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Active Iron(II) Catalysts toward *gem*-Specific Dimerization of Terminal Alkynes

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ABSTRACT We report the syntheses and catalytic activity of a series of piano-stool iron complexes with a general formula [FeClCp*(NHC)] (where NHC = *N*-heterocyclic carbene) toward the *gem*-specific dimerization of terminal alkynes. Compared to our first-generation catalyst, the newly synthesized catalyst is more active and features the same geminal specificity. Both the experimental and computational data are presented herein.

KEYWORDS *N*-heterocyclic carbene, iron, catalysis, alkyne dimerization, enyne, computation

INTRODUCTION

1,3-Enynes are important synthons for natural products, bioactive molecules, organic materials, and other complex molecules.[1-11] The general synthetic methods include metal-mediated cross-coupling reactions, Wittig reaction, and dehydration of propargyl alcohols.[12-18] The selective dimerization of terminal alkynes is the ideal route for enyne synthesis owing to its perfect atom

economy.[17-20] The main challenge of alkyne dimerization is the control of regioselectivity due to the competing formation of head-to-head (*E*/*Z*) and head-to-tail (*gem*) isomers.[1,17,18]

The catalytic dimerization of the terminal alkynes have been extensively established,[18,19] mostly based on precious metals[21-36] and f-block elements.[37-40] In contrast, iron-based catalysts are rarely reported.[41-47] The first example of iron-catalyzed alkyne dimerization uses a 30 mol% loading of $FeCl_3$ as the catalyst in the presence of 300 mol% of KO^{t}Bu at high temperatures to give *E*-enyne products.[41,42] Milstein and co-workers reported [Fe(PNP^{CH2})(H)(η^2-BH_4)] catalyst toward the dimerization of arylacetylenes, featuring good *Z*-selectivity, low catalyst loading, and mild reaction conditions (Chart 1, **I**).[43] Later, Kirchner and co-workers reported a [Fe(PNP^{NH})$(H)_2$(η^2-H_2)] catalyst giving high *Z*-selectivity for the dimerization of arylacetylenes with a remarkable increase of reaction rates (Chart 1, **II**).[44,45] The Mandal group reported a well-defined iron(0) complex capable of catalyzing the dimerization of arylacetylenes, but the reactions require a large excess of KO^{t}Bu and 120 °C and give poor to high *E* selectivity (Chart 1, **III**).[46] Huang, Hor, Zhao and co-workers reported the iron(II) complex of an *N*,*N*,*N*-tridentate ligand as the catalyst which requires the use of a large excess of a *t*-butoxide base and forcing conditions (Chart 1, **IV**).[47] Interestingly, NaO^{t}Bu and KO^{t}Bu give the opposite *E*/*Z* selectivity. The literature of the geminal selective dimerization of alkynes is dominated by Pd, Rh, Al, and early metal catalysts.[49-71] While the late transition metal catalysts displayed good functional group tolerance,[49-60] the early transition metal and Al catalysts are incompatible with polar functional groups such as NH and OH.[61-71]

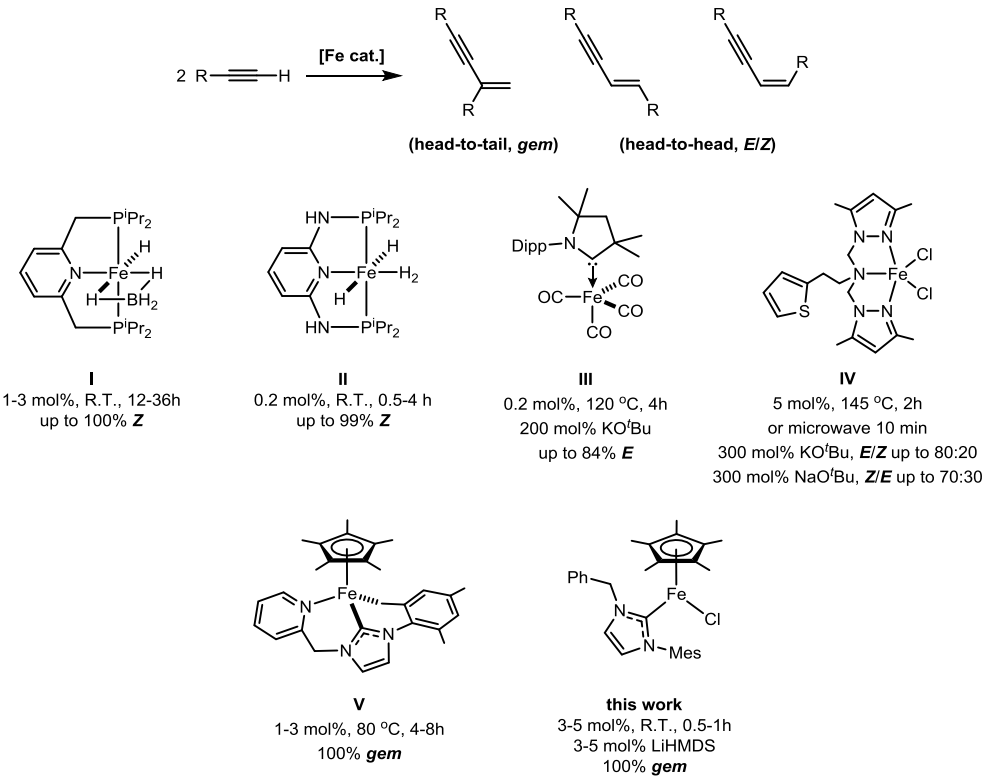


Chart 1. Well-defined iron catalysts for the dimerization of terminal alkynes.

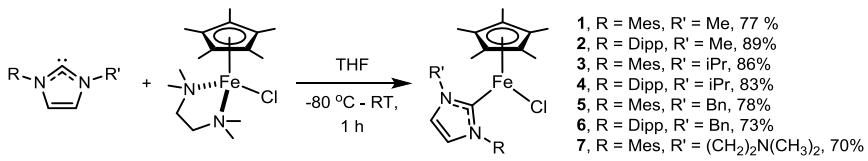
The NHC iron complexes are a versatile class of molecules for synthesis and catalysis.[72-78] Piano-stool iron NHC complexes, an important subclass of NHC iron complexes, are well known in organometallic chemistry.[79-86] Although the stoichiometric reactivity of such complexes has been intensively investigated, the catalytic counterpart remains rare.[79] Our group recently has developed a piano-stool iron catalyst featuring Cp* and picolyl *N*-heterocyclic carbene (NHC) ligands for the geminal specific dimerization of terminal alkynes (Chart 1, **V**).[48] This catalytic system features a broad substrate scope, i.e., both aryl and aliphatic alkynes are compatible and even substrates possessing an NH or OH group can be tolerated.[48] Our experimental and preliminary computational studies show that the bulky mesityl group on the NHC ligand is crucial for both the alkyne C–H activation and geminal specificity and that the pyridine group of the ligand

retards the catalytic activity by coordinating to metal center to generate stable off-cycle 18e species.[48] These results prompted us to replace the picolyl group of the NHC ligand with non-coordinating substituents. Herein we report the syntheses and structures of a series of half-sandwich iron complexes and our investigations into their catalytic reactivity toward alkyne dimerization. The half-sandwich iron complex of IMesBn (NHC with mesityl and benzyl substituents) turned out to be a highly active catalyst for the dimerization of terminal alkynes to yield geminal enynes exclusively.

