	Zn (10)	50	93 [**5a** (2.4 mol%)]
9	$Fe(acac)_3$	Zn (10)	50 °C	38
10[b]	$FeCl_2$	Zn (10)	50	~100 (entry 16, Table 1)
11	$FeCl_2$-$4H_2O$	Zn (10)	50	~100

[a] Yield was determined by ^1H NMR analysis of the crude mixture using an internal standard.
[b] Anhydrous iron salt was used.

2.5. Possible reaction mechanism

Although confirmation of the reaction mechanism must await further study, as illustrated in Scheme 6 we postulate the reaction course based on those proposed for the reported metal-catalyzed reactions [2]. Thus, in the solution prepared by mixing $FeCl_2$ or $FeCl_3$ and a ligand compound (L) such as **3a** and **5a**, the corresponding complexes L-$FeCl_{2\,or\,3}$ may be generated [7–9]. They can readily be reduced by Zn powder or EtMgBr to give the corresponding Fe(I) and/or Fe(0) complexes **9**. These complexes may be metastable and can quickly react with triynes **1** to give metallacyclopentadienes **10**, which may further be cyclized to **11** and/or **12** through an insertion or [4+2]-cycloaddition pathway, respectively. Reductive elimination reaction of **11** and/or **12** yields annulated benzenes **2** and regenerates the low valent complexes **9**. It is noteworthy that the active species should be generated in the presence of the



Scheme 4.

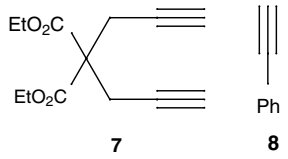
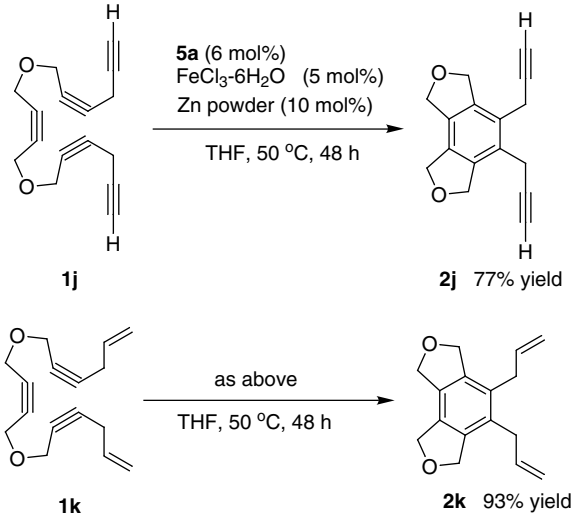
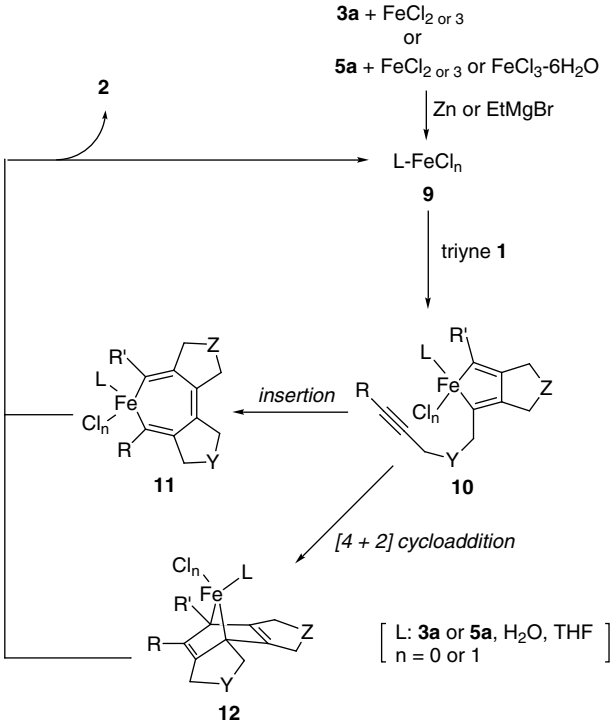


Fig. 1. Substrates for study of intermolecular reaction.

triyne substrate: after mixing of [**3a**+$FeCl_3$] or [**5a**+$FeCl_3$-$6H_2O$] with Zn powder in the absence of triyne **1a**, addition of **1a** to this mixture and the following stirring at 50 °C did not afford **2a**. The fact may suggest that the substrate alkynes could also act as a stabilizing ligand(s) for the metastable complexes **9**.



Scheme 5.



Scheme 6. Proposed reaction mechanism.

