

Iron carbenoid-mediated ylide reactions*

Xiu-Li Sun, Jun-Cheng Zheng, and Yong Tang‡

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032, China

Abstract: Electrophilic metal carbenoids, readily available from diazo compounds, prove to be good reagents for the preparation of ylides under neutral conditions. We have extended the strategy to synthesize allenes from diazoacetates with both stable and unstable ketenes in the presence of PPh_3 and $\text{Fe}(\text{TCP})\text{Cl}$ (0.5 mol %), which provided an easy access to optically active 4,4-disubstituted allenic esters by employing enantiopure phosphines. The mechanism involving the generation of ylide through catalytic transfer of an iron(II) carbene to phosphine was confirmed. A tandem Wittig–Nazarov cyclization reaction was further developed based on these results, culminating in a straightforward method for the construction of β -methylenecyclopentenones in a multistep one-pot manner without isolation of intermediates. By combining AsPh_3 and iron carbenoids, a catalytic Wittig reaction in toluene/water biphasic system was accomplished, affording α,β -unsaturated esters in high yields with *E/Z* above 50/1. Surprisingly, crotonate-derived phosphorus ylide reacted with electrophilic iron carbenoid, affording 1,1,4-trisubstituted 1,3-butadienes with high regio- and stereo-selectivities, where a new ylide generated via formal intermolecular carbenoid insertion into olefinic C–H bonds of the crotonate-derived phosphorus ylide was proposed.

Keywords: carbenoids; intramolecular cyclization; ring opening; tandem reactions; ylide reactions.

INTRODUCTION

Electrophilic metal carbenoids, readily available from diazo compounds, prove to be good reagents for the preparation of ylides under neutral conditions by reaction with nucleophilic heteroatom compounds such as phosphines, phosphites, and sulfide [1,2]. Since the pioneering work from Lu et al. on Wittig olefination reaction of aldehydes with diazoacetate catalyzed by a molybdenum complex [3], transition-metal complex-catalyzed olefination of aldehydes and ketones with diazo compounds under neutral conditions have been extensively studied recently [4]. Such a strategy has also been extended successfully to ylide epoxidation, aziridination, and cyclopropanation [2a,d]. In our study on ylide chemistry in organic synthesis [5], we documented that ketenes, which are unstable under basic condition, could react with ethyl diazoacetate (EDA) to give allenes in high yields in the presence of Ph_3P and catalytic tetra(*p*-chlorophenyl)porphyrin iron chloride [$\text{Fe}(\text{TCP})\text{Cl}$]. By employing chiral phosphine instead of PPh_3 , allenes could be synthesized with high enantioselectivity (93–98 % ee) in good yields [6]. Very recently, we found that crotonate-derived phosphorus ylide could react with elec-

*Paper based on a presentation at the 9th International Conference on Heteroatom Chemistry (ICHAC-9), 30 June–4 July 2009, Oviedo, Spain. Other presentations are published in this issue, pp. 505–677.

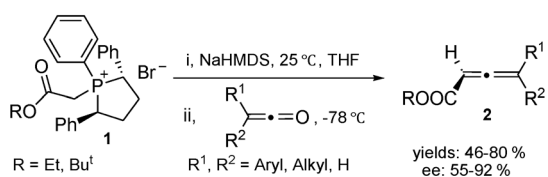
‡Corresponding author: E-mail: tangy@mail.sioc.ac.cn

trophilic iron carbenoid in a highly regio- and stereoselective manner, affording a new ylide via formal intermolecular carbenoid insertion into olefinic C–H bonds of the crotonate-derived phosphorus ylide [7]. On the basis of this finding, a one-pot olefination of aldehydes with methyl diazoacetate (MDA) has been developed, providing an easy access to 1,1,4-trisubstituted 1,3-butadienes with high stereoselectivity under mild conditions. In this paper, we wish to summarize our results on iron carbenoid-mediated ylide reactions.