RESULTS AND DISCUSSION

Synthesis and Characterization of Pre-catalysts. Complexes **1**–**7** were synthesized from the reaction of [FeClCp*(TMEDA)] with corresponding free NHC ligands in THF at −80 °C, and isolated in 70–89% yields (Scheme 1). The ^{1}H NMR spectra of **1**–**7** in C_6D_6 at room temperature show broadened and paramagnetically shifted resonances spanning the range of −25~110 ppm. The solution magnetic moments of **1**–**7** at room temperature (measured by Evans' method) were determined to be 3.0–3.7 μ_B, consistent with intermediate spin Fe(II) centers. The solid-state structures of **1**–**7** adopt two-legged piano-stool geometry (Figure 1). The Fe(1)−C(1), Fe(1)−Cl(1), and Fe(1)–Cp*$_{cent}$ distances for complexes **1**–**6** (Table 1) are comparable to those found in the closely related half-sandwich chloro NHC iron complexes.[82] Interestingly, the tertiary amine group in complex **7** shows no interaction with the iron center. The Fe(1)−C(1) (2.133(2) Å) and Fe(1)−Cl(1) (2.133(2) Å) bond lengths in complex **7** are slightly longer than those in complexes **1**–**6**, and the C(1)–Fe(1)–Cl(1) (106.50(5)º) bond angle is wider (Table 1). The Fe(1)–Cp$_{cent}$ distance of 1.986(1) Å significantly longer than those in complexes **1**–**6** (Table 1). At room temperature, complexes **1**–**7** slowly decompose into [$FeCl_2(NHC)_2$] and $FeCp^*_2$ in both solution and the solid state. They can be stored at −35 °C for months without significant decomposition.

Scheme 1. Syntheses of complexes **1**–**7**.



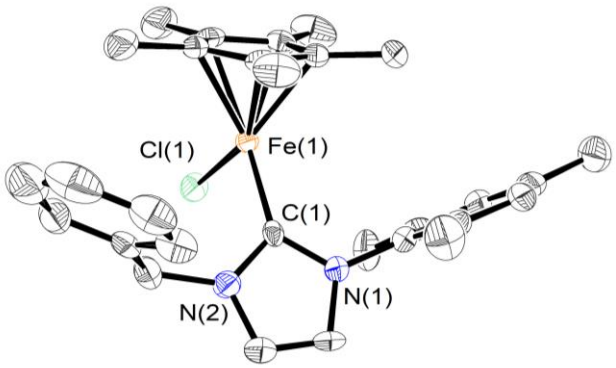


Figure 1. X-ray structures of **5**. Ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity.

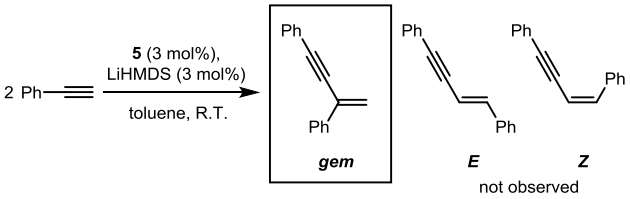
Table 1. Bond Lengths (Å) and Angles (deg) for 1–8.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Fe(1)–C(1)	1.966(3)	1.964(3)	1.980(4)	1.998(5)	1.980(4)	1.966(3)	2.133(2)	1.950(3)
Fe(1)–Cl(1)	2.272(1)	2.251(1)	2.264(1)	2.265(2)	2.267(1)	2.255(1)	2.2971(7)	-
C(1)–Fe(1)–Cl(1)	96.5(1)	94.9(1)	94.4(1)	96.9(1)	94.4(1)	96.41(9)	106.50(5)	-
Fe(1)–Cp*$_{cent}$	1.793(2)	1.793(2)	1.796(2)	1.823(2)	1.808(2)	1.790(2)	1.986(1)	1.7812(4)

Catalytic Dimerization of Phenylacetylene. We began by examining **1**–**7** in the catalytic dimerization of phenylacetylene, with a loading of 3 mol% of **[Fe]** pre-catalyst and 3 mol% of LiHMDS in toluene at room temperature as the standard conditions. No conversion was observed within 3 hours when **1** was used (Table 2, entry 1), presumably due to its instability. The bulkier **2** gives a moderate conversion of phenylacetylene to the *gem* dimer within 3 hours (Table 2, entry 2). Complex **3**, featuring an isopropyl and a mesityl substituents, gives the complete conversion of phenylacetylene to the geminal dimer within an hour (Table 2, entries 3–4). In contrast, complex

4, featuring an isopropyl and a 2,6-diisopropylphenyl (Dipp) substituents, only gives a 35% conversion in 3 hours (Table 2, entry 5). Complex **5** with benzyl and mesityl substituents leads to the full conversion within 0.5 hour (Table 2, entry 6). Similar to complexes **3** and **4**, complex **6** possessing a Dipp substituent displays a much lower activity (Table 2, entry 7) in comparison to its mesityl analogue **5**. Complex **7** possessing a tertiary amine side chain and a mesityl group is also an efficient catalyst, giving full conversion within 1 hour (Table 2, entry 9). Complex [FeClCp*(IMes)][82] (IMes = 1,3-dimesitylimidazol-2-ylidene) with mesityl groups as both R position and the precursor [FeClCp*(TMEDA)] shows no activity (Table 2, entry 10–11), showing that the asymmetric NHC ligands are crucial for this conversion. The two control experiments, i.e., with pre-catalyst **5** only and with base only, show little and no conversion, respectively (Table 2, entries 12–13).

Table 2. Testing of Complexes 1-7 for the Dimerization of Phenylacetylene[a]

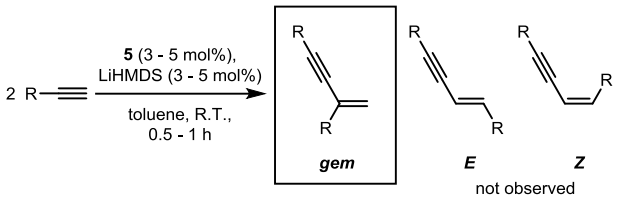


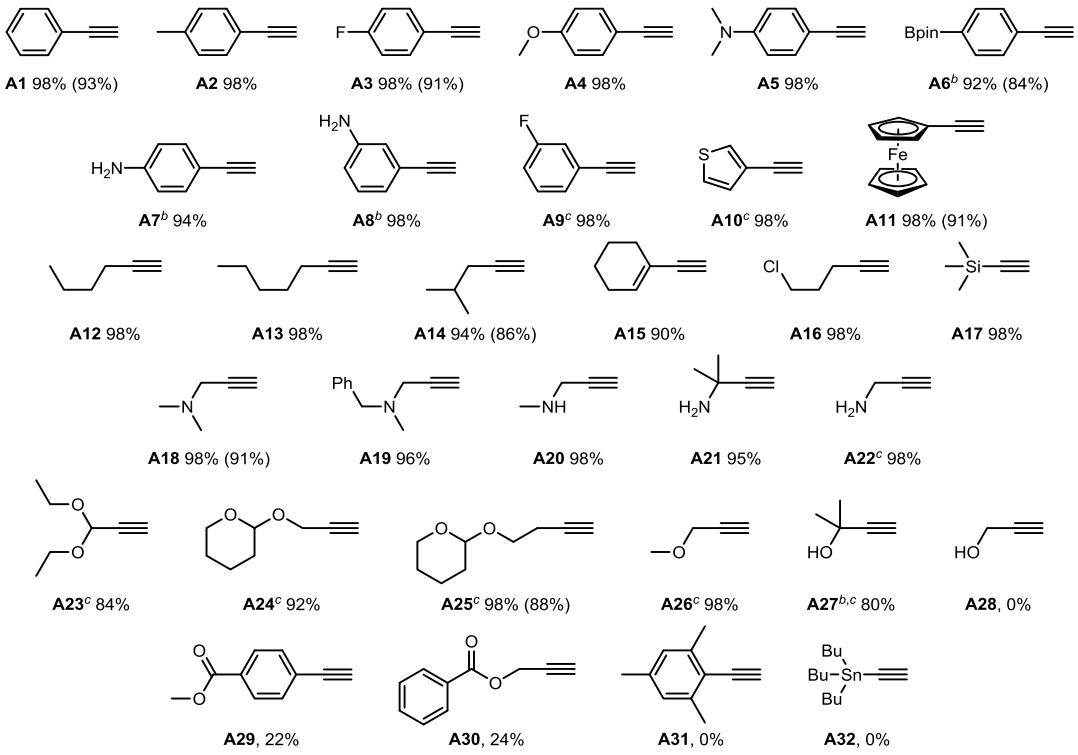
Entry	[Fe]	t (h)	Conv. (%)	Yield (%)
1	**1**	3	0	0
2	**2**	3	67	54
3	**3**	0.5	82	80
4	**3**	1	>99	98
5	**4**	3	35	32
6	**5**	0.5	>99	98
7	**6**	3	44	42
8	**7**	0.5	92	90
9	**7**	1	>99	98
10	**FeClCp*(IMes)**	3	0	0
11	**FeClCp*(TMEDA)**	3	0	0
12	**5** (no base)	3	<5	<5
13	base only	3	0	0

[a] General conditions: phenylacetylene (0.2 mmol), pre-catalyst (3 mol%), LiHMDS (3 mol%), toluene (1.0 mL), room temperature. The conversions and yields (of *gem* product) are based on the ^{1}H NMR integrations using mesitylene as the internal standard.

