ORGANOMETALLICS

Cyclic (Alkyl)amino Carbene Based Iron Catalyst for Regioselective Dimerization of Terminal Arylalkynes

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Supporting Information

ABSTRACT: $[(cAAC)Fe(CO)_4]$ (1) catalyzed head-to-head dimerization of terminal arylalkynes toward conjugated enynes in very high yield and high *E* selectivity (up to 84:16 *E:Z*). The protocol can be performed under extremely low catalyst loading down to 0.01 mol %, resulting in a high TON of 6500. A mechanistic pathway for arylalkyne dimerization has been proposed on the basis of a well-defined catalyst, an isolable intermediate, and quantum chemical calculations.



C onjugated 1,3-enynes are influential building blocks in organic synthesis for the preparation of natural products, polysubstituted aromatic rings, and the key structural unit in numerous biologically active molecules, drug intermediates, and organic electronic materials.¹ Owing to the widespread use of 1,3-enynes, development of novel methods toward their effective and economic preparation is a highly desirable goal

Scheme 1. Dimerization of Phenylacetylene Catalyzed by Complex 1 in Toluene



in catalysis research. Numerous methods for the synthesis of 1,3-enynes are well-known, including Sonogashira coupling of terminal alkynes with vinyl halides, cross-coupling of organo-





metallic alkynes with alkenes as well as terminal alkynes with preactivated alkenes, Wittig olefination of conjugated alkynals, Suzuki coupling of alkynyl halides with boronic acid, and dehydration of propargylic alcohols.² In comparison to these, an operationally simple and atom-economical dimerization of terminal alkynes or direct hydroalkynylation across the carbon–carbon triple bond to form conjugated enynes is a very practical method.³ The dimerization of terminal alkynes has been scrutinized primarily with a large number of transition-metal-based catalysts, mostly based on precious metals⁴ and f-block elements.⁵ However, the most recent trend deals with the development of catalysts using earth-abundant, nontoxic, and inexpensive metals such as iron for alkyne dimerization.

A thorough literature survey reveals that there have been only a few reports of iron catalysts employed for alkyne dimerization.⁶ The first iron-catalyzed alkyne dimerization used FeCl₃ as the catalyst in semistoichiometric loading (30 mol %).^{6a} Very recently, Milstein and co-workers^{6b} showcased that 1–3 mol % loading of iron catalyst can achieve chemo-, regio-, and stereoselective (*Z*-selective) alkyne dimerization without using base or other additives. This remarkable scarcity of iron-based catalyst strongly motivated us to develop an efficient iron-based catalyst for alkyne dimerization under very low catalyst loading condition. As a part of our ongoing research program to design organometallic catalysts using carbenes as ligands,⁷ we herein used a strong σ -donor ligand such as cyclic (alkyl)amino carbene (*c*AAC)⁸ to generate a robust catalytic platform. In this report, we describe an efficacious *E*-selective

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head-to-head dimerization of terminal arylalkynes (Scheme 1) with extremely low catalyst loading (0.2-0.01 mol %) of the iron(0) complex [(cAAC)Fe(CO)₄] (1), resulting in a high TON of 6500, which is impressive given the very few reports of iron-catalyzed alkyne dimerization reactions.⁶

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthesis of 1 was accomplished by the treatment of free cAAC with commercially available diiron nonacarbonyl $[Fe_2(CO)_9]$ in a 2:1 stoichiometric ratio in toluene at room temperature (Scheme 2). Analytically pure pale yellow crystals of 1 were obtained in 65% isolated yield from a concentrated toluene solution at -20 °C. Compound 1 readily dissolves in toluene, benzene, THF, and DMSO, and it shows limited solubility in hexane and pentane.

