

# SYNLETT Spotlight 248

## Application of Terminal Electrophilic Phosphinidene Complexes

Compiled by Manju Rani



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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### Introduction

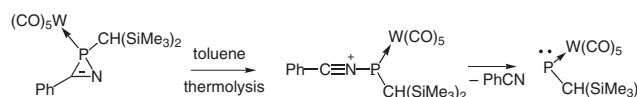
Phosphinidenes are phosphorus analogues of carbenes in which phosphorus is monovalent with an incomplete octet of electrons. Phosphinidene complexes readily react with alkenes, whereas free phosphinidenes do not react with alkenes. This indicates that the coordination of these unstable phosphorus compounds<sup>1</sup> with metallic species enhances their stability as well as reactivity by increasing the electrophilicity of the phosphorus atom. A number of precursors like phosphiranes,<sup>2</sup> phospholenes,<sup>2</sup> norbornadienes,<sup>3</sup> 2*H*-azaphosphirene<sup>4</sup> and phosphirene<sup>5</sup> metal complexes are known to generate terminal phosphinidene complexes in situ via their thermal or photochemical decomposition. These phosphinidene complexes are short-lived intermediates and their existence is proved by trapping them with substituted alkenes,<sup>6</sup> acetylenes,<sup>7</sup> and organic nitriles<sup>8</sup> via cycloaddition reactions resulting in the formation of a variety of P-heterocycles. Recently, insertion of phosphinidene complexes into carbon–halogen bonds has been established,<sup>9–11</sup> which affords a number of novel organophosphorus compounds.

### Preparation

In situ generation of phosphinidene intermediates is carried out under strictly anhydrous/moisture-free conditions, that is, in an inert atmosphere of dry nitrogen gas.

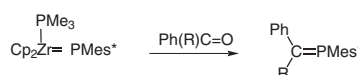
### Abstracts

(A) Phosphinidene complexes in the presence of alkenes<sup>6</sup> and substituted acetylenes<sup>7</sup> undergo [2+1]-cycloaddition reactions affording a variety of three-membered P-heterocycles.

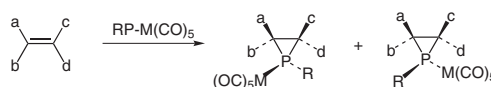


Scheme 1

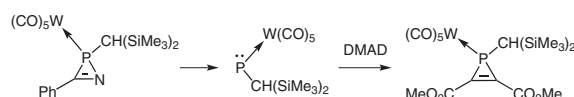
**Properties:** Phosphinidene complexes are highly unstable, short-lived intermediates and exhibit an inherent triplet<sup>12</sup> electronic state but the singlet<sup>13</sup> counterpart can be stabilised by substituents through both electronic and steric effects. Ligands with strong  $\sigma$ -donor capabilities increase the electron density on the P-atom and enhance its nucleophilicity. Ligands with strong  $\pi$ -acceptor capabilities increase the electropositive character of the P-atom. Nucleophilic phosphinidenes show Wittig-type reactivity<sup>14</sup> towards carbonyl derivatives and convert C=O into C=P double bonds (Scheme 2), while the electrophilic type appears to be unpredictable, but these phosphinidenes combine with the alkene to form cyclic compounds, namely phosphiranes (Scheme 3).



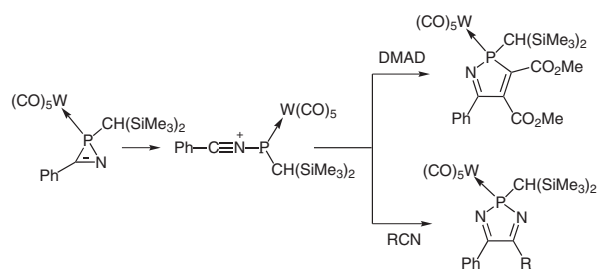
Scheme 2



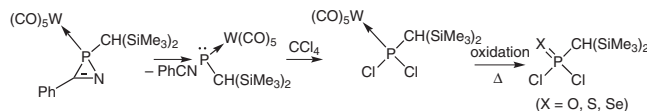
Scheme 3



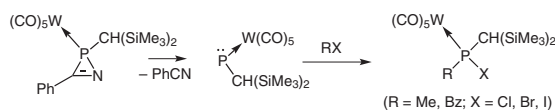
(B) A phosphinidene complex in the presence of an organic nitrile<sup>8</sup> yields a Lewis acid-base adduct which serves as a 1,3-dipole for [3+2] cycloaddition of the organic nitrile and the substituted acetylenes.<sup>7</sup>



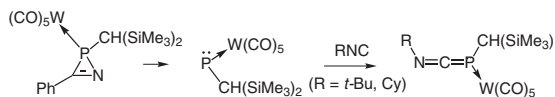
(C) A reaction of phosphinidene with CCl<sub>4</sub> results in transfer of a Cl atom of CCl<sub>4</sub> to the phosphorus atom giving dichloroorganophosphines.<sup>9</sup> Further, oxidation of these dichloroorganophosphines with chalcogens (O, S, Se) affords structurally characterised organophosphonic dichlorides, where thiophosphonic dichloride is the first example<sup>9</sup> of structurally characterised organothiophosphonic dichlorides.



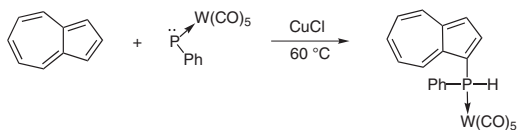
(D) Insertion of a phosphinidene complex into carbon-halogen bonds provides a novel route for the selective synthesis of prochiral phosphine complexes. A number of such complexes have been prepared and most of them have been structurally characterised<sup>10,11</sup> by single crystal X-ray crystallography.



(E) Terminal electrophilic phosphinidene complexes yield a P=C double bond with organic isocyanides.<sup>15</sup>



(F) Reactions of terminal electrophilic phosphinidene complexes with azulene, with or without a copper catalyst, are very interesting in view of insertion of a phosphinidene complex into a carbon-hydrogen bond.<sup>16</sup>



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