Catalytic Dimerization of Terminal Alkynes. Having identified complex **5** as the most promising pre-catalyst for terminal alkyne dimerization, we examined the substrate scope next. Pre-catalyst **5** shows high activity and excellent selectivity toward the dimerization of both aromatic and aliphatic terminal alkynes. The complete conversions of phenylacetylene and *p*-Me-, *p*-OMe-, *p*-F-, and *p*-NMe_2-substituted phenylacetylenes into the corresponding geminal products can be achieved within 0.5 h at room temperature (Table 3, entries A1–A5). With *p*-Bpin (Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl), *p*-NH_2 and *m*-NH_2-substituted phenylacetylenes, the reactions are slightly slower (Table 3, entries A6–A8). With *m*-F-phenylacetylene and 3-ethynylthiophene substrates, a 5 mol% loading of **5** and LiHMDS is needed to achieve full conversions in 0.5 h (Table 3, entries A9–A10). Ferrocenylacetylene, aliphatic alkynes including propargyl amines can also be converted into the corresponding *gem* products in good yields under the standard conditions (Table 3, entries A11–A21). A 5 mol % loading of **5** and LiHMDS is required for the unsubstituted propargyl amine (Table 3, entry A22). Furthermore, various oxygen-containing functional groups, such as acetals (Table 3, entries A23–A25), ether (entry A26), and tertiary alcohol (entry A27) are tolerated. In contrast to our previous catalytic system **V**,[48] unsubstituted propargyl alcohol shows no conversion (Table 3, entry A28). The catalytic activity ceased at 23% and 25% conversions with methyl 4-ethynylbenzoate and propargyl benzoate substrates, respectively (Table 3, entries A29–A30). In contrast, our previous catalytic system **V** shows no conversion of substrates containing ester functional groups.[48] The bulky mesitylacetylene and ethynyltributylstannane cannot dimerize under the same conditions (Table 3, entries A31–A32). The products from entries A11 and A29 were crystallographically characterized (Figures S25 and S26).

Table 3. Substrate Scope[a]





[a] General reaction conditions: substrate (0.2 mmol), **5** (3 mol%), LiHMDS (3 mol%), toluene (1.0 mL), room temperature, 0.5 h. The yields (of *gem* product) are based on ^{1}H NMR integration of the product peaks compared to those of the internal standard mesitylene. Isolated yields for reactions carried out with 1 mmol of the substrate are given in parentheses. [b] 1 h. [c] Reaction carried out with 5 mol% of **5** and 5 mol% of LiHMDS.

Coupling of Alkynes with *N*,*N*-Dimethyl-propargylamine. Selectively producing a single product is even more challenging when coupling two different alkynes, where 12 possible products may form (Scheme 2). Several strategies have been reported for the selective cross-dimerization of silyl alkynes with other alkynes.[31-35,43] Alkynes bearing an O or N-donor directing group have also been used as the acceptor alkyne to give high selectivity in cross-dimerizations.[48,58-61] The cross-dimerization of propargyl alcohols and amides with arylacetylene affords 2-en-4-yn-1-ols and 2-en-4-yn-1-yl amides (***E*-a**, where R^1 = aryl and R^2 = CH_2OH, CH_2NPg) in high selectivity

using a trialkyl phosphine-derived palladacycle catalyst under mild conditions.[58] Propargyl alcohols or amines provide high selectivity in cross-dimerization reactions to give ***gem*-a** enynes in high selectivity, using both late transition metals[49,59,60] and Ti(III)[61] catalysts.

Scheme 2. Possible enyne products in alkyne cross-dimerization reactions.

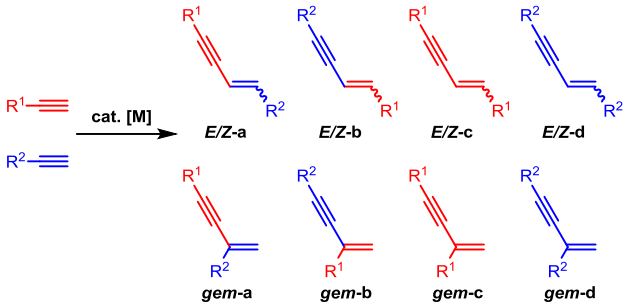
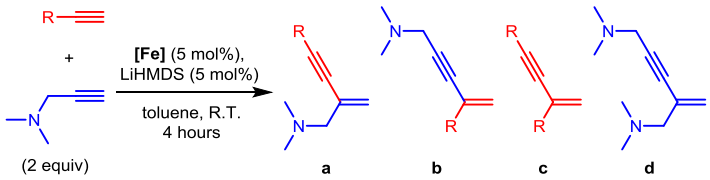
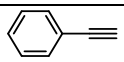
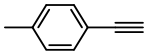
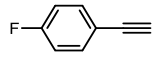
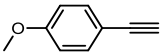
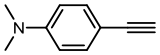
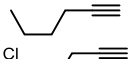
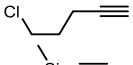


Table 4. Cross-dimerization of *N*,*N*-dimethylpropargylamine and other terminal alkynes[a]



		Yield (%)			
Entry	R	**a**	**b**	**c**	**d**
B1		76 (72)	6	14	61
B2		80 (78)	5	14	58
B3		70 (61)	6	18	62
B4		75 (70)	4	16	58
B5		80 (73)	4	16	57
B6		41	20	38	69
B7		29	35	36	66
B8		65	2	30	64

[a] General conditions: substrate (0.5 mmol), *N*,*N*-dimethyl-propargylamine (1.0 mmol), pre-catalyst (5 mol%), LiHMDS (5 mol%), toluene (2.5 mL), room temperature, 4 h. The yields (of *gem* product) are based on the ^{1}H NMR integrations using mesitylene as the internal standard. Yields of isolated product are given in parentheses.

The reaction of phenylacetylene (1 equiv) and *N*,*N*-dimethyl-propargyl amine (2 equiv) resulted in the complete conversion of the starting alkynes into a mixture of the cross-dimerization products **a** (76%) and **b** (6%) and the homo-dimerization products **c** (14%) and **d** (61%) (Table 4, entry B1) at ambient temperature with 4 h with a 5 mol% catalyst loading. Similar yields and selectivity were observed phenylacetylene was replaced with *p*-substituted phenylacetylenes (Table 4, entries B2–B5). Poor selectivity was observed when 1-hexyne and 5-chloro-1-pentyne were used instead of phenylacetylene (Table 4, entries B6–B7). When the bulky trimethylsilylacetylene was used, the yield of **a** was 65% (Table 4, entry B8).

Mechanistic Investigations. We first investigated the conversion of the pre-catalyst into the active species. The reaction between **5** and 1 equiv. of LiHMDS is slow and in 24 h gives a mixture where **5** is still the major species (Figure S95). The attempted isolation of the newly formed compounds was unsuccessful. In contrast, the reaction of **5** and PhC≡C−Li resulted in the clean formation of [FeCp*(C≡CPh)(IMesBn)], **8** instantaneously (Figure 2). The ^{1}H NMR spectrum of **8** in C_6D_6 shows paramagnetically broadened and shifted resonances. The magnetic moment of **8** in solution at room temperature (measured using the Evans' method) is 3.0 μ_B, consistent with a triplet spin state. The molecular structure of **8** was confirmed by X-ray crystallography (Figure 2). The Fe(1)–C(1) distance of 1.950(3) Å is slightly shorter compared to that in **5**.