IRON CARBENOID-MEDIATED YLIDE OLEFINATION OF KETENES

Enantioselective synthesis of allenic esters via ylide route [6]

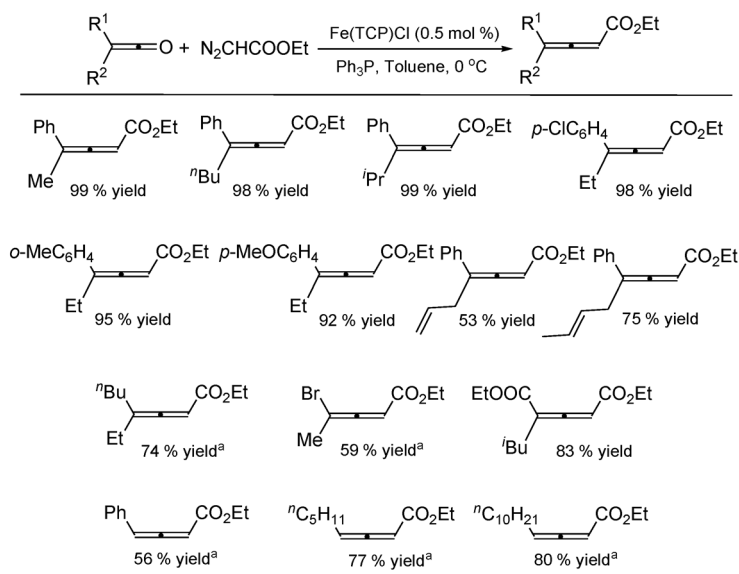
Allenes are versatile building blocks and the basic units of numerous natural products as well as biologically active compounds. Although the Wittig reaction or the Horner–Wadsworth–Emmons (HWE) reaction proves to be good for the preparation of allenes, only a few examples were involved in its asymmetric version. In our effort for the syntheses of optically active allenes, chiral phosphoniums **1** were designed, and it was found that, after deprotonation by NaHMDS, they could react with ketene to afford disubstituted allenic esters enantioselectively (Scheme 1). In this reaction, only moderate ee and yields were obtained in most cases [8].



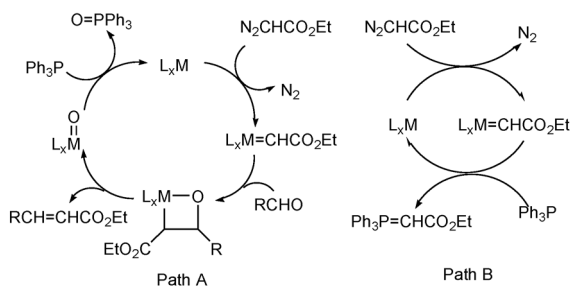
Scheme 1 Reaction of chiral phosphorus salts **1** with ketenes.

We speculated that the yield could be improved under neutral condition due to instability issue of ketenes. Thus, carbenoid-mediated olefination of ketenes was tested. Gratifyingly, high to excellent yields were achieved for the allenic esters when ketene was treated with EDA at 0 °C in the presence of PPh₃ and 0.5 mol % of Fe(TCP)Cl [6]. As shown in Scheme 2, pure disubstituted ketenes were suitable substrates to give the corresponding 4,4-disubstituted allenic esters. Further study revealed it was not necessary to prepare unstable ketenes in advance, and a facile one-pot protocol was involved, in which a mixture of acyl chlorides and Et₃N was added directly into the ylide generated in situ from phosphine and diazoacetate. Following this protocol, allenes formally derived from very unstable monosubstituted ketenes could also be obtained in good yields (Scheme 2).

With respect to the olefination mechanism of aldehydes with diazo compounds mediated by transition-metal complex, two different pathways have been proposed in literature as shown in Scheme 3, depending on metal complex. In path A, metal carbene reacts with aldehyde to afford the olefination product and PPh₃ acts as a reducing agent in the reaction system. In path B, however, formation of phosphorus ylide is suggested and the olefination reaction proceeds via a Wittig reaction. In the case of Fe(TCP)Cl employed, path B is believed to be the working mechanism. If this is the case, we envisaged that enantioenriched allenes would be formed by using optically active phosphine instead of triphenylphosphine.

