



Digest paper

Recent advances in diphosphination of alkynes and alkenes



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ABSTRACT

1,2-Bis(diphenylphosphino)ethenes and -ethanes (DPPEs) are among representative supporting ligands in transition metal catalysts, which can promote otherwise challenging organic transformations with high efficiency and selectivity. Such bidentately coordinating ligands are conventionally prepared by nucleophilic substitution reactions of halogenated carbon electrophiles with nucleophilic metal phosphides. However, they suffer from poor functional group compatibility and/or tedious preparation of highly functionalized starting substrates. In this context, additions of phosphines to readily available and simple alkynes and alkenes have recently received significant attention. This digest paper focuses on recent developments of diphosphination of alkynes and alkenes for the synthesis of DPPE-type ligands. The reported approaches are categorized into several types of reactions, and their scope, limitation, and mechanism are briefly summarized.

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Contents

Introduction	4317
Stepwise diphosphination of terminal alkynes	4318
Diphosphination of terminal alkynes with diphosphines	4319
Catalytic double hydrophosphination of alkynes	4319
Radical phosphinylphosphination of terminal alkenes	4320
Diphosphination of alkenes with silylphosphines	4321
Conclusion	4322
Acknowledgments	4322
References	4322

Introduction

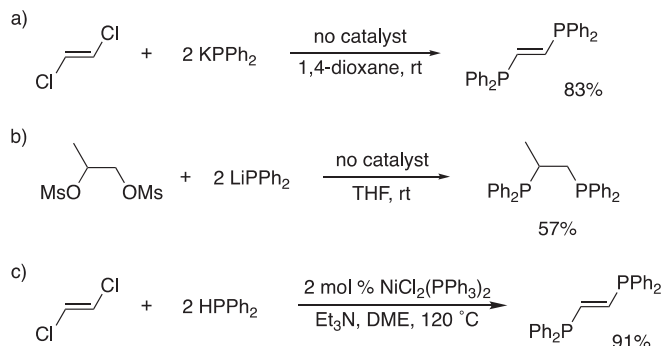
Phosphorus is one of indispensable main group elements in organic chemistry. It is a key element in bioactive molecules¹ and material science,² and organophosphines are invaluable synthetic reagents and intermediates, as exemplified by Wittig reaction, Horner-Wadsworth-Emmons reaction,³ and Appel reaction.⁴ Additionally, the phosphines are representative ancillary ligands for transition metal catalysts, which can promote otherwise greatly challenging organic transformations with high efficiency and selectivity.⁵ Particularly, bidentately coordinating 1,2-bis

(diphenylphosphino)ethenes and -ethanes (DPPEs) are frequently employed in coordination chemistry and organometallic chemistry because of their unique and rigid chelating nature. Such DPPE-type ligands are conventionally prepared by nucleophilic substitution of 1,2-dihalogenated ethenes and ethanes with phosphine nucleophiles. However, most protocols rely on the highly nucleophilic and basic metal phosphides such as Ph_2PK , which often suffers from functional group compatibility and hampers wide applications in the synthesis of complex molecules (Scheme 1a, b).⁶ The transition-metal-catalyzed cross-coupling reaction with moderately reactive hydrophosphines under milder conditions was also reported, but still functionalized starting materials such as 1,2-dichloroethenes are inevitable (Scheme 1c).⁷

On the other hand, additions of phosphino groups to C–C multiple bonds have recently received significant attention because

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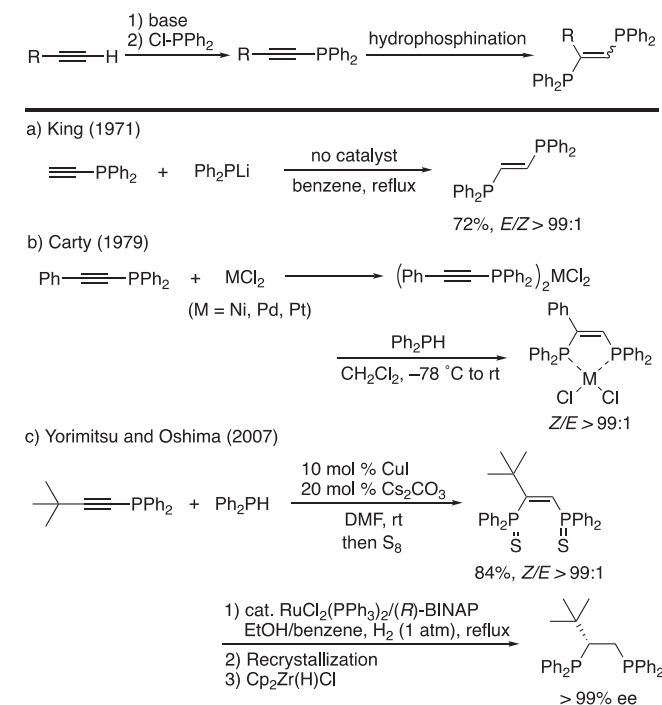


Scheme 1. Conventional protocols with 1,2-di(pseudo)halogenated carbon electrophiles and phosphide nucleophiles for the synthesis of DPPE-type ligands.