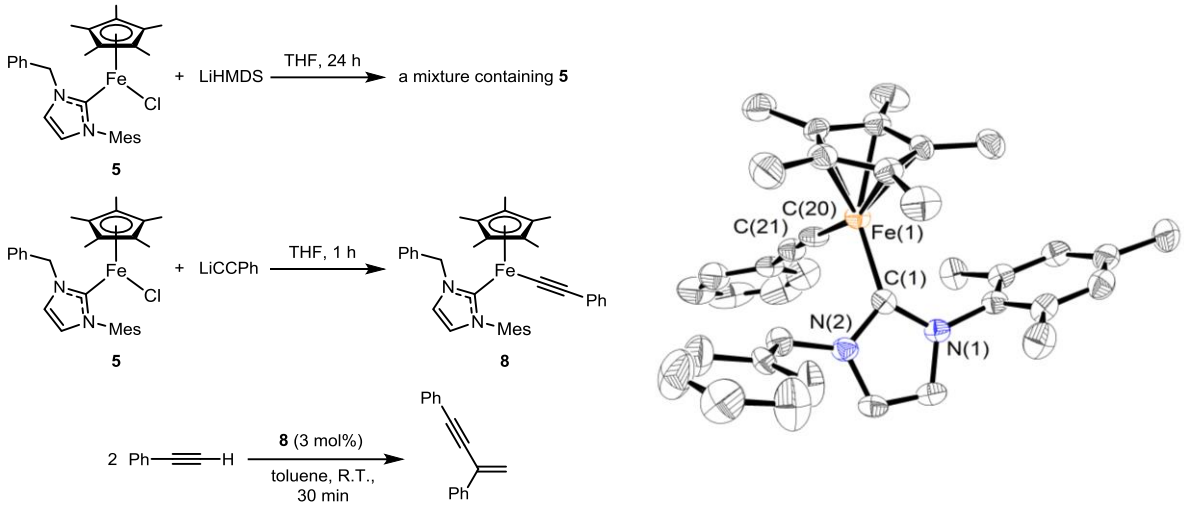


Figure 2. Synthesis of catalytic intermediate **8** (Left) and its X-ray structure (Right).

When **8** was used at a 3 mol% loading without the addition of LiHMDS, the catalytic performance toward the dimerization of phenylacetylene is comparable to that of the combination of **5** and LiHMDS under identical conditions (Figure 2). Complex **8** was used to study the mechanism further. The consumption of phenylacetylene follows a first-order decay curve (Figure S96), suggesting that the transition state of either the isomerization of an η^2-alkyne complex to an η^2-C–H σ-complex or alkyne C–H cleavage is turnover-determining. We observed a slightly slower rate for the dimerization of PhC≡C−D compared to that of PhC≡C−H using 3 mol% of **8** as the catalyst, with a secondary kinetic isotope effect (KIE) of k_H/k_D = 1.29 (Figure 3). This result is comparable to the value we previously observed for catalyst **V**, suggesting that the turnover-determining transition state is not associated with the alkyne C–H bond cleavage step. In the literature, such a normal secondary KIE was attributed to the isomerization of an η^2-alkyne complex to an η^2-C–H σ-complex being the rate-determining step, where the C–H bond is weakened in the transition state.[87] Our experimental results also suggest that the turnover-determining transition state is associated with the isomerization of an η^2-alkyne complex to an η^2-C–H σ-complex.

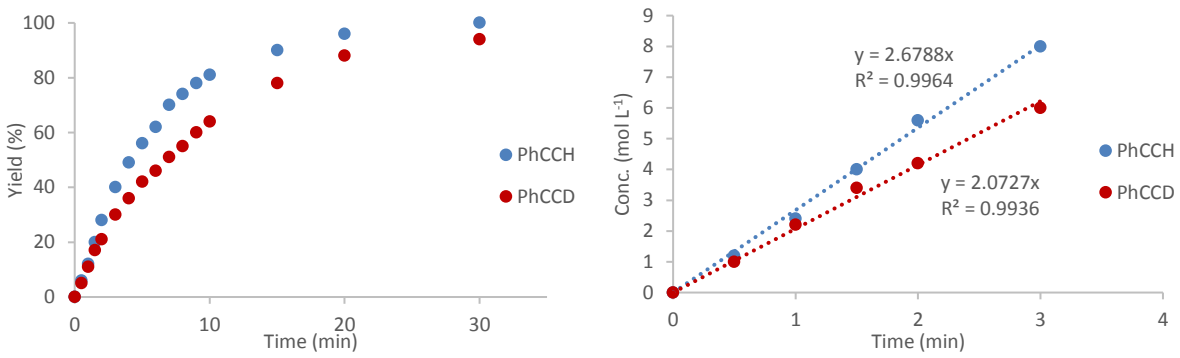
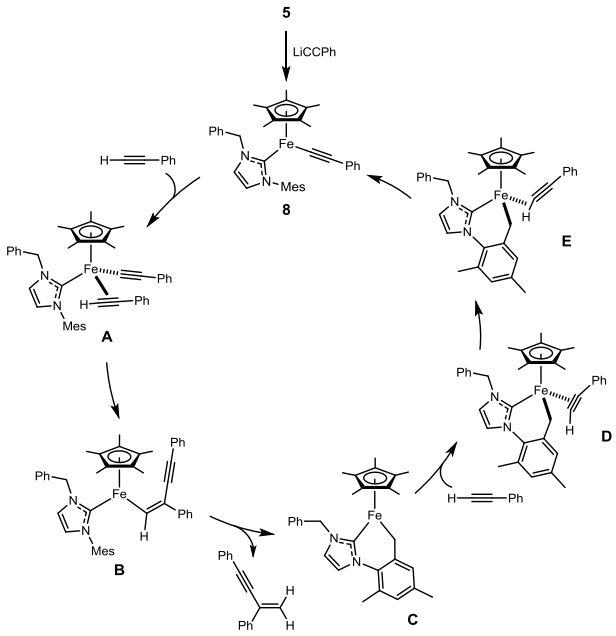


Figure 3. Left: Reaction profiles of the dimerization of phenylacetylene vs phenylacetylene-D catalyzed by 3 mol % of **8** (based on ^{1}H NMR integrations against mesitylene internal standard); Right: Linear regression of initial rates.

One possible mechanism is shown in Scheme 3. To enter the catalytic cycle, the pre-catalyst **5** reacts with *in situ* generated PhC≡C−Li to form **8**. The facile coordination of the alkyne substrate affords **A**, followed by a migratory insertion to give **B**. The subsequent σ-bond metathesis releases the enyne product and generates the cyclometallated intermediate **C**, which is converted into **D** via the facile coordination of the alkyne substrate in an η^2 fashion. The subsequent turnover-determining isomerization of **D** forms the σ-complex **E**, which undergoes another σ-bond metathesis to regenerate **8**.[88]



Scheme 3. Proposed catalytic cycle for phenylacetylene dimerization.

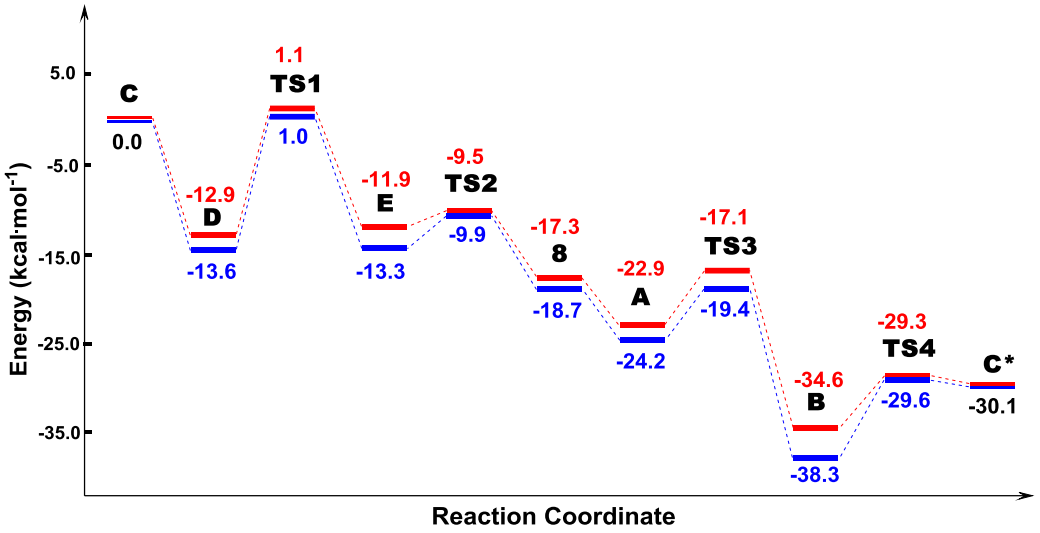
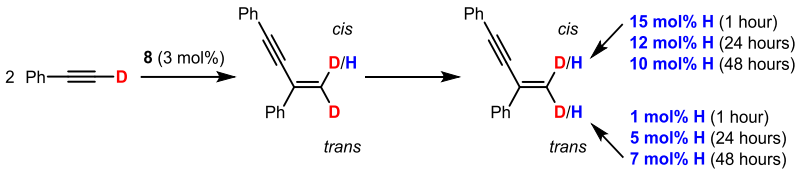