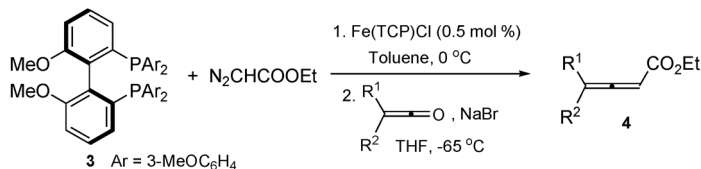


Scheme 2 Synthesis of allenic esters from the reaction of ketene with EDA in the presence of PPh_3 and Fe(TCP)Cl . *Reagents and conditions:* Olefination of ketene (1.0 equiv) with EDA (1.2 equiv) in the presence of Fe(TCP)Cl (0.5 mol %) and Ph_3P (1.2 equiv). ^aYlide was formed first from the reaction of Fe(TCP)Cl (0.5 mol %), Ph_3P (1.2 equiv), and EDA (1.2 equiv), then Et_3N (1.2 equiv) and acyl chloride (1.0 equiv) was added sequentially at -20°C to the reaction mixture.



Scheme 3 Two possible pathways involved in the carbenoid-mediated olefination of aldehydes.

As expected, enantioenriched allenic esters were obtained and excellent enantioselectivity was achieved when enantiopure diphosphine **3** was employed (Table 1). It not only provides an easy access to optically active 4,4-disubstituted allenic esters [6a], but also further confirms the mechanism that phosphorus ylide is generated through catalytic transfer of an iron(II) carbene to phosphine in the present reaction.

Table 1 Enantioselective synthesis of allenic esters.^a

Entry	R ¹ /R ²	Yield (%) ^b	ee (%) ^c
1	Ph/Me	72	93
2	Ph/Et	90	97
3	Ph ^m Pr	87	93
4	<i>o</i> -MeC ₆ H ₄ /Et	86	97
5	<i>p</i> -MeOC ₆ H ₄ /Et	81	96
6	<i>p</i> -ClC ₆ H ₄ /Et	83	97

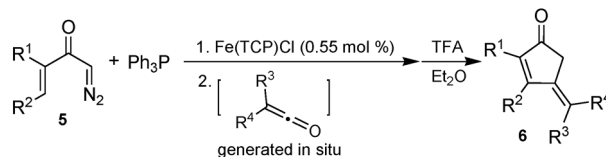
^aReagents and conditions. Ylide was formed first from EDA (2.0 equiv), Fe(TCP)Cl (0.5 mol %), **3** (1.0 equiv). The ylide was treated with NaBr (1.0 equiv) in THF and then ketene (1.0 equiv) at -65 °C.

^bIsolated yield.

^cDetermined by HPLC.

Multistep one-pot Wittig–Nazarov reaction for the construction of cyclopentenone from diazo compounds and acid chlorides [9]

Nazarov reaction provides a facile way for the construction of five-membered carbocycles [10], key subunits in many natural products and bioactive compounds. Since vinylallenyl ketones prove to be excellent substrates for the Nazarov reaction, we tried to combine the aforementioned allene synthesis with the Nazarov reaction to develop a tandem Wittig–Nazarov reaction for the synthesis of cyclopentenones. As shown in Table 2, under the optimized conditions, where both phosphorus ylides and ketenes were in situ prepared, the tandem Wittig–Nazarov reaction worked very well. These results demonstrated that there was no interference of byproducts Et₃N·HCl or Ph₃PO to the reaction. Various alkyl- and aryl-substituted β-methylenecyclopentenones could be synthesized in high yields with excellent stereoselectivity. For instance, ketene with homoallyl group gave alkenyl cyclopentenone in 76 % yield with *Z/E* ratio as 40/1 (entry 3). Notably, our method was also applicable in the preparation of fused carbocyclic rings from 1-cyclohexenyl-2-diazoethanone in high yields with good selectivities (Scheme 4). Thus, a facile Wittig–Nazarov cyclization reaction was developed, which offers a straightforward approach for the construction of β-methylenecyclopentenones in a multistep one-pot manner without isolation of intermediates.