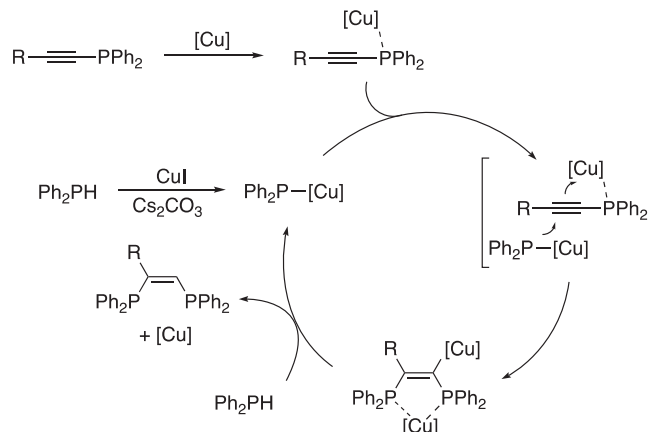
relatively simple hydrocarbons can be used as the starting platforms for the DPPE-type ligand synthesis. This digest paper highlights recent advances in diphosphination of alkynes and alkenes. The reactions are categorized into several approaches, and their scope, limitation, and mechanism are briefly summarized.

Stepwise diphosphination of terminal alkynes

Terminal alkynes are promising templates for the synthesis of DPPE-type ligands, because the alkyne C–H is relatively acidic and easily undergoes phosphination via a simple base-promoted deprotonation. Subsequent regioselective hydrophosphination can provide 1,2-bis(diphenylphosphino)ethenes in good overall yields (Scheme 2). The first proof of concept was reported by King, but only native diphenylethynylphosphine could be applicable, and (*E*)-isomer was exclusively formed (Scheme 2a).⁸ The (*E*)-isomer was somewhat less useful than the corresponding (*Z*)-isomer because the chelating coordination to metal center is impossible. This strategy was largely modified, by Carty, with nickel, palladium, and platinum salts, in which various substituted internal

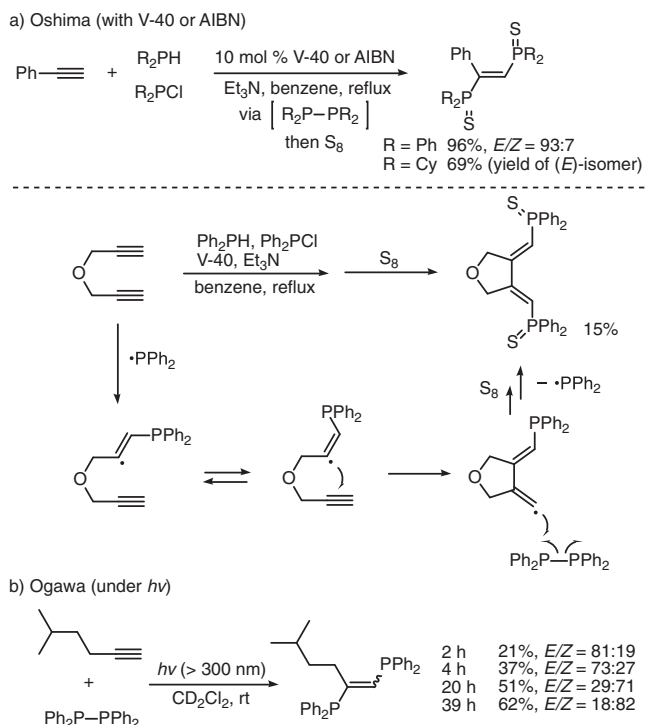


Scheme 2. Stepwise diphosphination approaches to 1,2-bis(diphenylphosphino)ethenes from terminal alkynes, including phosphination at the alkyne terminus and stereoselective hydrophosphination.



Scheme 3. Proposed mechanism for CuI/Cs₂CO₃-catalyzed *anti*-selective hydrophosphination of alkynylphosphines.

alkynylphosphines were viable, and (*Z*)-isomers were directly obtained as the corresponding metal-coordinated forms (Scheme 2b).⁹ However, one drawback is the use of stoichiometric amount of expensive transition metal salts. In 2007, Yorimitsu and Oshima developed the greatly improved methodology with inexpensive and abundant copper salt; the combination of CuI and Cs₂CO₃ catalyzed the *anti*-selective hydrophosphination of alkynylphosphines to form the (*Z*)-1,2-bis(diphenylphosphino)ethenes in high yields with high stereoselectivity (Scheme 2c).¹⁰ This deserves significant attention since the efficient turnover of CuI is feasible despite the conceivable catalyst poisonous nature of the diphosphinated product. The catalytic asymmetric hydrogenation followed by desulfidation can provide the optically active DPPE-type ligand of potent usefulness in asymmetric catalysis. The proposed mechanism includes the dual role of copper for the activation of alkynylphosphine and diphenylphosphine (Scheme 3).



Scheme 4. Radical diphosphination of terminal alkynes with tetraorganodiphosphines.

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