Figure 4. Computed singlet-state energetics: the proposed catalytic cycle in this work (in red) vs the catalytic cycle of catalyst **V** (in blue). NOTE: for the structure of each species in the catalytic cycle of catalyst **V**, replace the benzyl group on the NHC ligand of the corresponding species in Scheme 2 with a picolyl group.

Based on the mechanistic proposal above, the mechanism of the reaction has been computed using Gaussian 16, Revision A.03,[89] with PBEPBE[90] exchange-correlation functional. The TZVP[91] basis set was used for all elements. All structures were optimized with PCM solvent correction (solvent = toluene) and the D3 version of Grimme's dispersion correction with the original D3 damping function.[92] Frequency analysis was then performed to confirm that the structure is a ground state or a transition state as appropriate and to obtain the thermodynamic data. The 16e species (i.e., **8**, **B**, and **C**) in the catalytic cycle (Scheme 3) have triplet ground states with low lying singlet excited states, whereas the 18e species (i.e., **A**, **D**, and **E**) have single ground states. Although **8**, **B**, and **C** have triplet ground state, the facile alkyne binding would instantaneously convert **C** and **8** to the singlet **D** and **A**, respectively. Therefore, the reaction mechanism along the singlet surface was computed using the spin-restricted method and the energetics are plotted in a sequence starting with the cyclometallated intermediate **C**, where no

alkyne substrate is associated with the metal center for convenience (Figure 4). The free energy span of the catalytic cycle is 14.0 kcal·mol^{-1}, which is associated with the turnover-limiting isomerization of the η^2-alkyne complex **D** into the σ-complex **E**. The catalytic cycle of catalyst **V** was computed using the same method for comparison. As shown in Figure 4, the energetics of the two catalytic cycles are quite similar. However, for catalyst **V** the coordination of the dangling pyridine *N*-donor of the 16e intermediates produces the corresponding off-cycle 18e species, which are thermodynamically much more stable than the corresponding in-cycle species. For example, in the catalytic cycle of **V**, the off-cycle species related to intermediates **C** and **8** are 21.6 and 13.9 kcal·mol^{-1} more stable than **C** and **8**, respectively, in terms of free energy. Effectively, the off-cycle species are the dominant Fe-containing species in the reaction mixture and there is only a trace amount of the active species performing the catalysis. Consequently, catalyst **V** requires elevated temperatures to achieve moderate activity (i.e., TOF of 88 h^{-1} at 80 °C), whereas our new catalytic system is much more active (i.e., TOF of 800 h^{-1} at 25 °C).



Scheme 4. The *cis* and *trans*-H/D conversion used herein and the fate of exchangeable H.

For the dimerization of PhC≡C−D catalyzed by **8**, each molecule of **8** has six exchangeable protons (*i.e.*, two *ortho* CH_3 groups of mesityl). With a 3 mol% catalyst loading, there is 18 mol% of exchangeable proton from the catalyst. In addition, the PhC≡C−D substrate has a 99% deuteration level, providing an additional 1 mol% of exchangeable proton. Therefore, the total amount of exchangeable proton is 19 mol%. At the initial stage of the catalysis, when the catalyst is almost fully protio, only the signal of the *cis*-proton (with respect to the alkynyl group, Scheme

3) of the enyne product grows in intensity (Figure S97), indicating that the product release through cyclometallation is operational. The signal of the *trans*-proton (with respect to the alkynyl group, Scheme 4) of the enyne product starts to grow in intensity at 20 min (i.e. at ~90% yield of the enyne products), accompanied by the slow intensity decrease of the *cis*-proton. Such a phenomenon suggests the scrambling of the *cis*-H and *trans*-D of the enyne product, similar to that observed for the reaction catalyzed by **V**. Distinct from the reaction catalyzed by **V**, where the *cis*-H and *trans*-H signals become 1:1 ratio in intensity within 4 h under the conditions for catalysis, the reaction catalyzed by **8** showed much slower scrambling under the conditions for catalysis, i.e., after 48 h the *cis*-H signal is still slightly more intense (Figure S97). The scrambling of the *cis*-H and *trans*-D rate depends on the concentration of phenylacetylene but not the concentration of **8** (Table S3). It appears that the catalyst is not responsible for the scrambling between the *cis*-H and *trans*-D of the enyne product. Our attempt to isolate the D-labelled enyne product for further study by passing the reaction mixture through a short silica gel column (i.e., removing the catalyst) at 1 h gave an enyne sample with the *cis*- and *trans*-H signals of nearly equal intensity (Figure S98). The sum of the *cis*- and *trans*-H is ~16 mol% (Figure S98), ruling out the exchange between the enyne *trans*-D and the acidic protons from silica or moisture.

CONCLUSION

A series of NHCs ligand varying steric properties have been used to prepare piano-stool iron complexes [FeClCp*(NHC)], **1**–**7**, among which **5** with mesityl and benzyl group on the NHC ligand showed the highest catalytic activity toward terminal alkyne dimerization. Compared to our previous catalyst **V**, possessing a picolyl-NHC ligand, the new catalyst displays a much higher activity due to the lack of the stable off-cycle species. We tentatively attribute the normal secondary KIE to the turnover-limiting isomerization of an η^2-alkyne complex into a σ-complex,

which is further supported by our computational results. The scrambling between the *cis*-H and *trans*-D of the enyne product is not fully understood and will be studied further.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI:

Experimental procedures, selected crystallographic data tables, NMR and IR spectra (PDF), and details of computational studies.

Accession Codes

CCDC 1865872-1865880 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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REFERENCES

(1) *Modern Alkyne Chemistry* (Ed.: Trost, B. M.; Li, C.-J.), Wiley, Weinheim, **2015**.

(2) Zhang, W.; Zheng, S.; Liu, N.; Werness, J. B.; Guzei, I. A.; Tang, W. Enantioselective Bromolactonization of Conjugated (*Z*)-Enynes. *J. Am. Chem. Soc.* **2010**, *132*, 3664.

(3) Kong, J.-R.; Ngai, M.-Y.; Krische, M. J. Highly Enantioselective Direct Reductive Coupling of Conjugated Alkynes and α-Ketoesters via Rhodium-Catalyzed Asymmetric Hydrogenation. *J. Am. Chem. Soc.* **2006**, *128*, 718.

(4) Wessig, P.; Müller, G. The Dehydro-Diels−Alder Reaction. *Chem. Rev*. **2008**, *108*, 2051.

(5) Barday, M.; Ho, K. Y. T.; Halsall, C. T.; Aïssa, C. Regioselective Synthesis of 3-Hydroxy-4,5-alkyl-Substituted Pyridines Using 1,3-Enynes as Alkynes Surrogates. *Org. Lett*. **2016**, *18*, 1756.

(6) Kumar, R.; Tamai, E.; Ohnishi, A. Nishimura, A.; Hoshimoto, Y.; Ohashi, M.; Ogoshi, S. Nickel-Catalyzed Enantioselective Synthesis of Cyclobutenes via [2+2] Cycloaddition of α,β-Unsaturated Carbonyls with 1,3-Enynes. *Synthesis* **2016**, 2789.