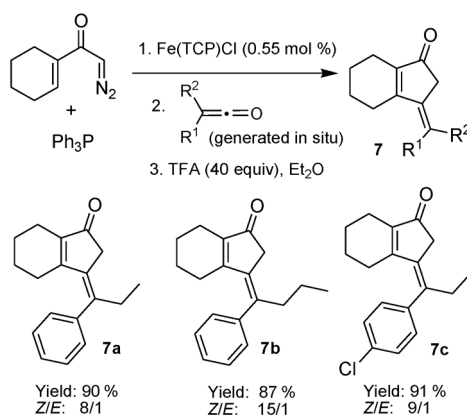
Table 2 One-pot synthesis of β -methylene-cyclopentenones from diazo-compounds and acid chlorides.^a

Entry	R ¹ /R ²	R ³ /R ⁴	Yield (%) ^b	Z/E ^c	Entry	R ¹ /R ²	R ³ /R ⁴	Yield (%) ^b	Z/E ^c
1	Me/Ph	Ph/Me	90	2.5/1	9	Me/ <i>p</i> -MeOC ₆ H ₄	Ph/Et	87	10/1
2	Me/Ph	Ph/ ^{<i>i</i>} Pr	86	12/1	10	Me/C ₆ H ₅	Ph/Et	95	12/1
3	Me/Ph	Ph/homoallyl	76	40/1	11	Me/ <i>p</i> -ClC ₆ H ₄	Ph/Et	82	17/1
4	Me/Ph	Ph/Ph	68	–	12	Me/2-furyl	Ph/Et	80	15/1
5	Me/Ph	<i>p</i> -MeO-C ₆ H ₄ /Et	84	10/1	13	Me/C ₆ H ₄ CH=CH	Ph/Et	71	24/1
6	Me/Ph	<i>p</i> -Cl-C ₆ H ₄ /Et	93	18/1	14	Me/C ₅ H ₁₁	Ph/Et	90	15/1
7	Me/Ph	<i>p</i> -Br-C ₆ H ₄ /Et	65	9/1	15	Me/cyclohexyl	Ph/Et	63	11/1
8	Me/Ph	1-naphthyl/Et	59	23/1					

^aReagents and conditions: ylide was formed first from Fe(TCP)Cl (0.55 mol %), PPh₃ (1.2 equiv), and diazoketone (1.0 equiv), which was subsequently treated with ketene prepared in situ from acid chloride (2.2 equiv) and Et₃N (2.4 equiv) at 0 °C. The reaction was quenched with cooled (0 °C) TFA in Et₂O.

^bIsolated yield.

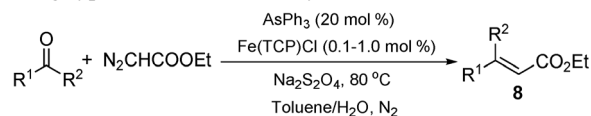
^cDetermined by ¹H NMR.

**Scheme 4** One-pot synthesis of hexahydroindenone.

Although iron porphyrin-catalyzed ylide olefination of ketenes has been developed and applied successfully to one-pot Wittig–Nazarov cyclization, stoichiometric amount of triphenylphosphine was required in the reaction. In order to improve atom-economy of our chemistry, we set out to realize the aforementioned reaction using a catalytic amount of a heteroatom species. In view of the great efficiency achieved in telluronium compound-catalyzed olefination of aldehydes with bromoacetates (up to 0.5 mol % catalyst loading) [11], attempts were made firstly to adapt telluronium compound-catalyzed olefination to allenes but with little success. One of the possible reasons was that basic conditions employed in the catalytic telluronium ylide olefination could kill the ketene. So we turned our attention on the transition-metal-mediated ylide olefination, which was carried out under neutral conditions, and considering the fact that triphenylphosphine oxide is very hard to be reduced under mild conditions, AsPh₃ was chosen as a substitute. Thus, a AsPh₃-catalyzed Wittig reaction with diazoacetate as a starting material was first examined [12]. As shown in Table 3, in the presence of

sodium hydrosulfite and AsPh_3 (20 mol %) and $\text{Fe}(\text{TCP})\text{Cl}$ (0.5 mol %), the catalytic ylide olefination with EDA proceeded well in toluene/water biphasic system to give the corresponding α,β -unsaturated esters in high yields with E/Z above 50/1. Aromatic aldehydes and aliphatic aldehydes all are suitable substrates. Trifluoromethyl ketone gave the corresponding β -trifluoromethyl α,β -unsaturated ester with 99/1 E/Z ratio in 85 % yield, providing an easy access to trifluoromethylvinyl compounds.