The nature of the complex has been probed by an array of spectroscopic methods (¹H, ¹³C NMR, and IR), as well as by elemental analysis and single-crystal X-ray diffraction studies. The ¹³C NMR spectrum of 1 reveals a resonance at 215.8 ppm, assignable to the C1 carbon bound to the iron center which is significantly shifted upfield upon metal coordination from the corresponding chemical shift of free *c*AAC (304.2 ppm).^{8b} To unambiguously ascertain the expected bond connectivities, a crystal was analyzed via single-crystal X-ray diffraction (Figure 1).⁹ As anticipated, the X-ray crystal structure of 1 exhibits



Figure 1. View of the molecular structure of **1**. Ellipsoids are set at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Fe1–C1, 1.995(2); Fe1–C21, 1.813(2); Fe1–C22, 1.779(2); Fe1–C23, 1.793(2); Fe1–C24, 1.793(2); C21–Fe1–C1, 99.36(9); C22–Fe1–C1, 173.86(9); C24–Fe1–C1, 86.65(9); C23–Fe1–C1, 92.72(9).

iron(0) trapped in a distorted-trigonal-bipyramidal environment and bonded to the cAAC and four carbonyl moieties. The Fe–C(carbene) bond distance is 1.995(2) Å, which compares well with that of the previously crystallographically analyzed [(IMes)Fe(CO)₄] (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene).¹⁰

Having well understood the structure of the complex, we used **1** as a precatalyst for dimerization of terminal alkynes to 1,3-enynes. When a solution of complex **1** (0.2 mol %) and phenylacetylene in toluene was stirred in the presence of 2 equiv of potassium *tert*-butoxide (KO^tBu) at room temperature for 4 h, a 36% (*E:Z* 70:30) yield of 1,4-diphenyl-1-buten-3-yne was realized (Table 1, entry 2). Upon further optimization of solvent and temperature, a quantitative yield of the head-to-

Table 1. Optimization Study for Iron-CatalyzedDimerization of Phenylacetylene a

Ph-	 Н + 2 ко	0.2 mol 0.2 mol Toluene 120 °C	Fe(CO) ₄ % ; 4 h C	P + 2 a	h Ph + F	O ^t Bu
	1 (2				Ph	3
entry	base (2 equiv)	cat. I (mol %)	solvent	(°C)	(2a:2b:3)	TON
1	KO ^t Bu (2)	0.2	DMSO	RT	25, 66:34:0	
2	$KO^{t}Bu$ (2)	0.2	toluene	RT	36, 70:30:0	
3	KO ^t Bu (2)	0.2	toluene	90	65, 81:19:0	
4	KO ^t Bu (2)	0.2	toluene	120	98, 82:18:0	490
5	KO ^t Bu (2)	0.2	hexane	80	83, 38:50:0	
6	KO ^t Bu (2)	0.2	Et_2O	40	15, 15:9:0	
7	KO ^t Bu (2)	0.2	THF	80	95, 79:21:0	
8	KO ^t Bu (2)	0.2	benzene	95	90, 50:48:0	
9	$K_{2}CO_{3}(2)$	0.2	toluene	120	70, 65:35:0	
10	Na_2CO_3 (2)	0.2	toluene	120	55, 58:42:0	
11	$\begin{array}{c} \mathrm{Cs}_2\mathrm{CO}_3 \\ (2) \end{array}$	0.2	toluene	120	65, 71:29:0	
12	KOAc (2)	0.2	toluene	120	60, 60:40:0	
13	NaOAc (2)	0.2	toluene	120	65, 52:48:0	
14	$K_{3}PO_{4}(2)$	0.2	toluene	120	60, 64:36:0	
15	-	0.2	toluene	120	_	
16	KO ^t Bu (2)	-	toluene	120	5, 68:32:0	
17 ^c	KO ^t Bu (2)	0.2	toluene	120	36, 78:22:0	
18	KO ^t Bu (1)	0.2	toluene	120	67, 74:26:0	
19	KO ^t Bu (3)	0.2	toluene	120	97, 65:30:5	
20	KO ^t Bu (4)	0.2	toluene	120	96, 65:21:14	
21	$KO^{t}Bu$ (2)	0.1	toluene	120	98, 62:38:0	980
22	$KO^{t}Bu$ (2)	0.05	toluene	120	84, 53:47:0	1680
23	$KO^{t}Bu$ (2)	0.01	toluene	120	65, 49:51:0	6500
^a React	ion conditio	ons unless	specified	otherwis	e: phenylacety	vlene (1

mmol), KO'Bu (2 mmol), complex 1, toluene (1 mL), 120 °C, 4 h. ^bIsolated yield. ^cFe(CO)₅ instead of complex 1.