(7) Zhou, X.; Huang, C.; Zeng, Y.; Xiong, J.; Xiao, Y.; Zhang, J. Silver-Catalysed Tandem Hydroamination and Cyclization of 2-Trifluoromethyl-1,3-enynes with Primary Amines: Modular Entry to 4-Trifluoromethyl-3-pyrrolines. *Chem. Commun*. **2017**, *53*, 1084.

(8) Campbell, K.; Kuehl, C. J.; Ferguson, M. J.; Stang, P. J.; Tykwinski, R. R. Coordination-Driven Self-Assembly: Solids with Bidirectional Porosity. *J. Am. Chem. Soc*. **2002**, *124*, 7266.

(9) Nicolaou, K. C.; Dai, M. W.; Tsay, S. C.; Estevez, V. A.; Wrasidlo, W. Designed Enediynes: A New Class of DNA-Cleaving Molecules with Potent and Selective Anticancer Activity. *Science* **1992**, *256*, 1172.

(10) Goldberg, I. H. Mechanism of Neocarzinostatin Action: Role of DNA Microstructure in Determination of Chemistry of Bistranded Oxidative Damage. *Acc. Chem. Res*. **1991**, *24*, 191.

(11) Kim, H.; Lee, H.; Lee, D.; Kim, S.; Kim, D. Asymmetric Total Syntheses of (+)-3-(*Z*)-Laureatin and (+)-3-(*Z*)-Isolaureatin by "Lone Pair−Lone Pair Interaction-Controlled" Isomerization. *J. Am. Chem. Soc*. **2007**, *129*, 2269.

(12) Negishi, E.; Anastasia, L. Palladium-Catalyzed Alkynylation. *Chem. Rev*. **2003**, *103*, 1979.

(13) Chinchilla, R.; Nájera, C. The Sonogashira Reaction: A Booming Methodology in Synthetic Organic Chemistry. *Chem. Rev*. **2007**, *107*, 874.

(14) Ranu, B. C.; Adak, L.; Chattopadhay, K. Hydroxyapatite-Supported Palladium-Catalyzed Efficient Synthesis of (*E*)-2-Alkene-4-ynecarboxylic Esters. Intense Fluorescence Emission of Selected Compounds. *J. Org. Chem*. **2008**, *73*, 5609.

(15) Deussen, H.-J.; Jeppesen, L.; Schärer, N.; Junager, F.; Bentzen, B.; Weber, B.; Weil, V.; Mozer, S. J.; Sauerberg, P. Process Development and Scale-Up of the PPAR Agonist NNC 61-4655. *Org. Process Res. Dev*. **2004**, *8*, 363.

(16) Yan, W.; Ye, X.; Akhmedov, N. G.; Petersen, J. L.; Shi, X. 1,2,3-Triazole: Unique Ligand in Promoting Iron-Catalyzed Propargyl Alcohol Dehydration. *Org. Lett*. **2012**, *14*, 2358.

(17) Zhou, Y.; Zhang, Y.; Wang, J. Recent Advances in Transition-Metal-Catalyzed Synthesis of Conjugated Enynes. *Org. Biomol. Chem*. **2016**, *14*, 6638.

(18) Trost, B. M.; Masters, J. T. Transition Metal-Catalyzed Couplings of Alkynes to 1,3-Enynes: Modern Methods and Synthetic Applications. *Chem. Soc. Rev*. **2016**, *45*, 2212.

(19) Trost, B. M. The Atom Economy--A Search for Synthetic Efficiency. *Science* **1991**, *254*, 1471.

(20) Trost, B. M. Atom Economy—A Challenge for Organic Synthesis: Homogeneous Catalysis Leads the Way. *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 259.

(21) Yi, C. S.; Liu, N. Homogeneous Catalytic Dimerization of Terminal Alkynes by $C_5Me_5Ru(L)H_3$ (L = PPh_3, PCy_3, PMe_3). *Organometallics* **1996**, *15*, 3968.

(22) Yi, C. S.; Liu, N. The Ruthenium Acetylide Catalyzed Cross-Coupling Reaction of Terminal and Internal Alkynes: Isolation of a Catalytically Active β-Agostic Intermediate Species. *Organometallics* **1998**, *17*, 3158.

(23) Ogata, K.; Toyota, A. Iridium(I) Complex of Chelating Pyridine-2-thiolate Ligand: Synthesis, Reactivity, and Application to the Catalytic *E*-Selective Terminal Alkyne Dimerization via C–H Activation. *J. Organomet. Chem.* **2007**, *692*, 4139.

(24) Conifer, C.; Gunanathan, C.; Rinesch, T.; Hçlscher, M.; Leitner, W. Solvent-Free Hydrosilylation of Terminal Alkynes by Reaction with a Nonclassical Ruthenium Hydride Pincer Complex. *Eur. J. Inorg. Chem*. **2015**, 333.

(25) Powała, B.; Pietraszuk, C. Regio- and Stereoselective Homodimerization of Monosubstituted Acetylenes in the Presence of the Second Generation Grubbs Catalyst. *Catal. Lett*. **2014**, *144*, 413.

(26) Kawata, A.; Kuninobu, V.; Takai, K. Rhenium-Catalyzed Regio- and Stereoselective Dimerization and Cyclotrimerization of Terminal Alkynes. *Chem. Lett.* **2009**, *38*, 836.

(27) Bassetti, M.; Pasquini, C.; Raneri, A.; Rosato, D. Selective Dimerization of Arylalkynes to (*E*)-1,4-Diaryl Enynes Catalyzed by the [Ru(*p*-cymene)Cl_2]$_2$/Acetic Acid System under Phosphine-Free Conditions. *J. Org. Chem.* **2007**, *72*, 4558.

(28) Hijazi, A.; Parkhomenko, K.; Djukic, J.-P.; Chemmi, A.; Pfeffer, M. Head-to-Head Homo-Coupling of Arylethynes Catalysed by (Dicarbonyl)ruthenium Chloride Metallacycles: Selective Synthesis of *(E)*-1,4-Diarylbut-1-en-3-ynes. *Adv. Synth. Catal*. **2008**, *350*, 1493.

(29) Xu, D.; Sun, Q.; Quan, Z.; Wang, X.; Sun, W. Cobalt-Catalyzed Dimerization and Homocoupling of Terminal Alkynes. *Asian J. Org. Chem*. **2018**, *7*, 155.

(30) Ostrowska, S.; Szymaszek, N.; Pietraszuk, C. Selective Dimerization of Terminal Acetylenes in the Presence of PEPPSI Precatalysts and Relative Chloro- and Hydroxo-Bridged *N*-Heterocyclic Carbene Palladium Dimers. *J. Organomet. Chem.* **2018**, *856*, 63.

(31) Ogata, K.; Oka, O.; Toyota, A.; Suzuki, N.; Fukuzawa, S.-i. Phosphine-Dependent Selective Cross-Dimerization between Terminal Alkylacetylene and Silylacetylene by Iridium(I) Guanidinate Complex-Phosphine System. *Synlett* **2008**, 2663.

(32) Katagiri, T.; Tsurugi, H.; Satoh, T.; Miura, M. Rhodium-Catalyzed (*E*)-Selective Cross-Dimerization of Terminal Alkynes. *Chem. Commun*. **2008**, 3405.

(33) Azpíroz, R.; Rubio-Pérez, L.; Castarlenas, R.; Pérez-Torrente, J. J.; Oro, L. A. *gem*-Selective Cross-Dimerization and Cross-Trimerization of Alkynes with Silylacetylenes Promoted by a Rhodium–Pyridine–*N*-Heterocyclic Carbene Catalyst. *ChemCatChem* **2014**, *6*, 2587.

(34) Ogoshi, S.; Ueta, M.; Oka, M.; Kurosawa, H. Dimerization of Terminal Alkynes Catalyzed by a Nickel Complex Having a Bulky Phosphine Ligand. *Chem. Commun*. **2004**, 2732.

(35) Katayama, H.; Yari, H.; Tanaka, M.; Ozawa, F. (*Z*)-Selective Cross-Dimerization of Arylacetylenes with Silylacetylenes Catalyzed by Vinylideneruthenium Complexes. *Chem. Commun.* **2005**, 4336.