Table 3 Ph_3As -catalyzed Wittig-type olefination of aldehydes with diazoacetate.^a



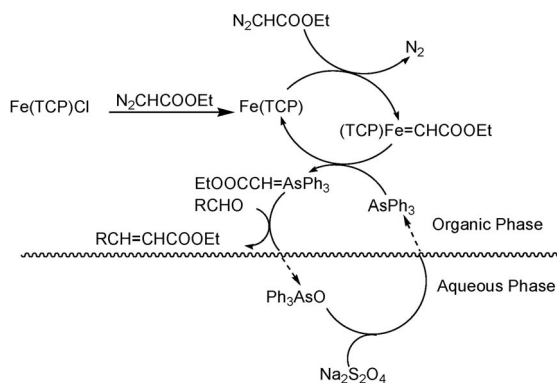
Entry	R ¹ /R ²	Yield (%) ^b	E/Z	Entry	R ¹ /R ²	Yield (%) ^b	E/Z
1	4-ClC ₆ H ₄ /H	97	99/1	9	4-MeC ₆ H ₄ /H	81	99/1
2	3-ClC ₆ H ₄ /H	95	99/1	10	4-MeOCC ₆ H ₄ /H	81	99/1
3	4-MeOCC ₆ H ₄ /H	99	99/1	11 ^b	2-(but-3-enyl)C ₆ H ₄ /H	78	99/1
4	4-CF ₃ C ₆ H ₄ /H	89	99/1	12	2-furyl/H	87	99/1
5	4-FC ₆ H ₄ /H	92	99/1	13 ^c	CH ₃ (CH ₂) ₇ /H	80	99/1
6	2,4-Cl ₂ C ₆ H ₃ /H	96	99/1	14	Cyclohexyl/H	78	50/1
7	2,6-Cl ₂ C ₆ H ₃ /H	71	99/1	15	4-CH ₃ COC ₆ H ₄ /H	93	99/1
8	C ₆ H ₅ /H	86	99/1	16	CF ₃ /4-ClC ₆ H ₄	85	99/1

^aReagent and conditions: method A: carbonyl compounds (1.0 equiv), EDA (2.0 equiv), $\text{Fe}(\text{TCP})\text{Cl}$ (0.1–1.0 mol %), $\text{Na}_2\text{S}_2\text{O}_4$ (2.0 equiv), toluene/ H_2O (2.5/1, v/v), 80 °C. EDA was slowly added via a syringe pump or in portions.

^bMethod B. $\text{Fe}(\text{TCP})\text{Cl}$ was added in portions and EDA (3.0 equiv) was added via a syringe pump or in portions.

^cIsolated yield.

To shed light on the mechanism, we did several control experiments and found that olefination product was not observed in the reaction of *p*-chlorobenzaldehyde with EDA without Ph_3As even in the presence of a stoichiometric amount of $\text{Fe}(\text{TCP})\text{Cl}$. And no desired product was isolated in the absence of $\text{Fe}(\text{TCP})\text{Cl}$. These results suggested that the catalytic olefination proceeded via arsonium ylide route. Toluene/water biphasic system was also crucial as the reaction could not proceed in the absence of water. The proposed AsPh_3 -catalyzed olefination catalytic cycle is shown in Scheme 5: $\text{Fe}(\text{TCP})\text{Cl}$ is in situ reduced by EDA to give $\text{Fe}(\text{TCP})$, which decomposes diazoacetate to form iron-carbene intermediate, followed by converting AsPh_3 to arsonium ylide, a subsequent Wittig reaction with aldehyde affords olefin and Ph_3AsO . Ph_3AsO is deoxygenated by $\text{Na}_2\text{S}_2\text{O}_4$ in the aqueous phase, regenerating triphenylarsine to complete a catalytic cycle.

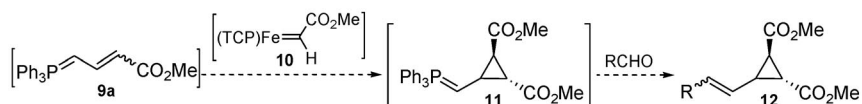


Scheme 5 Proposed mechanism of Ph_3As -catalyzed Wittig-type olefination in biphasic system.

Unfortunately, attempts to extend substrates from aldehydes to ketenes failed and a combination of the current reaction with Nazarov reaction for one-pot synthesis of β -methylenecyclopentenones proved to be inefficient.

