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Selective Double-Carbomagnesiation of Internal Alkynes Catalyzed by Iron-N-Heterocyclic Carbene Complexes: A Convenient Method to Highly Substituted 1,3-Dienyl Magnesium Reagents

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Supporting Information Placeholder

ABSTRACT: Controlled multi-carbometalation of alkynes has been envisaged as an efficient synthetic method for dienyl and polyenyl metal reagents, but effective catalyst enabling the transformation has remained elusive. Herein, we report that an iron(II)-N-heterocyclic carbene (NHC) complex (IEt₂Me₂)₂FeCl₂ ($IEt_2Me_2 = 1,3$ -diethyl-4,5-dimethylimidazol-2-ylidene) can serve as precatalyst for the double-carbometalation of internal unsymmetrical alkynes with alkyl Grignard reagents, producing highly substituted 1,3-dienyl magnesium reagents with high regioand stereo-selectivity. Mechanistic studies suggest the involvement of low-coordinate organoiron(II)-NHC species as the in-cycle intermediates. The strong σ -donating nature of IEt₂Me₂ and its appropriate steric property are thought the key factors endowing the iron-NHC catalyst fine performance.

Transition-metal-catalyzed carbometalation is a useful method for generating organometallic compounds that are valuable nucleophiles in organic synthesis.¹ Currently, the most successfully developed carbometalation reaction is the monocarbometalation of alkyne, being used for the stereo- and regioselective synthesis of vinyl lithium, magnesium, aluminum, and zinc reagents (a in Figure 1). Ideally, the vinyl metal reagent formed from a mono-carbometalation reaction might undergo further carbometalation reactions with alkynes to produce di-, tri-, and even polyenyl metal reagents. While a controlled di- or multicarbometalation method to selectively produce dienyl- or polyenyl metal reagents has not been reported yet, its feasibility can be inferred from the formations of 1,3-diene byproducts in transitionmetal-catalyzed carbometalation and hydrosilylation of alkynes.², Moreover, the uncontrolled polymerization of terminal alkynes catalyzed by Ti(OBuⁿ)₄/AlEt₃ (1:4) and Fe(acac)₃/AlEt₃ (1:3) is thought to be a carbometalation reaction of alkynes (b in Figure 1).⁴ Thus, controlling the degree of alkyne insertion is a key issue. In this regard, we report herein the achievement of selective double-carbometalation reaction of unsymmetrical internal alkynes with alkyl Grignard reagents using an iron(II)-Nheterocyclic carbene complex as catalyst (c in Figure 1). The ironcatalyzed reaction furnishes 1,3-dienyl magnesium reagents with high regio- and stereoselectivity, which are useful synthons for the preparation of highly substituted 1,3-diene derivatives.

Noting the capability of Fe(acac)₃/AlEt₃ in promoting the polymerization of terminal alkynes ^{4a, b} and the fine performance of Fe(acac)₃/IPr (IPr = 1,3-di(2',6'-diisopropylphenyl)imidazol-2-



Figure 1. Transformations of Alkynes under Carbometalation Conditions

Table 1. Carbometalation of Phenyl(methyl)acetylene Followed by Hydrolysis^{*a*, *b*}

——————————————————————————————————————		5 mol% <mark>Fe</mark> cat H	I₂O	Ph	+
		THF rt, 15 min	F	^p h 1a	Ph 2
	Entry	Catalyst	Conv. (%)	GC Yield (%)	
1				1 a	2
	1	(IEt ₂ Me ₂) ₂ FeCl ₂	99	88	2
	2	(IMe ₂ Me ₂) ₂ FeCl ₂	87	57	4
í	3	(IPr ₂ Me ₂) ₂ FeCl ₂	99	81	12
4	4 ^c	(IMes) ₂ FeCl ₂	91	20	4
:	5 ^c	$FeCl_2 + 2 IPr$	80	7	2
(6 ^c	$FeCl_2 + 2 PPh_3$	44	4	2
,	7 ^c	FeCl ₂	40	1	3
8	8 ^c	Fe(acac) ₃	46	2	3
9	9	none	0	0	0

^a The reactions were carried out in THF (1.0 mL) at rt under a nitrogen atmosphere using 1.0 mmol of phenyl(methyl)acetylene and 0.70 mmol of MeMgBr with 5 mol% catalyst loading. ^b Conversions and GC yields were based on the alkyne with *n*-dodecane as the internal standard. ^c Polyalkynes were formed.