head dimerization product 2 (Table 1, entry 4) was achieved in toluene at 120 °C. After optimization of different bases (Table 1, entries 4 and 9-14), quantitative yield and higher selectivity were realized when 2 equiv of KO^tBu was used in the presence of toluene at 120 °C for 4 h (Table 1, entry 4). The reaction does not proceed in absence of bases (Table 1, entry 15). A control experiment without catalyst 1 yielded only 5% of 1,3enyne product with 2 equiv of KO^tBu (Table 1, entry 16), which clearly indicates that the presence of our catalyst is required for the reaction. To further test the necessity of a cAAC-bound Fe(0), the catalysis was executed in the presence of $[Fe(CO)_5]$ and base instead of catalyst 1, giving a 36% yield of the dimerized product with moderate selectivity (Table 1, entry 17). This unequivocally establishes that cAAC plays an important role during the catalysis. To our delight, the catalyst can even perform the reaction well with extremely low catalyst loading (0.01 mol %) at 120 °C, leading to a considerably high TON value of 6500 with moderate yield (65%, Table 1, entry 23).

A preliminary kinetic plot of yield as a function of time revealed that the reaction goes to near completion within 3 h (see the Supporting Information for details). Further, the scope of the dimerization of several terminal arylalkynes to 1,3-enynes (Table 2) was investigated. It is noteworthy that the reaction

		Ar						
		(cAAC)Fe(CO) ₄ (0.2 mol	(cAAC)Fe(CO)₄ (0.2 mol%)					
Ar∙	— <u>—</u> —H	2 KO ^t Bu; Toluene ; 4 h 120 ^o C	Ar E	+ Ar Z A				
_	Entry	Substrate	Conv. ^b [%]	Yield [%] ^c , (<i>E</i> : <i>Z</i>)				
_	1		>99	98, 82:18				
	2 Me	,-{	>99	98, 74:26				
	3		>99	92, 64:36				
	4 MeC		>99	96, 60:40				
	5		82	56, 44:56				
	6	OMe	>99	95, 77:23				
	7 F		>99	90, 73:27				
	8 Br		>99	92, 74:26				
	9		>99	92, 77:23				
	10	F ₃ C CF ₃	>99	60, 17:83				
	11 ^d		>99	98, 84:16				
	12		77	66, 5:95				

Table 2. Dimerization of Terminal Arylalkynes Catalyzed by 1^a

^{*a*}Reaction conditions unless specified otherwise: arylalkyne (1 mmol), KO'Bu (2 mmol), complex 1 (0.2 mol %), toluene (1 mL), 120 °C, 4 h. The conversion and ratio of *E:Z* isomers are based on ¹H NMR spectroscopic analysis of the crude reaction mixture. ^{*b*1}H NMR spectroscopic conversion. ^cIsolated yield. ^{*d*}The reaction was carried out with 0.15 mmol of the substrate instead of 1.0 mmol.

showcases exclusive regioselectivity favoring only head-to-head product. Under the standardized conditions, the presence of both an electron-donating and an electron-withdrawing group furnished the dimerized product **2** in good to excellent yield (56-98%) along with good stereoselectivity. The *E*:*Z* ratio of the product is somewhat dependent on the nature of the alkyne and varies from 60:40 to 84:16 in favor of the *E* isomer in most cases (Table 2, except for entries 5, 10, and 12).

Substrate Scope of Arylalkynes. The presence of an electron-donating methyl group at the para or meta position of the phenylacetylene moiety afforded high yield and good selectivity to an *E:Z* mixture of the dimerized product (Table 2, entries 2 and 3). The presence of methoxy group at the ortho position of phenylacetylene dramatically lowered both the yield and selectivity in comparison to that for a para substituent, presumably because of the steric congestion at the ortho position of methoxyphenylacetylene (Table 2, entries 4 and 5).