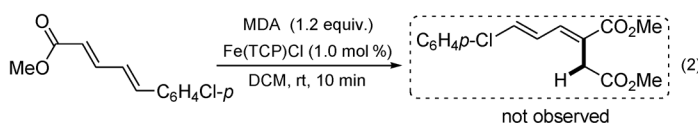
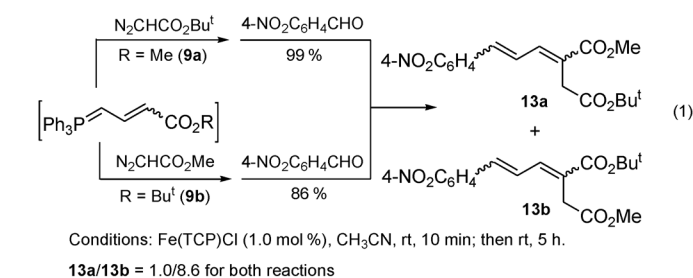
Reaction of allylic phosphoranones with iron porphyrin carbenoids: Formal carbenoid insertion into olefinic C–H bonds [7]

In our previous study on ylide chemistry, we have developed efficient methods for stereoselective synthesis of vinylcyclopropanes, important subunits in some biologically active compounds as well as intermediates in the synthesis of complex molecules. However, this direct allylic ylide cyclopropanation suffers from substrate limitations. In view of the fact that iron carbenoid can react with olefins to afford cyclopropanes, a new strategy as shown in Scheme 6 was designed to access such compounds. It was envisioned that phosphorus ylide **9a** could react with iron carbenoid **10** affording ylide **11**, which was supposed to be trapped by aldehydes to provide disubstituted vinylcyclopropanes.

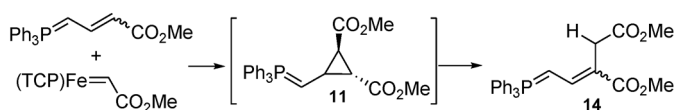


Scheme 6 Hypothesized reaction between ylide **9a** and metal carbene **10**.

Treatment of crotonate-derived phosphorus ylide **9** with electrophilic iron carbenoid **10**, followed by aldehyde, unexpectedly, afforded 1,1,4-trisubstituted 1,3-butadienes and no desired product was observed. Further studies demonstrated that both the reaction of ylide **9a** with *tert*-butyl diazoacetate (BDA) and the reaction of ylide **9b** with MDA led to the same product distribution in the cross experiments (eq. 1 in Scheme 7). In addition, (*2E,4E*)-methyl 5-(4-chlorophenyl)penta-2,4-dienoate did not react with MDA in the presence of Fe(TCP)Cl under the same conditions (eq. 2 in Scheme 7). These results suggested that the reaction proceeded probably via cyclopropanation of ylide, followed by ring opening as shown in Scheme 8.



Scheme 7 Cross-over experiments of different combinations between conjugated double bonds and diazo compounds.



Scheme 8 Possible working pathway of the formal carbenoid insertion into olefinic C–H bond.

To make the present reaction more practicable, a one-pot reaction starting with the phosphonium salt instead of ylide **9a** has been developed. As shown in Table 4, the reaction of phosphorous bromide **15** with MDA and aldehydes, in the presence of a base, worked very well to produce 1,1,4-trisubstituted 1,3-butadienes in moderate to good yields. Noticeably, optically active aldehyde *O,O*-isopropylidene-*D*-glyceraldehyde furnished the product without loss of ee. Compared with the reaction of triphenylphosphine ylide **9a**, the stereoselectivity in the one-pot reaction was improved greatly (Table 4).

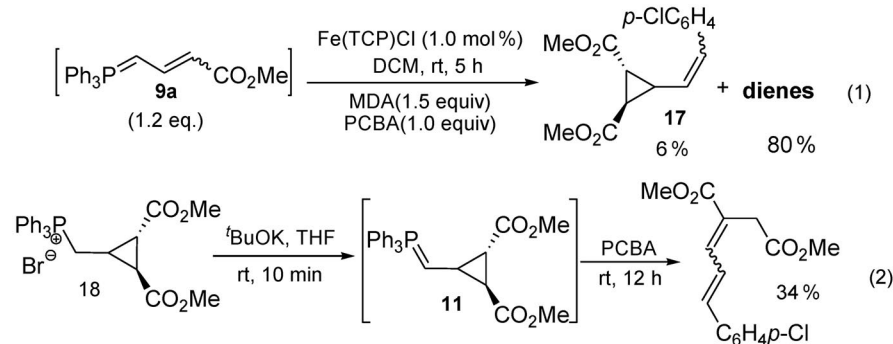
Table 4 One-pot synthesis of 1,3-butadienes via catalytic carbenoid insertion of allylic ylide.^a