ylidene) in catalyzing the arylmagnesiation of unactivated internal alkynes,⁵ we targeted iron-NHC catalysts for controlled multicarbometalation of alkynes.⁶ After screening a series of iron-NHC complexes for the reaction of phenyl(methyl)acetylene with MeMgBr, the N-ethyl carbene complex (IEt₂Me₂)₂FeCl₂ proved an effective catalyst for the double-carbometalation reaction. The reaction of phenyl(methyl)acetylene with 0.70 equiv of MeMgBr and 5 mol% of the iron catalyst in THF at room temperature for 15 min, followed by hydrolysis, gives the diene, (E)-2,4-dimethyl-1,3-diphenyl-1,3-pentadiene (1a), and the mono-ene, 2-methyl-1phenylpropene (2a), in 88% and 2% GC yields, respectively (entry 1 in Table 1), and the isomers of 1a being trace. The identity of 1a was confirmed by NMR and mass spectroscopy characterization,⁷ as well as by single-crystal X-ray diffraction studies on its derivatives (vide infra). The E-configuration of 1a implies the syn-addition nature of the double-carbometalation reaction, at least for the second carbometalation step.



Chart 1. The NHC Ligands Used in the Study

The use of NHCs with appropriate steric bulkiness is essential to ensure the selective double-carbometalation reaction. Under similar reaction conditions, the reaction using (IMe₂Me₂)₂FeCl₂ that bears the less bulky NHC ligand IMe_2Me_2 (IMe_2Me_2 = 1,3,4,5-tetramethylimidazol-2-ylidene, Chart 1) gives 1a in lower yield (entry 2), wherein alkyne polymerization as indicated by thickening of the mixture during the reaction course was noticed. The use of the bulkier NHC-iron catalyst (IPr₂Me₂)₂FeCl₂ $(IPr_2Me_2 = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, Chart$ 1) leads to the decrease of the double-/mono-carbometalation selectivity (entry 3). The reactions employing the more steric demanding NHC ligands, IMes (IMes = 1,3-dimesitylimidazol-2ylidene) and IPr, mainly afford polyalkynes (entries 4 and 5).⁷ Similarly, the trials with FeCl₂/PPh₃, FeCl₂ and Fe(acac)₃ as catalysts have alkyne polymerization being dominating (entries 6-8). A control experiment without the addition of any iron catalyst indicates the inertness of phenyl(methyl)acetylene toward MeMgBr (entry 9).



Scheme 1. Transformations of the Resultant 1,3-Dienyl Magnesium Reagent

The evidence supporting the formation of the 1,3-dienyl magnesium reagent was gained from the quenching experiment with D_2O , which yielded the deuterated product **1a-D** in 82% yield with 98% deuterium incorporation at the olefinic carbon position (Scheme 1). The *in-situ* formed 1,3-dienyl magnesium

species can also be trapped by I_2 , paraformaldehyde, and allyl bromide to form the 1,3-dienyl iodide **3a**, the homoallylic alcohol **4**, and the cross-coupling product **6**, respectively, in good yields (Scheme 1), reflecting the synthetic utility of the double-carbometallation reaction. The esterization of **4** gives **5**. A single-crystal X-ray diffraction study confirmed its stereochemistry as an *E*-isomer (Figure S1), supporting the *syn*-addition nature of the carbometalation reaction.

Table 2. Synthesis of Highly Substituted 1,3-Diene Derivatives from Iron-Catalyzed Double-Carbometalation of Internal Alkynes^{*a.b*}



^{*a*} The reaction was carried out in THF (1.0 mL) at rt for 15 min under a nitrogen atmosphere using 1.0 mmol of an alkyne, 0.70 mmol of RMgBr, and 0.050 mmol of (IEt₂Me₂)₂FeCl₂, and then quenched with H₂O at room temperature (method A) or with 0.75 mmol of I₂ at -5 °C (method B). ^{*b*} Isolated yields based on the alkyne, and the yields in the brackets are the GC yields. ^{*c*} The carbometalation step was conducted in THF at 0 °C for 1 h. ^{*d*} The carbometalation step was conducted in THF at 50 °C for 8h.