2.6. Conclusion

We have demonstrated that $FeCl_n$ ($n = 2$ or 3)/Zn with an imidazol-2-ylidene **3** or a 2-iminomethylpyridine **5** ligand was effective as a catalyst for intramolecular trimerization of triynes by the instant protocol. The catalysis with a **3**/$FeCl_n$/Zn reagent is the first example of imidazol-2-ylidene iron complex-catalyzed reaction other than polymerization reaction [7]. From the viewpoint of practicality, it is noteworthy that hydrates of $FeCl_n$ as well as their anhydrous ones could be used in the reaction with a ligand **5**.

3. Experimental

3.1. General

NMR spectra were recorded in $CDCl_3$ at 600, 500 and 270 MHz for ^1H and 150, 125 and 67.5 MHz for ^{13}C, respectively, on JEOL JNM-ECA600, 500 and -EX270 spectrometers. Chemical shifts are reported in parts per million (ppm, δ) relative to Me_4Si (δ 0.00) or residual $CHCl_3$ (δ 7.26) for ^1H and $CDCl_3$ (δ 77.0 for ^{13}C). IR spectra were recorded on an FT-IR spectrometer (HITACHI 270-30) and are reported in wave numbers (cm^{-1}). All reactions sensitive to oxygen and/or moisture were performed under an argon atmosphere. Imidazolium salts, i.e., 1,3-bis(2,6-diisopropylphenyl)-3H-imidazol-1-ium chloride and 1,3-bis(2,4,6-trimethylphenyl)-3H-imidazol-1-ium chloride were prepared from the corresponding amines according to the reported procedures [10]. 2-(aryl)Iminomethylpyridine (**5a**)–(**5c**) was prepared from aniline

derivatives and pyridine 2-carboxaldehyde according to the reported procedure [11]. Other ligands **4a**,**b** [11], **4c**–**e** [12], **4f** [13] and **6a**–**c** [14] were prepared according to the reported procedure. The alkyne substrates were prepared by the conventional reactions. Dry solvents (THF and ethyl ether) were purchased from Kanto Chemicals. Other chemicals including iron salts and zinc powder were used as received. A THF solution of $FeCl_n$-$m(H_2O)$ and a ligand was prepared prior to use.

3.2. Cyclotrimerization reactions catalyzed by an imidazol-2-ylidene *3a*-$FeCl_3$/Zn reagent

3.2.1. General procedure

To a mixture of anhydrous $FeCl_3$ (16.2 mg, 0.1 mmol) and THF (2 mL) was added a solution of 1,3-bis(2,6-diisopropylphenyl)-3*H*-imidazol-2-ylidene **3a** (0.12 mmol) in THF (2 mL), prepared from 1,3-bis(2,6-diisopropylphenyl)-3*H*-imidazol-1-ium chloride (51.0 mg, 0.12 mmol) and *n*-BuLi (0.076 mL, 1.58 M in hexanes, 0.12 mmol) in THF, at 0 °C to give a clear brown solution as a solution of catalyst precursor [9].

To a suspension of triyne **1** (1.0 mmol) and Zn powder (6.5 mg, 0.1 mmol) in THF (1 mL) was added a solution of catalyst precursor involving **3a** and $FeCl_3$ (prepared above, 0.8–2 mL, 0.02–0.05 mmol, 2–5 mol%) at room temperature. The resulting mixture was stirred for 24–48 h at room temperature ~THF-reflux temperature. After being cooled to room temperature, the mixture was filtered through a pad of Celite with ether and saturated aqueous NH_4Cl (10 mL) was added. The mixture was extracted with ether (2×10 mL), washed with brine, dried over $MgSO_4$, concentrated in vacuo. The residue was chromatographed on silica gel to give the corresponding annulated benzene **2**.

3.3. Cyclotrimerization reaction catalyzed by a 2-(iminomethyl)pyridine *5a*-$FeCl_3$-$6H_2O$/Zn reagent

3.3.1. General procedure

To a mixture of zinc powder (6.5 mg, 0.10 mmol) and **1** (1.0 mmol) in THF (2.5 mL) was added a solution of $FeCl_3$-$6H_2O$ (13.5 mg, 0.05 mmol) and 2-(2,6-diisopropylphenyl)iminomethylpyridine (**5a**) (16.0 mg, 0.06 mmol) in THF (1.5 mL) [9]. The resulting mixture was stirred at 50 °C. After being cooled to ambient temperature, Et_2O (10 mL) was added and the mixture was filtered through a pad of Celite with ether. The filtrate was concentrated in vacuo and chromatographed on silica gel to give the corresponding annulated benzene **2**.

1,3,6,8-Tetrahydro-2,7-dioxa-*as*-indacene (**2a**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 2H, Ar), 5.13 (s, 4H, $ArCH_2O$), 5.04 (s, 4H, $ArCH_2O$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 132.3, 119.9, 73.4, 72.2; IR (KBr): 2854, 1464, 1386, 1038, 1018 cm^{-1}. Mp 83–85 °C. Anal. Calc. for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.70; H, 6.09%.