R	Yield (%)	3 <i>E</i> ,5 <i>E</i> /3 <i>E</i> ,5 <i>Z</i>	R	Yield (%)	3 <i>E</i> ,5 <i>E</i> /3 <i>E</i> ,5 <i>Z</i>
4-ClC ₆ H ₄	62	92/8	<i>E</i> -C ₆ H ₅ CH=CH	45	90/10
4-BrC ₆ H ₄	61	94/6	Cy	72	92/8
4-NO ₂ C ₆ H ₄	54	97/3	Ph(Me)CH	66	94/6
4-CNC ₆ H ₄	53	92/8	C ₃ H ₁₁	69	87/13
C ₆ H ₅	61	95/5		65	75/25
4-MeC ₆ H ₄	67	94/6			

(96 % ee for 3*E*,5*E* isomer)

^aReagents and conditions: phosphorous salt **15** (1.25 equiv), toluene (2.0 ml), rt, LiHMDS (1.5 equiv), Fe(TCP)Cl (0.5 mol %), MDA (1.5 equiv), aldehyde (1.0 equiv).

To further confirm the mechanism, we tried to trap the intermediate **11**. By adding the mixture of *p*-ClC₆H₄CHO (PCBA) and MDA to ylide **9a** in CH₂Cl₂ (DCM) in the presence of [Fe(TCP)Cl], vinylcyclopropane **17** (*E/Z*, 15/85) was isolated albeit in 6 % yield (Scheme 9). Furthermore, we synthesized the intermediate ylide **11**, which was found to undergo the ring-opening reaction rapidly, and reacted



Scheme 9 Evidences for cyclopropanation, ring-opening mechanism of the formal carbenoid insertion.

with PCBA to give the desired diene in 34 % yield. These results supported the mechanism proposed in Scheme 8.

OUTLOOK

Traditionally, ylide reactions are carried out under basic conditions, which is usually harmful to substrates sensitive to base. Transition-metal-mediated ylide formation by decomposing diazo compounds paves a way to run ylide reaction under neutral conditions and provides a solution to extend ylide reaction to some unstable substrates. Furthermore, the neutral and mild conditions allow developing ylide-mediated multistep reactions in one-pot such as the Wittig–Nazarov reaction described in this paper, in which four reactions are combined in one-pot. In addition, ylide proves to possess the possibility to react with electrophilic metal carbenoids and which will extend the application of ylides in organic synthesis.

ACKNOWLEDGMENTS

We are grateful for the financial support from the Natural Sciences Foundation of China (Grant Nos. 20821002 and 20932008), the Major State Basic Research Development Program (Grant No. 2006CB806105), the Chinese Academy of Sciences, and The Science and Technology Commission of Shanghai Municipality.