Figure 2. Molecular structures of **15** showing 30% probability ellipsoids and a partial atom scheme. Selected distances (Å) and angles (deg): C1-I1 2.137(4), C1-C2 1.330(6), C2-C3 1.514(6), C3-C4 1.331(6), C1-C2-C3-C4 76.9(6).

Substrate scope study revealed that the $(IEt_2Me_2)_2FeCl_2$ catalyzed double-carbometalation reaction can be extended to a series of aryl(alkyl)acetylenes, enabling the stereoselective synthesis of versatile highly substituted 1,3-dienes.⁸ As shown in Table 2, the reactions of MeMgBr with aryl(methyl)acetylenes having electron-donating or -withdrawing groups on the *para*position of phenyl ring can all afford the 1,3-dienes (**1a-1e**) and 1

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1,3-dienyl iodides (3a, 3c, and 3e) in good isolated yields (65-85%), along with trace amount of the mono-carbometalation products and the isomers of the dienes. The high yields of the dienes with p-chloro- and p-bromo-phenyl substitutes (1d, 1e, and 3e) reflects the compatibility of the iron-catalyzed reaction to aryl halides, being contrast to the reported iron-catalyzed dehalogenation reactions of aryl halides with organometallic reagents.⁹ Due to the steric demanding nature of (otolyl)(methyl)acetylene, its reaction produces the doublecarbometalation product 7 in low yield. In addition to the phenyl substituted acetylenes, the heteroarene substituted acetylene (2thienyl)(methyl)acetylene, is also effective for the iron-catalyzed double-carbometalation reaction, affording the 1,3-dithienyl-1,3dienes, 8 and 9, in 54% and 41% isolated yields, respectively. Phenyl(alkyl)acetylenes with long and/or substituted alkyl chain are also suitable to the double-carbometalation reaction. The attainment of the dienes 10-22, among which the structure of 15 is established by X-ray crystallographic study (Figure 2), unambiguously confirms the syn-addition character of the carbometalation reaction. The low yield of the tert-butyl substituted diene 16, again, indicates that the iron-catalyzed reaction is sensitive to steric nature of alkynes. The obtainment of the chloroalkyl substituted dienes 21 and 22 suggests that the iron-catalyzed carbometalation reaction is competitive to crosscoupling reactions.¹⁰ Probably due to steric effects, the methylmagnesiation of diphenyl acetylene and the alkylmagnesiation reactions with Me₃SiCH₂MgBr and Bu^tCH₂MgBr give the dienes 23-25 in low yields. The ongoing revealed studv the (IEt₂Me₂)₂FeCl₂-catalyzed doublecarbometalation reactions of phenyl(methyl)acetylene with EtMgBr and PhMgBr merely afford trace amounts of the dienes, which might be related to the instability of IEt₂Me₂-supported iron ethyl and phenyl species.11



Scheme 2. The Reactions of (IEt₂Me₂)₂FeMe₂ with Phenyl(methyl)acetylene



Scheme 3. (IEt₂Me₂)₂FeCl₂ and FeCl₂/IEt₂Me₂ Catalyzed Double-Carbometalation Reactions

The achievement of the iron-catalyzed double-carbometalation reaction posed the questions on the identity of the in-cycle organoiron intermediates and the factors rendering the high double-carbometalation selectivity. For the former question, lowcoordinate iron(II)-NHC methyl and alkenyl species seem the reasonable intermediates. Our previous study showed that