In the case of a meta derivative of methoxyphenylacetylene, excellent yield and selectivity were retained (Table 2, entry 6). The dimerization of 4-fluorophenylacetylene afforded 90% yield with a 73:27 mixture of the *E*:*Z* dimers (Table 2, entry 7). Under similar reaction conditions, 4-bromophenylacetylene gave the corresponding product in 92% yield with comparable selectivity (E:Z = 74:26, Table 2, entry 8). An electronwithdrawing trifluoromethyl substituent at the ortho position of phenylacetylene yielded 92% of the corresponding dimer with good selectivity (E:Z = 73:27, Table 2, entry 9). However, the presence of two electron-withdrawing substituents in the same ring, such as trifluoromethyl at both the 3- and 5-positions of phenylacetylene offered a moderate yield (60%) of the corresponding dimer with inverted selectivity (E:Z = 17:83) (Table 2, entry 10). We surmise that the presence of two strongly electron withdrawing groups makes the arylalkynes sufficiently electron poor that binding to Fe(0) is disfavored (see Mechanistic Understanding). A terminal alkyne containing a heterocyclic ring such as pyridine lowered the yield of the dimerized product and favored the Z isomer of the corresponding dimer (Table 2, entry 12).

Mechanistic Understanding. To explore the mechanistic course of the alkyne dimerization reaction catalyzed by 1, we ventured on a tandem experimental and computational approach. As is intuitive, the generation of electronic unsaturation to 1 requires driving one CO ligand out, which is an energy-uphill process, given the strong binding of the CO ligand. Indeed, upon heating a mixture of 1 and phenylacetylene at 90 °C, unsaturation at the iron center is created, promoting the alkyne binding. This fact is in strong accord with either a thermal or photochemical reaction toward the generation of unsaturation for similar catalytic systems.¹⁰ The alkyne-bound intermediate 3 (Figure 2) was isolated from a benzene solution and thoroughly characterized by NMR, IR, and mass spectroscopic studies. Intermediate 3 displays its characteristic ¹³C NMR resonances at δ 78.7 and 82.2 ppm, representing alkyne carbons. Furthermore, the resonance at 82.2 ppm vanishes on the DEPT-135 pulse sequence, suggesting this carbon to be the phenyl-substituted atom. Computationally (M06/lanl2dz+6-31G* for C, H, N, and O)¹¹ we were also able to optimize 3 (see Figure 2), where alkyne binds the iron in an η^2 fashion, displaying C–Fe bond distances of 2.04 and 2.13 Å, respectively. Not surprisingly, the C-C bond of the alkyne clearly elongates to 1.27 Å from 1.21 Å for the parent alkyne. We probed a further sequence of events computationally and inferred that the alkynide, generated from deprotonation of the alkyne by KO^tBu, binds to the metal upon creating further unsaturation. Expelling the second CO requires energy, but the amount is smaller than that of the first step since the already bound phenylacetylene can mitigate the effect of electron loss, forming a metallacyclopropene type intermediate. Upon alkynide binding, intermediate 4 is generated (Figure 2), where alkyne and alkynide are perfectly oriented toward C-C bond formation, leading to the dimerization of alkyne. The exclusive formation of a head-tohead isomer in this dimerization reaction can be nicely explained from an atomic polar tensor (APT) charge analysis of the intermediate 4 (Figure 3a). As alkynide behaves as a nucleophile, its attack will be facilitated at a center which possesses more positive charge. In 4, the unsubstituted carbon bears a charge of -0.178e, in comparison to -0.638e at the phenyl-substituted carbon of the bound alkyne (Figure 3). From the charge analysis, it is intuitive to surmise that the other



Figure 2. Free energy landscape of the alkyne dimerization reaction catalyzed by 1. Asterisks designate the transition states which were not exactly located but are shown for the purposes of illustration only. In the inset is shown 4-TS, in which the newly formed C…C bond distance is 1.88 Å.