REFERENCES

1. (a) M. P. Doyle, M. A. McKervey, T. Ye. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley-Interscience, New York (1998); (b) B. M. Trost, L. S. Melvin Jr. *Sulfur Ylides*, Chap. 7, Academic Press, New York (1975).
2. For some reviews, see (a) J. R. Fulton, V. K. Aggarwal, J. de Vincente. *Eur. J. Org. Chem.* 1479 (2005); (b) D. M. Hodgson, F. Y. T. M. Pierard, P. A. Stupple. *Chem. Soc. Rev.* **30**, 50 (2001); (c) M. P. Doyle, D. C. Forbes. *Chem. Rev.* **98**, 911 (1998); (d) T. Ye, M. Anthony McKervey. *Chem. Rev.* **94**, 1091 (1994).
3. X. Lu, H. Fang, Z. Ni. *J. Organomet. Chem.* **373**, 77 (1989).
4. Some recent examples, see: (a) H. Lebel, V. Paquet, C. Proulx. *Angew. Chem., Int. Ed.* **40**, 2887 (2001); (b) G. A. Mirafzal, G. Cheng, L. K. Woo. *J. Am. Chem. Soc.* **124**, 176 (2002); (c) Y. L. Chen, M. Huang, A. Ranade, X. P. Zhang. *J. Org. Chem.* **68**, 3714 (2003); (d) A. M. Santos, C. C. Romao, F. E. Kuhn. *J. Am. Chem. Soc.* **125**, 2414 (2003); (e) V. K. Aggarwal, J. R. Fulton, C. G. Sheldon, J. de Vincente. *J. Am. Chem. Soc.* **125**, 6034 (2003); (f) A. M. Santos, F. M. Pedro, A. A. Yogalekar, I. S. Lucas, C. C. Romao, F. E. Kuhn. *Chem. Eur. J.* **10**, 6313 (2004).
5. (a) X.-L. Sun, Y. Tang. *Acc. Chem. Res.* **41**, 937 (2008); (b) Q.-G. Wang, X.-M. Deng, B.-H. Zhu, L.-W. Ye, X.-L. Sun, C.-Y. Li, C.-Y. Zhu, Q. Shen, Y. Tang. *J. Am. Chem. Soc.* **130**, 5408 (2008); (c) X.-M. Deng, P. Cai, S. Ye, X.-L. Sun, W.-W. Liao, K. Li, Y. Tang, Y.-D. Wu, L.-X. Dai. *J. Am. Chem. Soc.* **128**, 9730 (2006); (d) Y. Tang, S. Ye, X.-L. Sun. *Synlett* 2720 (2005); (e) W.-W. Liao, X.-M. Deng, Y. Tang. *Chem. Commun.* **13**, 1516 (2004); (f) S. Ye, Z.-Z. Huang, C.-A. Xia, Y. Tang, L.-X. Dai. *J. Am. Chem. Soc.* **124**, 2432 (2002); (g) Y. Tang, S. Ye, Z.-Z. Huang, Y.-Z. Huang. *Heteroatom Chem.* **13**, 463 (2002).
6. (a) C.-Y. Li, X.-B. Wang, X.-L. Sun, Y. Tang, J.-C. Zheng, Z.-H. Xu, Y.-G. Zhou, L.-X. Dai. *J. Am. Chem. Soc.* **129**, 1494 (2007); (b) C.-Y. Li, B.-H. Zhu, L.-W. Ye, Q. Jing, X.-L. Sun, Y. Tang, Q. Shen. *Tetrahedron* **63**, 8046 (2007).
7. S. R. Wang, C.-Y. Zhu, X.-L. Sun, Y. Tang. *J. Am. Chem. Soc.* **131**, 4192 (2009).
8. C.-Y. Li, X.-L. Sun, Q. Jing, Y. Tang. *Chem. Commun.* 2980 (2006).
9. P. Cao, X.-L. Sun, B.-H. Zhu, Q. Shen, Z. Xie, Y. Tang. *Org. Lett.* **11**, 3048 (2009).

10. For recent reviews, see: (a) H. Pellissier. *Tetrahedron* **61**, 6479 (2005); (b) A. J. Frontier, C. Collison. *Tetrahedron* **61**, 7577 (2005); (c) M. A. Tius. *Eur. J. Org. Chem.* 2193 (2005); for selected examples, see: (d) D. Song, A. Rostami, F. G. West. *J. Am. Chem. Soc.* **129**, 12019 (2007); (e) M. Rueping, L. W. Andrey, B. J. Nachtsheim. *Angew. Chem., Int. Ed.* **46**, 2097 (2007); (f) W. He, I. R. Herrick, T. A. Atesin, P. A. Caruana, C. A. Kellenberger, A. J. Frontier. *J. Am. Chem. Soc.* **130**, 1003 (2008).
11. (a) Z.-Z. Huang, S. Ye, W. Xia, Y.-H. Yu, Y. Tang. *J. Org. Chem.* **67**, 3096 (2002); (b) Z.-Z. Huang, S. Ye, W. Xia, Y. Tang. *Chem. Commun.* 1384 (2001); (c) Z.-Z. Huang, Y. Tang. *J. Org. Chem.* **67**, 5320 (2002).
12. P. Cao, C.-Y. Li, Y.-B. Kang, Z. Xie, X.-L. Sun, Y. Tang. *J. Org. Chem.* **72**, 6628 (2007).