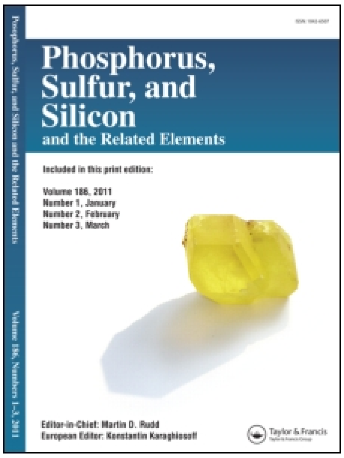
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Ambident Phosphinomethanide Ligands: From Robust Complexes to Fragile Frameworks

Hans. H. Karsch; Roland Richter; Eva Witt

To cite this Article Karsch, Hans. H. , Richter, Roland and Witt, Eva(1996) 'Ambident Phosphinomethanide Ligands: From Robust Complexes to Fragile Frameworks', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 165 — 168

To link to this Article: DOI: 10.1080/10426509608545116

URL: http://dx.doi.org/10.1080/10426509608545116

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.

Phosphorus, Sulfur, and Silicon, 1996, Vols. 109–110, pp. 165–168
Reprints available directly from the publisher
Photocopying permitted by license only

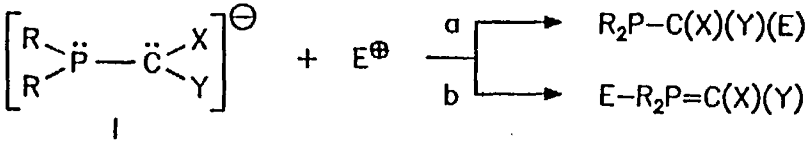
AMBIDENT PHOSPHINOMETHANIDE LIGANDS: FROM ROBUST COMPLEXES TO FRAGILE FRAMEWORKS

HANS. H. KARSCH*, ROLAND RICHTER and EVA WITT
Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

Abstract The ambidentate nature of phosphinomethanides leads to a broad variety of coordination modes to metal centers. For instance, high phosphine coordination numbers are achieved with diphosphinomethanide ligands. Furthermore, phosphinomethanides undergo readily rearrangements on reaction with electrophiles, leading to a manifold of new compounds with unexpected structural features, e.g. novel heterocycles. In addition, redox reactions with oxidative coupling of the phosphinomethanides are often encountered, which again lead to novel heterocyclic structures with group 15 element oxidants like PCl_3 or $AsCl_3$.

INTRODUCTION

Whereas carbon commonly is regarded as the typical element of the second period in the periodic table, phosphorus can be regarded as representative for the heavier elements. A comparison of both elements with regard to their chemical properties should use a system, which comprises the same number of bonds and electrons for both elements. This requirement is met by phosphinomethanides I, where both elements are connected directly together, which has the additional advantage, that the reactivity can be evaluated with one single component. Both reaction at carbon as well as at phosphorus is possible and tunable by the appropriate choice of substituents R, X and Y (eq. 1).

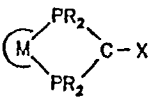


I

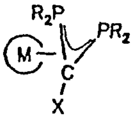
(1)

HIGH COORDINATION NUMBERS

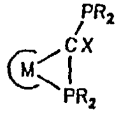
Simple phosphinomethanides (X = Y = H) will react with most kind of electrophiles via carbon (a). With heteroelement substituents at carbon, ylide formation (b) is also possible. Thus, with diphosphinomethanides (Y = PR_2), complexes of s/p,d,f elements with high phosphine coordination numbers and with numerous kinds of coordination modes are accessible, e.g. II-VIII.



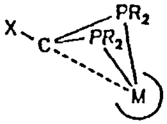
II



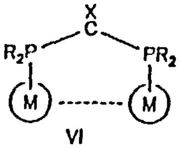
III



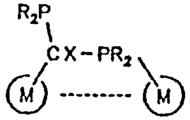
IV



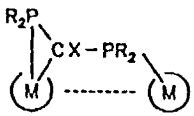
V



VI



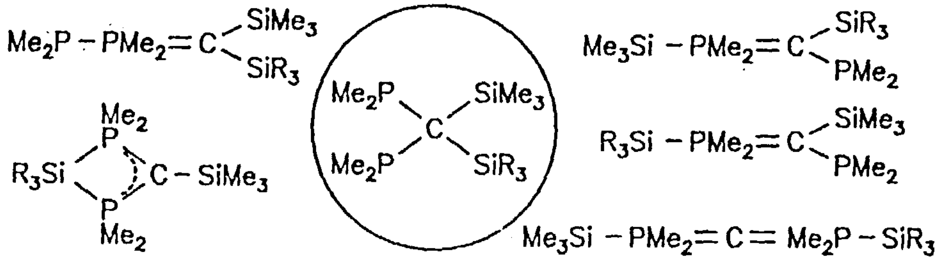
VII



VIII

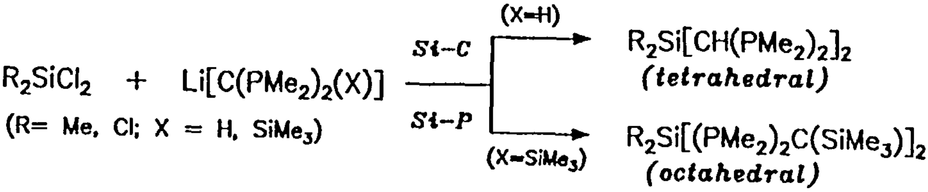
SKELETON REARRANGEMENTS/MONOFUNCTIONAL SYSTEMS

The coordination of heteroelement substituted phosphinomethanides to (formal) silicenium or phosphenium type of electrophiles depends on reaction conditions and substitution patterns. Quite frequently, the initially formed products are not stable and rearrange to thermodynamically more stable products. Thus combining $Li[C(PMe_2)_2(SiMe_3)]$ with R_3SiCl, potentially six different isomers are possible and - at least in part - indeed observed:



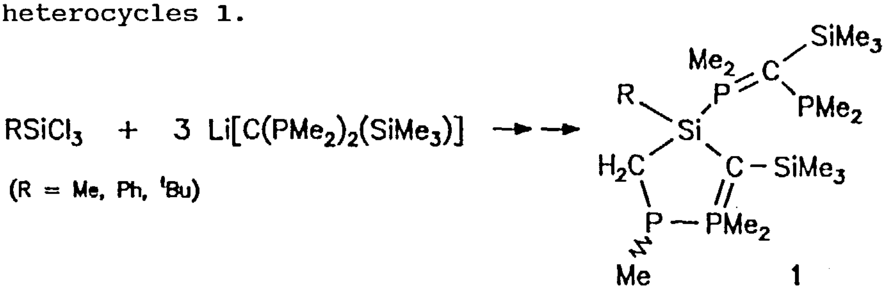
SKELETON REARRANGEMENTS/MULTIFUNCTIONAL SYSTEMS

The interaction of a silicon center with more than one phosphinomethanide ligand again will result in different kind of products (eq. 2):



(2)

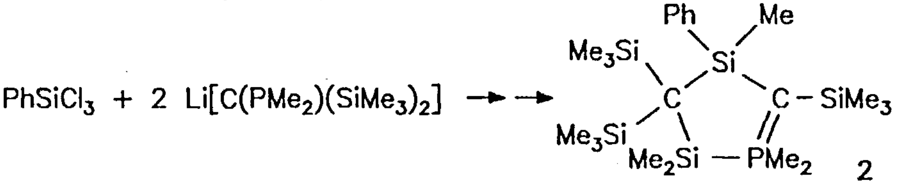
Rearrangement and additional metalation is observed in the case of eq. (3), resulting in the novel, fluctional heterocycles 1.



1

(3)

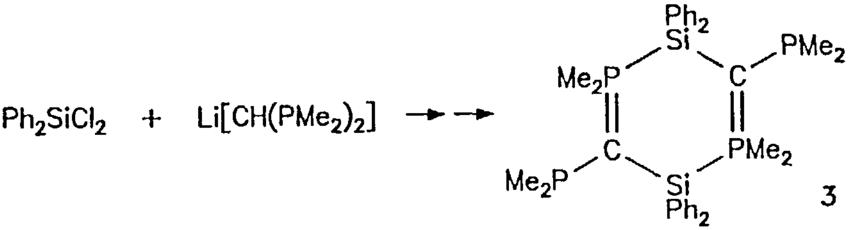
A methyl migration from one silicon to the other and chlorophosphine elimination are the key steps in the formation of the novel heterocycle 2, probably via a silene intermediate (eq. 4)



2

(4)

A silene intermediate also may be involved in the formation of the novel heterocycle 3 (eq. 5)

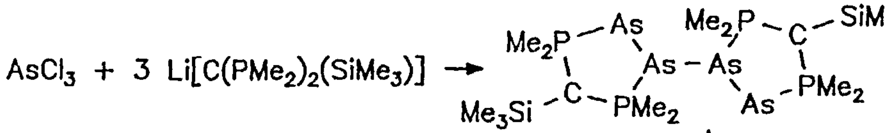


3

(5)

OXIDATIVE COUPLING OF PHOSPHINOMETHANIDES

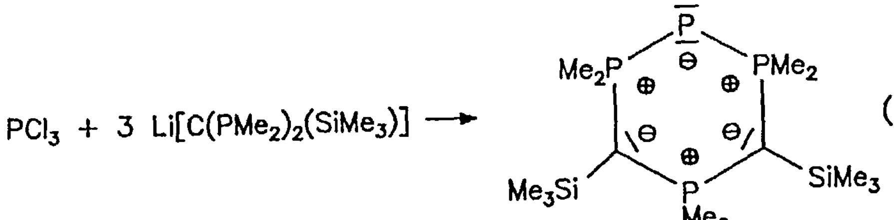
P-P, P-C and C-C coupling reactions are observed in the reaction of titanocene dichloride with lithium phosphinomethanides. Similar coupling reactions are also observed in the reactions with group 15 element halides.
Thus, for instance, the tetranuclear arsenic derivative 4 is obtained according to eq. (6).



(6)

4

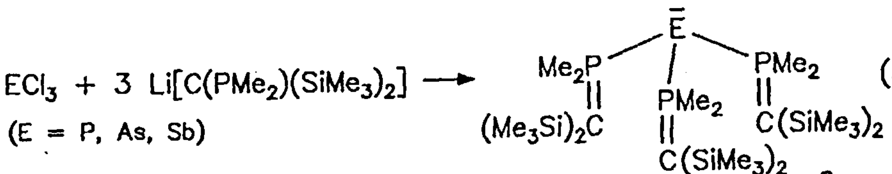
With PCl_3, a variety of heterocycles with low coordinate phosphorus is obtained, e.g. according to eq. (7).



(7)

5

The postulated intermediate, a trisylidic phosphine derivative can be characterized as well as its heavier congeners by slight changes in the substitution pattern eq.(8).



(8)

6

Compounds, 1-6 have been characterized by NMR spectroscopy and X-ray diffraction.

REFERENCE

H.H. Karsch, Russ. Chem. Bull. 1993, 42, 1937