Figure 3. (a) APT charge distribution in 4. (b) Plausible mechanism for Z to E isomerization via a metallacarbene type intermediate structure.

head-to-tail isomer of the enyne product will require significantly higher energy due to the assembly of two negatively charged centers. The free energy landscape is shown in Figure 2, accumulating all the computational information. The C–C bond formation via 4-TS overcomes a small energy barrier of 6.43 kcal/mol, leading to the σ -enynyl intermediate 5, which forms after alkyne binding to the vacant coordination site at iron (Figure 2). The formation of 5 is highly exergonic and justifies the strong thermodynamic drive behind the dimerization reaction. The σ -enynyl intermediate can easily be protonated by the bound alkyne to realize the 1,4-disubstituted enyne. The protonation of the anionic form of the enyne by an alkyne has been invoked in several previous reports.¹²

Moreover, the potential energy surface of the alkyne dimerization reaction suggests that the major amount of energy required for the reaction is in fact expended to drive CO out to create unsaturation from the stable 1. To prove this conjecture further as well as to authenticate the competence of 3, we performed catalysis with isolated 3. Indeed, catalysis starting from 3 can happen at a far lower temperature, 50 °C, converting the phenylacetylene completely to its dimerized product in quantitative yield. Notably, the *E* isomer of the dimerized product is slightly thermodynamically more stable than the kinetically controlled *Z* isomer. The *Z* to *E* isomerization can be facilitated via iron–carbenoid resonance

structures (Figure 3b).¹³ Interestingly, we observed *E* to *Z* product interconversion as a time-dependent phenomenon, since the *E*:*Z* ratio at 1 h (64:36) can be increased to 82:18 after 4 h (Table S2, entry 3, in the Supporting Information). Our proposed mechanism has a very close resemblance to previous proposals for Zr- and Ru-catalyzed dimerization of arylalkynes to 1,3-enynes.¹⁴

CONCLUSIONS

Herein we have reported an efficient base-metal catalyst, which can convert terminal arylalkynes to the corresponding dimerized enyne products in excellent yield and good E:Z ratio. The small amount of catalyst loading for this dimerization translates into a high TON of 6500. Isolation of a reaction intermediate, further catalysis with this intermediate, and highlevel DFT calculations have helped to build a convincing mechanistic sketch for this atom-economical reaction.

EXPERIMENTAL SECTION

Methods. All reactions and manipulations were carried out under a dry and oxygen-free atmosphere (N_2) using standard Schlenk techniques or inside a glovebox maintained below a 0.1 ppm level of O2 and H2O. All glassware were oven-dried (130 °C) and evacuated while hot prior to use. All solvents were distilled from Na/ benzophenone prior to use. All other chemicals were purchased from commercial sources and used as received. Elemental analyses were carried out using a Perkin Elmer 2400 CHN analyzer, and samples were prepared by keeping them under reduced pressure (10^{-2}) mbar) overnight. The melting points were measured in a sealed glass tube on a Büchi B-540 melting point apparatus and are uncorrected. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on Merck 60 silica gel (100-200 mesh). Deuterated benzene was purchased from Sigma-Aldrich, dried by sodium/potassium alloy, and stored over 4 Å molecular sieves prior to use. NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer or a Bruker Avance III 500 MHz spectrometer. All chemical shifts are reported in ppm using tetramethylsilane as a reference. Chemical shifts (δ) downfield from the reference standard are assigned positive values. Crystallographic

data for the structural analysis of 1 have been deposited at the Cambridge Crystallographic Data Center (CCDC number 1497028). These data can be obtained free of charge from the Cambridge Crystallographic Data Center.

