

This article was downloaded by:

On: 30 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### Synthesis of Functionalized $\Delta^3$ Phosphabenzenes by Means of Diels Alder Reaction with Phosphaalkenes

Y. Y. C. Yeung<sup>a</sup>; Lam Ko<sup>a</sup>; P. Cosquer<sup>a</sup>; P. Pellon<sup>a</sup>; J. Hamelin<sup>a</sup>; R. Carrie<sup>a</sup>

<sup>a</sup> Groupe de Physicochimie Structurale, U.A. C.N.R.S. 704, Université de Rennes, Rennes, FRANCE

**To cite this Article** Yeung, Y. Y. C. , Ko, Lam , Cosquer, P. , Pellon, P. , Hamelin, J. and Carrie, R.(1987) 'Synthesis of Functionalized  $\Delta^3$  Phosphabenzenes by Means of Diels Alder Reaction with Phosphaalkenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 523 — 526

**To link to this Article:** DOI: 10.1080/03086648708080635

**URL:** <http://dx.doi.org/10.1080/03086648708080635>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# SYNTHESIS OF FUNCTIONALIZED $\lambda^3$ PHOSPHABENZENES BY MEANS OF DIELS ALDER REACTION WITH PHOSPHA-ALKENES.

Y.Y.C. YEUNG LAM KO, P. COSQUER, P. PELLON, J. HAMELIN and R. CARRIE

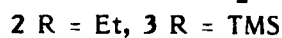
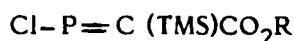
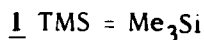
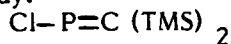
Groupe de Physicochimie Structurale, U.A. C.N.R.S. 704, Université de Rennes, Campus de Beaulieu, 35042 Rennes, FRANCE.

**Abstract** Diels Alder reaction provides an easy and general access to functionalized  $\lambda^3$  phosphabenzenes after aromatization with the possibilities of introducing the functional group either with the diene or the phosphaaalkene.

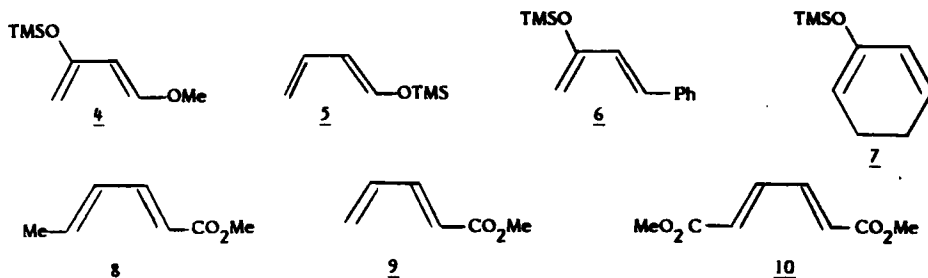
The synthesis of  $\lambda^3$  phosphabenzenes has been reviewed by G.Märkl<sup>1</sup>. A survey of the literature shows that functional  $\lambda^3$  phosphabenzenes<sup>2-5</sup> are still scarce compared to alkyl or aryl substituted ones.

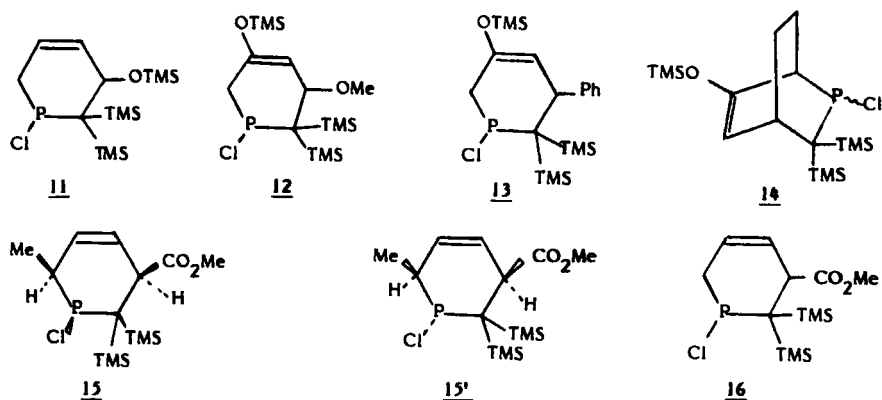
Märkl *et al.*<sup>6</sup> have already shown that the reaction of  $\text{TMS(Ph)C=P-Cl}$ , with cyclopentadienones or  $\alpha$ -pyrones leads to phosphabenzenes. Furthermore, the possibility of aromatization of the adduct from **1** and 2,3 dimethylbutadiene has been described<sup>7</sup>. However, drastic conditions were used and yields were rather low.