(IEt₂Me₂)₂FeCl₂ can react with MeMgBr (2 equiv) to form the high-spin iron(II) methyl complex (IEt₂Me₂)₂FeMe₂.¹¹ The iron(II) methyl complex (0.20 mmol) then proved reactive toward phenyl(methyl)acetylene, producing the double-carbometalation product in 0.05 mmol (13% yield relative to the amount of methyl anion in (IEt₂Me₂)₂FeMe₂) in 12 h (Scheme 2). Notably, the addition of 1 equiv of MgBr₂ Et₂O to the mixture can significantly accelate the rate, and upon which the reaction in 15 min can furnish the double-carbometalation product in 70% yield (0.28 mmol, the yield is relative to the amount of methyl anion in (IEt₂Me₂)₂FeMe₂) and the mono-carbometalaion product in 24% vield (0.09 mmol) (Scheme 2). The enhanced rate and increased vield of the double-carbometallation product hint the higher reactivity of the three-coordinate iron(II) methyl species, which can be formed by NHC-abstraction from (IEt₂Me₂)₂FeMe₂ by MgBr₂, toward alkyne insertion. A quenching experiment using D₂O indicated the formations of the deuterated products **1a-D** and 2-D (Scheme 2). These observations suggest that the threecoordinate iron(II) methyl species (IEt_2Me_2)FeXMe (A, X = Me or vinyl) could be the genuine speices performing carbometalation reaction with alkyne, and that the three-coordinate iron(II) vinyl species (IEt₂Me₂)FeX(CPh=CMe₂) (**B**, X = Me or vinyl) and $(IEt_2Me_2)FeX(CPh=CMeCPh=CMe_2)$ (C, X = Me or vinyl) are the intermediate and product, respectively, in these stoicheometric reactions. The capability of open-shell organoiron(II) species to undergo alkyne insertion reaction is also supported by previously reported hydrometalation of alkynes by Holland's β -diketiminato iron(II) hydride¹² and the carbometalation of alkynes by our iron(II) phenyl species $(IPr_2Me_2)_2FePh_2$.¹³ In addition to these stoicheometric reactions, both (IEt₂Me₂)₂FeMe₂ and the 1:1 mixture of FeCl₂/IEt₂Me₂ proved efficient catalysts for the double-carbometalation reaction (Scheme 3).



Scheme 4. Proposed Catalytic Cycle for the Iron-Catalyzed Carbometalation Reaction

Accordingly, a catalytic cycle involving three-coordinate organoiron(II)-NHC species shown in Scheme 4 is proposed for the iron-catalyzed double-carbometalation reaction. Under the catalytic reaction condition, the interaction of the precatalyst (IEt₂Me₂)₂FeCl₂ with MeMgBr produces the three-coordinate iron(II) methyl species A, which then performs carbometalation with an alkyne molecule to give the iron(II) alkenyl species **B**. Intermediate **B** reacts with another alkyne molecular to give the iron(II) dienyl species C that undergoes transmetalation with MeMgBr to yield the dienyl magnesium reagent and regenerate A. During the course, the high stereo- and regio-selectivity of the carbometalation reaction should originate from the cis-addition nature of the migratory insertion and steric nature of the aryl(alkyl)acetylens. Bergman has used the latter factor to account the regioselective insertion reaction of nickel(II) methyl species (acac)Ni(PPh₃)Ph with phenyl(alkyl)acetylenes.¹⁴ In terms of the high double-carbometalation selectivity, the strong σ -donating nature of the NHC ligand in combination with its appropriate steric property of IEt_2Me_2 should be the key contributing factors.¹⁵ Benefited from these features, the ligand displacement of IEt_2Me_2 by carboanions or an alkyne molecule might be hard to occur on the organoiron intermediates **A-C**, thereby depressing the side reaction of uncontrolled multi-carbometalation to form oligomers or polymers.⁴ On the other hand, the appropriate steric property of IEt_2Me_2 could allow the iron alkenyl species **B** to react with a molecule of alkyne, leading to double-carbometalation, but render the further reaction of the iron dienyl species **C** with alkyne difficult due to steric repulsion between the NHC ligand and the highly substituted 1,3-dienyl group. The molecular structures of **5** and **15** clearly indicate the highly substituted dienes have non-planar 1,3-diene cores and are steric demanding.

In summary, we found that iron(II)-NHC complexes can serve as catalysts for the double-carbometalation reactions of unsymmetrical internal alkynes with alkyl Grignard reagents. The high regio- and stereoselectivity of the iron-catalyzed reaction enables the selective synthesis of highly substituted 1,3-dienyl magnesium reagents. The achievement of the doublecarbometalation reaction demonstrates the feasibility of controlling the degree of multi-carbometalation of alkynes upon judicious selection of catalysts. Inspired by this, we are now pursuing iron-catalyzed controlled triple-carbometalation reaction for the production of 1,3,5-trienyl metal reagents.

ASSOCIATED CONTENT

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

Experimental procedures, characterization data, NMR, and GC spectra (PDF)

Crystallographic data (CIF)

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Notes

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