Trimethyl(1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacen-4-yl)-silane (**2b**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (s, 1H, Ar), 5.17 (s, 2H, $ArCH_2O$), 5.14 (s, 2H, $ArCH_2O$), 5.03 (s, 4H, $ArCH_2O$), 0.29 (s, 9H, TMS); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 143.9, 138.2, 133.4, 131.9, 131.5, 125.2, 73.9, 73.5, 72.3, 71.9, −0.98; IR (KBr) 2956, 2895, 2855, 1767, 1251, 1059 cm^{-1}. Mp 116–117 °C. Anal. Calc. for $C_{13}H_{18}O_2Si$: C, 66.62; H, 7.74. Found: C, 66.63; H, 7.68%.

tert-Butyldimethyl(1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacen-4-ylmethoxy)silane (**2c**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (s, 1H, Ar), 5.12 (s, 4H, $ArCH_2O$), 5.02 (s, 4H, $ArCH_2O$), 4.66 (s, 2H, $ArCH_2OTBS$), 0.93 (s, 9H, *t*-Bu), 0.10 (s, 6H, $Si(CH_3)_2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 136.3, 134.3, 132.4, 130.9, 117.6, 73.4, 72.7, 72.14, 72.09, 63.6, 25.9, 18.4, −5.4; IR (KBr) 2954, 2930, 2857, 1762, 1466, 1348, 1007, 839 cm^{-1}. Mp 84–85 °C. Anal. Calc. for $C_{17}H_{26}O_3Si$: C, 66.62; H, 8.55. Found: C, 66.99; H, 8.48%.

4,5-Diphenyl-1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacene (**2d**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 – 7.22 (m, 10H, Ph), 5.14 (s, 4H, $ArCH_2O$), 4.99 (s, 4H, $ArCH_2O$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 138.4, 134.1, 131.2, 129.4, 127.9, 126.8, 73.6, 72.7; IR (KBr) 2922, 2847, 1446, 1429, 1352, 1063, 1043 cm^{-1}. Mp 188–193 °C. Anal. Calc. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.71; H, 5.76%.

4,5-Dibutyl-1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacene (**2e**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.11 (s, 4H, $ArCH_2O$), 5.02 (s, 4H, $ArCH_2O$), 2.49–2.53 (m, 4H, $ArCH_2CH_2$), 1.37–1.50 (m, 8H, $CH_2CH_2CH_3$), 0.95 (t, 6H, $J = 7.0$ Hz, $CH_2CH_2CH_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.3, 133.3, 129.3, 73.0, 72.7,32.7, 29.6, 23.0, 13.9; IR (KBr) 2956, 2930, 2866, 1461, 1056 cm^{-1}. Mp 93–95 °C. Anal. Calc. for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.54; H, 9.70%.

4,5-Bis(trimethylsilyl)-1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacene (**2f**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.17 (s, 4H, $ArCH_2O$), 4.95 (s, 4H, $ArCH_2O$), 0.40 (s, 18H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 138.9, 132.4, 74.8, 71.2, 3.6; IR (neat) 2950, 2900, 2855, 1728, 1251, 1059 cm^{-1}. Mp 134–136 °C. Anal. Calc. for $C_{16}H_{26}O_2Si_2$: C, 62.69; H, 8.55. Found: C, 62.80; H, 8.48%.

1-Methyl-1,3,6,8-tetrahydroindeno[4,5-*c*]furan-7,7-dicarboxylic acid diethyl ester (**2g**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, 1H, $J = 8.0$ Hz, Ar), 7.02 (d, 1H, $J = 8.0$ Hz, Ar), 5.33 (m, 1H, $ArCH(CH_3)$), 5.11 (d, 1H, $J = 12.0$ Hz, $ArCH_2O$), 4.99 (d, 1H, $J = 12.0$ Hz, $ArCH_2O$), 4.22 (q, 2H, $J = 6.5$ Hz, CH_2CH_3), 4.20 (q, 2H, $J = 6.5$ Hz, CH_2CH_3), 3.62 (d, 1H, $J = 16.5$ Hz, $ArCH_2C$), 3.59 (d, 1H, $J = 16.5$ Hz, $ArCH_2C$), 3.55 (d, 1H, $J = 16.5$ Hz, $ArCH_2C$), 3.46 (d, 1H, $J = 16.5$ Hz, $ArCH_2C$), 1.50 (d, 3H, $J = 6.0$ Hz, $CH(CH_3)$), 1.27 (t, 3H, $J = 6.5$ Hz, CH_2CH_3), 1.25 (t, 3H, $J = 6.5$ Hz, CH_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4 (2C), 139.7, 138.8, 138.1, 132.9, 123.2, 119.6, 79.4, 72.2, 61.7 (2C), 60.6, 39.8, 38.2, 20.6, 13.93, 13.91; IR (KBr) 2978,

1746, 1733, 1715, 1467, 1450, 1218, 1240, 1184, 1157, 1070 cm^{-1}. Anal. Calc. for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.64; H, 7.06%.