Functionalized  $\lambda^3$  phosphabenzenes are obtained from phosphaaalkenes **1**, **2** and **3** via the Diels Alder reaction. **2** and **3** are generated in an original way.



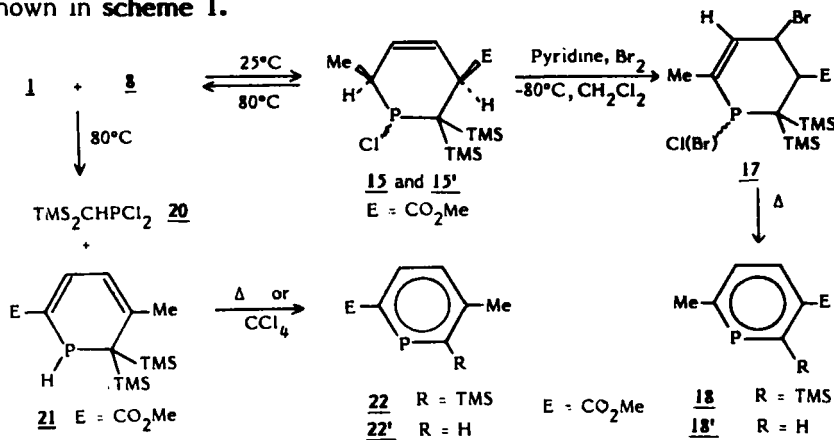
At room temperature, **1** reacts almost quantitatively with electron-rich or -poor dienes such as **4** - **9** leading to the corresponding adducts **11** - **16** but does not react with **10**.





The results of the second order perturbation theory calculations are in agreement with the experimental observations.

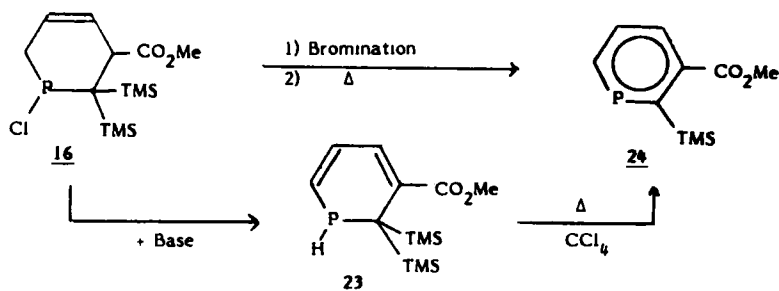
If the Diels Alder works well at least in the case of dienes **4** - **9**, the aromatization of the adducts is less easy in certain cases. Adducts **15** and **15'** are transformed into phosphabenzenes **18** and **18'** (4/1 mixture, yield 42 %/1) and their regioisomers **22** and **22'** (4/1 mixture, yield 32%/8) as shown in **scheme 1**.



**Scheme 1**

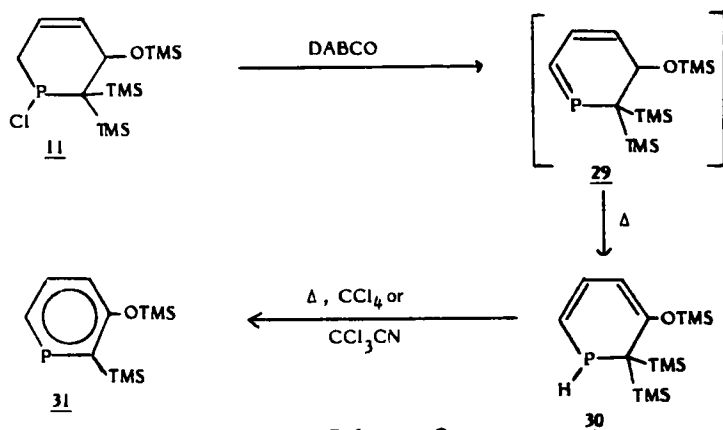
When **15** and **15'** are heated with diene **4**, cycloreversion is shown by trapping phosphalkene **1** with **4**, more reactive than methyl sorbate **8** to yield **12** and **27** (see after). Phosphabenzenes **18** and **22** are protodesilylated by formic acid in refluxing  $\text{CCl}_4$ . These results show the synthetic potentiality of the reversible Diels Alder reaction. It enables the synthesis of one or the other isomer **18** or **22**, depending on reaction conditions.