(36) Żak, P.; Bołt, M.; Lorkowski, J.; Kubicki, M.; Pietraszuk, C. Platinum Complexes Bearing Bulky N-Heterocyclic Carbene Ligands as Efficient Catalysts for the Fully Selective Dimerization of Terminal Alkynes. *ChemCatChem* **2017**, *9*, 3627.

(37) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. Novel *Z*-Selective Head-to-Head Dimerization of Terminal Alkynes Catalyzed by Lanthanide Half-Metallocene Complexes. *J. Am. Chem. Soc*. **2003**, *125*, 1184.

(38) Komeyama, K.; Kawabata, T.; Takehira, K.; Takaki, K. Rare-Earth Silylamide-Catalyzed Selective Dimerization of Terminal Alkynes and Subsequent Hydrophosphination in One Pot. *J. Org. Chem*. **2005**, *70*, 7260.

(39) Ge, S.; Norambuena, V. F. Q.; Hessen, B. Highly Efficient Regio- and Stereoselective Dimerization of (Hetero)aromatic Terminal Alkynes by Organo Rare-Earth Metal Catalysts. *Organometallics* **2007**, *26*, 6508.

(40) Platel, R. H.; Schafer, L. L. Zirconium Catalyzed Alkyne Dimerization for Selective *Z*-Enyne Synthesis. *Chem. Commun*. **2012**, *48*, 10609.

(41) Midya, G. C.; Paladhi, S.; Dhara, K.; Dash, J. Iron Catalyzed Highly Regioselective Dimerization of Terminal Aryl Alkynes. *Chem. Commun*. **2011**, *47*, 6698.

(42) Midya, G. C.; Parasar, B.; Dhara, K.; Dash, J. Ligand Mediated Iron Catalyzed Dimerization of Terminal Aryl Alkynes: Scope and Limitations. *Org. Biomol. Chem.* **2014**, *12*, 1812.

(43) Rivada-Wheelaghan, O.; Chakraborty, S.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. Z-Selective (Cross-)Dimerization of Terminal Alkynes Catalyzed by an Iron Complex. *Angew. Chem. Int. Ed*. **2016**, *55*, 6942. This report includes *gem*-selective dimerization of trimethylsilylacetylene.

(44) Gorgas, N.; Alves, L. G.; Stöger, B.; Martins, A. M.; Veiros, L. F.; Kirchner, K. Stable, Yet Highly Reactive Nonclassical Iron(II) Polyhydride Pincer Complexes: *Z*-Selective Dimerization and Hydroboration of Terminal Alkynes. *J. Am. Chem. Soc*. **2017**, *139*, 8130.

(45) Gorgas, N.; Stöger, B.; Veiros, L. F.; Kirchner, K. Iron(II) Bis(acetylide) Complexes as Key Intermediates in the Catalytic Hydrofunctionalization of Terminal Alkynes. *ACS Catal.* **2018**, *8*, 7973.

(46) Bhunia, M.; Sahoo, S. R.; Vijaykumar, G.; Adhikari, D.; Mandal, S. K. Cyclic (Alkyl)amino Carbene Based Iron Catalyst for Regioselective Dimerization of Terminal Arylalkynes. *Organometallics* **2016**, *35*, 3775.

(47) Xue, F.; Song, X.; Lin, T. T.; Munkerup, K.; Albawardi, S. F.; Huang, K.-W.; Hor, T. S. A.; Zhao, J. Dimerization of Terminal Aryl Alkynes Catalyzed by Iron(II) Amine-Pyrazolyl Tripodal Complexes with *E*/*Z* Selectivity Controlled by *tert*-Butoxide. *ACS Omega* **2018**, *3*, 5071.

(48) Liang, Q.; Osten, K. M.; Song, D. Iron-Catalyzed gem-Specific Dimerization of Terminal Alkynes. *Angew. Chem. Int. Ed*. **2017**, *56*, 6317.

(49) Islas, R. E.; Cárdenas, J.; Gaviño, R.; García-Ríos, E.; Lomas-Romerob, L.; Morales-Serna, J. A. Phosphinito Palladium(II) Complexes as Catalysts for the Synthesis of 1,3-Enynes, Aromatic Alkynes and Ynones. *RSC Adv.* **2017**, 7, 9780.

(50) Sabourin, E. T. The Selective Head-to-Tail Dimerization of α-Hydroxy Terminal Acetylenes. *J. Mol. Catal*. **1984**, *26*, 363.

(51) Gevorgyan, V.; Radhakrishnan, U.; Takeda, A.; Rubina, M.; Rubin, M.; Yamamoto, Y. Palladium-Catalyzed Highly Chemo- and Regioselective Formal [2 + 2 + 2] Sequential

Cycloaddition of Alkynes: A Renaissance of the Well Known Trimerization Reaction? *J. Org. Chem.* **2001**, *66*, 2835.

(52) Dzhemilev, U. M.; Khusnutdinov, R. I.; Shchadneva, N. A.; Nefedov, O. M.; Tolstikov, G. A. Some New Transformations of Cyclopropylacetylene Catalyzed by Rhodium, Palladium, and Cobalt Complexes. *Russ. Chem. Bull*. **1989**, *38*, 2171.

(53) Chen, T.; Guo, C.; Goto, M.; Han, L.-B. A Brønsted Acid-Catalyzed Generation of Palladium Complexes: Efficient Head-to-Tail Dimerization of Alkynes. *Chem. Commun*. **2013**, *49*, 7498.

(54) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Rühter, G. Palladium-Catalyzed Additions of Terminal Alkynes to Acceptor Alkynes. *J. Am. Chem. Soc.* **1997**, *119*, 698.

(55) Trost, B. M.; Chan, C.; Rühter, G. Metal-Mediated Approach to Enynes. *J. Am. Chem. Soc*. **1987**, *109*, 3486.

(56) Mochizuki, K.; Sakai, K.; Kochi, T.; Kakiuchi, F. Rhodium-Catalyzed Dimerization of Arylacetylenes and Addition of Malonates to 1,3-Enynes. *Synthesis* **2013**, *45*, 2088.

(57) Trost, B. M.; Masters, J. T.; Le Vaillant, F.; Lumb, J.-P. Synthesis of a 1,3-Bridged Macrobicyclic Enyne via Chemoselective Cycloisomerization Using Palladium-Catalyzed Alkyne–Alkyne Coupling. *J. Org. Chem*. **2016**, *81*, 10023.

(58) Lauer, M. G.; Headford, B. R.; Gobble, O. M.; Weyhaupt, M. B.; Gerlach, D. L.; Zeller, M.; Shaughnessy, K. H. A Trialkylphosphine-Derived Palladacycle as a Catalyst in the Selective Cross-Dimerization of Terminal Arylacetylenes with Terminal Propargyl Alcohols and Amides. *ACS Catal*. **2016**, *6*, 5834.

(59) Trost, B. M.; McIntosh, M. C. An Unusual Selectivity in Pd Catalyzed Cross-Coupling of Terminal Alkynes with "Unactivated" Alkynes. *Tetrahedron Lett*. **1997**, *38*, 3207.

(60) Xu, H.-D.; Zhang, R.-W.; Li, X.; Huang, S.; Tang, W.; Hu, W.-H. Rhodium-Catalyzed Chemo- and Regioselective Cross-Dimerization of Two Terminal Alkynes. *Org. Lett*. **2013**, *15*, 840.

(61) Oshovsky, G. V.; Hessen, B.; Reek, J. N. H.; de Bruin, B. Electronic Selectivity Tuning in Titanium(III)-Catalyzed Acetylene Cross-Dimerization Reactions. *Organometallics* **2011**, *30*, 6067.

(62) den Haan, K. H.; Wielstra, Y.; Teuben, J. H. Reactions of Yttrium-Carbon Bonds with Active Hydrogen-Containing Molecules. A Useful Synthetic Method for Permethylyttrocene Derivatives. *Organometallics* **1987**, *6*, 2053.

(63) Heeres, H. J.; Teuben, J. H. Catalytic Oligomerization of Terminal Alkynes by Lanthanide Carbyls $(\eta^5\text{-}C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = Y, La, Ce). *Organometallics* **1991**, *10*, 1980.