(1,3,6,8-Tetrahydro-2,7-dioxa-*as*-indacen-4-yl)methanol (**2h**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (s, 1H, Ar), 5.16 (s, 2H, $ArCH_2O$), 5.10 (s, 2H, $ArCH_2O$), 5.01 (brs, 4H, $ArCH_2O$), 4.65 (d, 2H, $J = 5.4$ Hz, $ArCH_2OH$), 2.06 (t, 1H, $J = 5.4$ Hz, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.3, 137.0, 133.7, 132.6, 131.5, 118.4, 73.3, 72.5, 72.14, 72.08, 63.3; IR (KBr) 3400, 2855, 1640, 1618, 1086, 1040 cm^{-1}. Mp 135–137 °C. Anal. Calc. for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.49, H, 6.41%.

5,5′-Bis-benzyloxymethyl-1,3,6,8,1′,3′,6′,8′-octahydro[4,4′]bi[2,7-dioxa- *as*-indacenyl] (**2i**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24–7.29 (m, 6H, Ph), 7.13–7.16 (m, 4H, Ph), 5.20 (d, 2H, $J = 14.0$ Hz, $ArCH_2O$), 5.17 (d, 2H, $J = 14.0$ Hz, $ArCH_2O$), 5.03–5.11 (m, 8H, $ArCH_2O$), 4.72 (d, 2H, $J = 12.0$ Hz, $ArCH_2O$), 4.64 (d, 2H, $J = 12.0$ Hz, $ArCH_2O$), 4.32 (d, 2H, $J = 11.5$ Hz, $ArCH_2OBn$), 4.29 (d, 2H, $J = 11.5$ Hz, $ArCH_2OBn$), 4.12 (d, 2H, $J = 11.0$ Hz, $PhCH_2O$), 4.08 (d, 2H, $J = 11.0$ Hz, $PhCH_2O$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7, 138.2, 137.5, 132.5, 131.9, 130.0, 129.0, 128.3, 127.74, 127.71, 73.3, 73.2, 73.1, 72.8, 72.2, 67.6; IR (KBr) 3057, 3032, 2889, 2855, 1775, 1767, 1458, 1450, 1350, 1087, 1048 cm^{-1}. Mp 150–159 °C. Anal. Calc. for $C_{36}H_{34}O_6$: C, 76.85; H, 6.09. Found: C, 76.87, H, 6.06%.

4,5-Diprop-2-ynyl-1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacene (**2j**): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.20 (s, 4H, CH_2O), 5.04 (s, 4H, CH_2O), 3.55 (d, 4H, $J = 2.9$ Hz, $CH_2C\equiv C$), 2.08 (t, 2H, $J = 2.9$ Hz, $C\equiv CH$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.1, 132.4, 128.3, 81.0, 73.8, 73.6, 71.0, 20.2; IR (neat) 3244, 2854, 1060, 1041 cm^{-1}. Since **2j** was somewhat unstable, it was converted by hydrogenation with 10% Pd/C under atmospheric H_2 to 4,5-dipropyl-1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacene, the structure of which was confirmed by comparison of its spectroscopic data with the data of that derived from **2k** by the same procedure. 4,5-dipropyl-1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacene: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.04 (s, 4H, OCH_2), 4.95 (s, 4H, OCH_2), 2.42 (t, 4H, $J = 8.1$ Hz, $ArCH_2CH_2$), 1.44 (sext, 4H, $J = 8.1$ Hz, CH_2CH_3), 0.93 (t, 6H, $J = 8.1$ Hz, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 133.9, 130.0, 73.7, 73.3, 32.7, 24.4, 15.1; MS (EI) *m*/*z* (relative intensity) 246 (100, M^+), 217(58, $M^+-CH_2CH_3$), 203 (61, $M^+-CH_2CH_2CH_3$).

4,5-Diallyl-1,3,6,8-tetrahydro-2,7-dioxa-*as*-indacene (**2k**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.81–5.89 (m, 2H, $CH{=}CH_2$), 5.08 (s, 4H, CH_2O), 5.01–5.05 (m, 6H, CH_2O and $CH{=}CH_2$), 4.91 (d, 2H, $J = 9.6$ Hz, $CH{=}CH_2$), 3.30 (d, 4H, $J = 6.0$ Hz, $ArCH_2CH$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1, 135.1, 130.3, 130.1, 115.7, 72.9, 72.7, 33.9; IR (KBr): 3071, 2847, 1636, 1055 cm^{-1}. Mp 53–55 °C. Anal. Calc. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.29; H, 7.20%.

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