Similarly, adduct **16** after bromination and thermolysis gives **24** (yield 10% after chromatography). A better route to **24** (80%, NMR evaluation) via **23** is under present investigation (**scheme 2**).



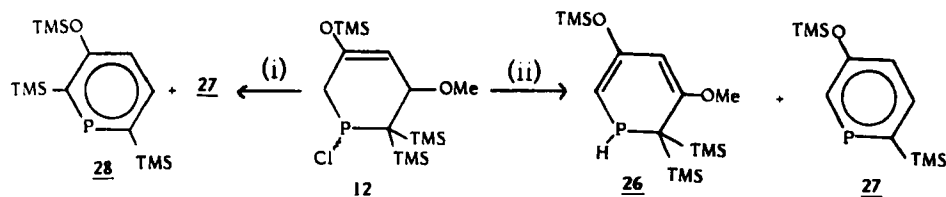
Scheme 2

With DABCO in refluxing benzene, **11** gives almost quantitatively the secondary phosphine **30** which is converted in refluxing  $\text{CCl}_4$  or by  $\text{CCl}_3\text{CN}$  at room temperature into **31** (yield 60 %/**11**) (scheme 3).



Scheme 3

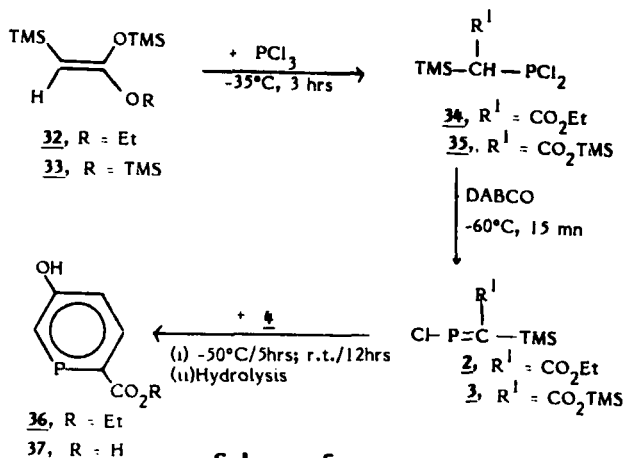
Adduct **12** leads to different phosphabenzenes **27** and **28** depending on the reaction conditions. Heating **12** in a solution of DABCO in benzene at reflux leads almost quantitatively to **27** with about 5 % of phosphine **26**. When **12** is added to pyridine in refluxing benzene, a 3/7 mixture of **27** and



Scheme 4, (i) Benzene + pyridine, 80°C,  
(ii) DABCO, benzene 20°C  $\rightarrow$  80°C

28 is obtained. The detail of the mechanism(s) of the reaction is not clear at the present time. However, the formation of 28 implies the migration of the trimethylsilyl moiety.

The functionality can be introduced by the dienophile. The unknown phosphaaalkenes 2 and 3 are generated *in situ* and trapped by diene 4 to give phosphabenzenes 36 and 37 in an overall yield of 60-70 %/32 or 33 (scheme 5).



Scheme 5

The structure of the products is established by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR and mass spectrometry.

This study shows that phosphaaalkenes  $\text{TMS}-\text{C}=\text{P}-\text{Cl}$  allow a rather easy route to functionalized  $\lambda^3$  phosphabenzenes. The Diels Alder reaction provides a quantitative access to primary adducts which may be subsequently aromatized in satisfactory yields.

The functional group may be introduced either with the diene or the phosphaaalkenes.

## REFERENCES

- <sup>1</sup>G. Märkl in *Houben-Weyl, Methoden der organische chemie*, G.Thieme Verlag, band E1, p.72(1982).
- <sup>2</sup>G. Märkl, G. Adolin, F.Kees and G. Zander, *Tetrahedron Lett.*, 3445 (1977).
- <sup>3</sup>G.Märkl and K.Hock, *Tetrahedron Lett.*, 2645(1983).
- <sup>4</sup>G. Märkl and K.Hock, *Tetrahedron Lett.*, 5051(1983).
- <sup>5</sup>G.Märkl and K. Hock, *Tetrahedron Lett.*, 5055(1983).
- <sup>6</sup>G.Märkl, E.Silbereisen and G.Y.Jin, *Angew. Chem. Supplement*,881 (1982).
- <sup>7</sup>Y.Y.C. Yeung Lam Ko and R. Carrié, *J. Chem. Soc., Chem. Comm.*, 1640(1984).
- <sup>8</sup>R.Appel and A. Westerhaus, *Tetrahedron Lett.*, 2159 (1981).