Synthesis of (cAAC)Fe(CO)₄ (1). In a glovebox, an oven-dried 50 mL Schlenk flask was charged with Fe₂(CO)₉ (200 mg, 0.55 mmol) and cyclic (alkyl)amino carbene (cAAC) (286 mg, 1 mmol). Then the Schlenk flask was taken out from the glovebox, connected to the Schlenk line and dry toluene (25 mL) was added via a cannula at 25 °C under an argon atmosphere to this reaction mixture. The reaction mixture was stirred overnight, and during the course of the reaction, the color changed to yellow. Then the reaction mixture was filtered through a celite pad and concentrated to ca. 5 mL. Storage of this reaction mixture at -20 °C for 3 days afforded yellow crystals (185 mg, 0.43 mmol, 43%). Anal. Calcd for C₂₄H₃₁FeNO₄: C, 63.58; H, 6.89; N, 3.09. Found: C, 63.62; H, 6.82; N, 3.04. IR (film, γ_{CO} in cm⁻¹): 2005, 1922, 1884. ¹H NMR (C₆D₆, 500 MHz, 298 K): δ 7.22 (t, 1H, J = 8 Hz), 7.08 (d, 2H, J = 7.5 Hz), 2.65 (sept, 2H, J = 6.5 Hz),1.49 (d, 6H, J = 6.5 Hz), 1.48 (s, 6H), 1.43 (s, 2H), 1.11 (d, 6H, J = 6.5 Hz), 0.84 (s, 6H) ppm. ¹³C NMR (C_6D_6 , 125 MHz, 298 K): δ 215.8, 146.7, 137.9, 130.4, 128.4, 126.1, 78.5, 60.0, 51.5, 31.5, 29.3, 29.2, 25.9, 24.6 ppm.

Synthesis of (cAAC)Fe(CO)₃(PhCCH) (3). In a glovebox, an ovendried 25 mL Schlenk flask was charged with complex 1, (cAAC)Fe- $(CO)_4$ (70 mg, 0.1544 mmol), in 3 mL of benzene. Then phenylacetylene (22.0 μ L, 0.2 mmol, 1.3 equiv) was added, and the reaction mixture was heated to 90 °C for 10 h. After completion of the reaction, the dark red solution was separated from the reaction mixture simply by decantation. Then the supernatant was evaporated to dryness and washed twice with cold hexane to afford the dark red complex 3 (36.6 mg, 0.0694 mmol, 48%). ESI-MS: *m*/*z* calcd for $C_{31}H_{37}FeNO_3H [M + H]^+$ 528.2201, found 528.2206. IR (film, γ_{CO} in cm⁻¹): 2039, 1988, 1926. ¹H NMR (C_6D_6 , 400 MHz, 298 K): δ 7.60 (br s, 1H), 7.39 (br s, 1H), 7.11-6.78 (m, 6H), 3.37 (br s, 2H), 3.05 (br s, 1H), 2.16-1.75 (m, 2H), 1.47-1.16 (m, 6H), 1.16-0.96 (m, 12H), 0.87–0.77 (m, 6H) ppm. ¹³C NMR (C₆D₆, 125 MHz, 298 K): δ 222.8, 208.7, 171.9, 132.2, 130.9, 129.0, 128.8, 128.0, 127.4, 127.2, 122.7, 96.2, 82.2, 79.9, 78.7, 66.5, 59.4, 32.1, 29.2, 28.3, 26.4 ppm. DEPT-135 (C₆D₆, 125 MHz, 298 K): δ 132.2, 129.0, 128.8, 127.4, 127.2, 96.2, 78.7, 66.5, 59.4 (CH₂), 32.1, 29.2, 28.3 ppm.

General Procedure for Catalytic Dimerization of Arylalkynes to 1,3-Enynes by $(cAAC)Fe(CO)_4$ (1). In an oven-dried 25 mL sealed tube equipped with a magnetic stirrer inside the glovebox, complex 1 (0.2 mol %) was dissolved in 1.0 mL of toluene followed by addition of KO^tBu (224.4 mg, 2.0 mmol, 2 equiv). Then arylacetylene (1.0 mmol, 1 equiv) was added. The mixture was heated to 120 °C for 4 h. After cooling the reaction mixture, the solvent was removed and the crude product was purified by silica gel column chromatography using distilled *n*-hexanes as eluent to give (E+Z)-1,4-diarylbut-1,3-enyne.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00703.

Experimental procedure, spectroscopic data, and scanned spectra (PDF)

X-ray crystallographic data for 1 (CIF)

Calculations and Cartesian coordinates of calculated structures (XYZ)

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The authors declare no competing financial interest.

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