(64) Horton, A. D. Unprecedented Isolation of Alk-1-en-3-yn-1-yl Intermediates in the Catalytic Oligomerisation of Alk-1-ynes by Cationic Lewis Base-Free Zirconocene Complexes. *J. Chem. Soc. Chem. Commun.* **1992**, 185.

(65) Horáček, M.; Štěpnička, P.; Kubišta, J.; Gyepes, R.; Mach, K. Reactions of Substituted Zirconocene−Bis(trimethylsilyl)ethyne Complexes with Terminal Alkynes. *Organometallic* **2004**, *23*, 3388.

(66) Yoshida, M.; Jordan, R. F. Catalytic Dimerization of Terminal Alkynes by a Hafnium Carboranyl Complex. A "Self-Correcting" Catalyst. *Organometallics* **1997**, *16*, 4508.

(67) Sun, S.; Kroll, J.; Luo, Y.; Zhang, L. Gold-Catalyzed Regioselective Dimerization of Aliphatic Terminal Alkynes. *Synlett* **2012**, 54.

(68) Korolev, A. V.; Guzei, I. A.; Jordan, R. F. Reactivity of Cationic Organoaluminum Aminotroponiminate Compounds with Unsaturated Substrates. Formation of Dinuclear Dicationic Aluminum Complexes. *J. Am. Chem. Soc.* **1999**, *121*, 11605.

(69) Dash, A. K.; Eisen, M. S. Chemo- and Regioselective Dimerization of Terminal Alkynes Promoted by Methylaluminoxane. *Org. Lett*. **2000**, *2*, 737.

(70) Yamaguchi, M.; Hayashi, A.; Hirama, M. Alkynyldichlorogalliums are Unstable in Hydrocarbon Solvents Dimerization of Alkynyldichlorogalliums *via* Carbogallation. *Chem. Lett.* **1995**, *24*, 1093.

(71) Akita, M.; Yasuda, H.; Nakamura, A. Regioselective Homo- and Codimerization of 1-Alkynes Leading to 2,4-Disubstituted 1-Buten-3-ynes by Catalysis of a $(\eta^5\text{-}C_5Me_5)_2TiCl_2$/RMgX System. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480.

(72) Riener, K.; Haslinger, S.; Raba, A.; Högerl, M. P.; Cokoja, M.; Herrmann, W. A.; Kühn, F. E. Chemistry of Iron *N*-Heterocyclic Carbene Complexes: Syntheses, Structures, Reactivities, and Catalytic Applications. *Chem. Rev.* **2014**, *114*, 5215.

(73) Ingleson, M. J.; Layfield, R. A. *N*-Heterocyclic Carbene Chemistry of Iron: Fundamentals and Applications. *Chem. Commun*. **2012**, *48*, 3579.

(74) Bézier, D.; Sortais, J.-B.; Darcel, C. N-Heterocyclic Carbene Ligands and Iron: An Effective Association for Catalysis. *Adv. Synth. Catal*. **2013**, *355*, 19.

(75) Liu, Y.; Wang, L.; Deng, L. Selective Double Carbomagnesiation of Internal Alkynes Catalyzed by Iron-N-Heterocyclic Carbene Complexes: A Convenient Method to Highly Substituted 1,3-Dienyl Magnesium Reagents. *J. Am. Chem. Soc.*, **2016**, *138*, 112.

(76) Liang, Q.; Janes, T.; Gjergji, X.; Song, D. Iron Complexes of a Bidentate Picolyl-NHC Ligand: Synthesis, Structure and Reactivity. *Dalton Trans.* **2016**, *45*, 13872.

(77) Fleischauer, V. E.; Muñoz III, S. B.; Neate, P. G. N.; Brennessel, W. W.; Neidig, M. L. NHC and Nucleophile Chelation Effects on Reactive Iron(II) Species in Alkyl–Alkyl Cross-Coupling. *Chem. Sci.* **2018**, *9*, 1878.

(78) Liang, Q.; Liu, N. J.; Song, D. Constructing Reactive Fe and Co Complexes from Isolated Picolyl-Functionalized *N*-Heterocyclic Carbenes. *Dalton Trans.* **2018**, *47*, 9889.

(79) Johnson, C.; Albrecht, M. Piano-Stool *N*-Heterocyclic Carbene Iron Complexes: Synthesis, Reactivity and Catalytic Applications. *Coord. Chem. Rev*. **2017**, *352*, 1.

(80) Chakraborty, U.; Demeshko, S.; Meyer, F.; Rebreyend, C.; de Bruin, B.; Atanasov, M.; Neese, F.; Mühldorf, B.; Wolf, R. Electronic Structure and Magnetic Anisotropy of an Unsaturated Cyclopentadienyl Iron(I) Complex with 15 Valence Electrons. *Angew. Chem. Int. Ed*. **2017**, *56*, 7995.

(81) Reiners, M.; Baabe, D.; Zaretzke, M.-K.; Freytag, M.; Walter, M. D. Reversible Dinitrogen Binding to [Cp′ Fe(NHC)] Associated with an N_2-Induced Spin State Change. *Chem. Commun.* **2017**, *53*, 7274.

(82) Ohki, Y.; Hatanaka, T.; Tatsumi, K. C−H Bond Activation of Heteroarenes Mediated by a Half-Sandwich Iron Complex of *N*-Heterocyclic Carbene. *J. Am. Chem. Soc*. **2008**, *130*, 17174.

(83) Hatanaka, T.; Ohki, Y.; Tatsumi, K. C–H Bond Activation/Borylation of Furans and Thiophenes Catalyzed by a Half-Sandwich Iron N-Heterocyclic Carbene Complex. *Chem. - Asian J.* **2010**, *5*, 1657.

(84) Hatanaka, T.; Ohki, Y.; Tatsumi K. Coupling of an *N*-Heterocyclic Carbene on Iron with Alkynes to Form η^5-Cyclopentadienyl-Diimine Ligands. *Angew. Chem. Int. Ed*. **2014**, *53*, 2727.

(85) Liang, Q.; Song, D. Reactivity of Fe and Ru Complexes of Picolyl-Substituted *N*-Heterocyclic Carbene Ligand: Diverse Coordination Modes and Small Molecule Binding. *Inorg. Chem*. **2017**, *56*, 11956.

(86) Liang, Q.; Salmon, A.; Kim, P. J.; Yan, L.; Song, D. Unusual Rearrangement of an *N*-Donor-Functionalized *N*-Heterocyclic Carbene Ligand on Group 8 Metals. *J. Am. Chem. Soc.* **2018**, *140*, 1263.

(87) Li, X.; Vogel, T.; Incarvito, C. D.; Crabtree, R. H. Electronic and Steric Effects in the Insertion of Alkynes into an Iridium(III) Hydride. *Organometallics* **2005**, *24*, 62.

(88) Perutz, R. N.; Sabo-Etienne, S. The Sigma-CAM Mechanism: Sigma Complexes as the Basis of Sigma-Bond Metathesis at Late-Transition-Metal Centers. *Angew. Chem. Int. Ed*. **2007**, *46*, 2578.

(89) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich,

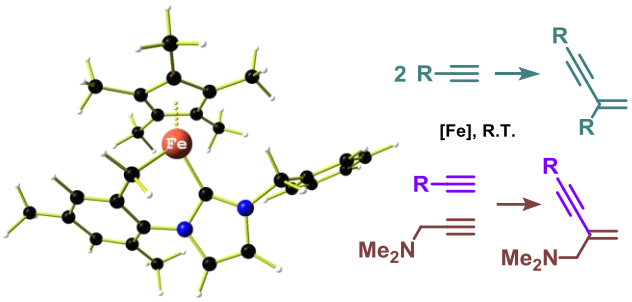
A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.;Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.;Foresman, J. B.; Fox, D. J. *Gaussian 16*, *Revision A.03*, Gaussian, Inc., Wallingford CT, 2016.

(90) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(91) Schafer, A.; Huber, C.; Ahlrichs, R. Fully Optimized Contracted Gaussian Basis Sets of Triple Zeta Valence Quality for Atoms Li to Kr. *J. Chem. Phys.* **1994**, *100*, 5829.

(92) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate *Ab Initio* Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H–Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

Graphic TOC



We report an iron-catalyzed geminal-specific dimerization of terminal alkynes at ambient temperature.