

This article was downloaded by:

On: 29 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>

[2 2] Cycloaddition Reactions of Phosphenium Complexes with Isocyanates and Isothiocyanates

Alexander Fried^a; Wolfgang Malisch^a; Martin Schmeusser^a; Udo Weis^a

^a Institut für Anorganische Chemie der Universität Würzburg, Am Bub land, Würzburg, Bundesrepublik Deutschland

To cite this Article Fried, Alexander , Malisch, Wolfgang , Schmeusser, Martin and Weis, Udo(1992) '[2 2] Cycloaddition Reactions of Phosphenium Complexes with Isocyanates and Isothiocyanates', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 65: 1, 75 – 78

To link to this Article: DOI: 10.1080/10426509208055322

URL: <http://dx.doi.org/10.1080/10426509208055322>

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.

[2 + 2] Cycloaddition Reactions of Phosphenium Complexes with Isocyanates and Isothiocyanates

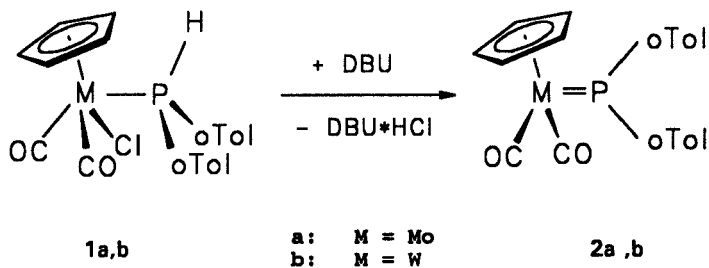
**Alexander Fried, Wolfgang Malisch*, Martin Schmeusser
 and Udo Weis**

**Institut für Anorganische Chemie der Universität
 Würzburg, Am Hubland, D-8700 Würzburg, Bundesrepublik
 Deutschland.**

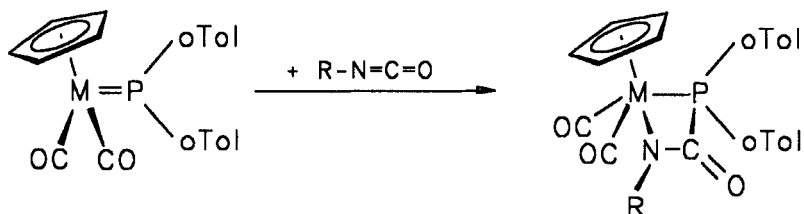
As a part of a systematic study concerning phosphenium complexes of the type $\text{Cp}(\text{OC})_2\text{M}=\text{PR}_2$ ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{alkyl}, \text{aryl}$) reactions with isocyanates and isothiocyanates were performed in order to get information with respect to regioselectivity.

$\text{M}=\text{P}$ - complexes can be obtained either via decarbonylation of the corresponding metallophosphane (**a**) or via base-assisted dehydrohalogenation of the bifunctional phosphane metal complexes $\text{Cp}(\text{OC})_2(\text{R}_2(\text{H})\text{P})\text{M}-\text{Cl}$ (**b**).¹

Route (b) can be successfully applied for conversion of **1a,b** to the *o*-tolyl-substituted phosphenium complexes **2a,b**, which are isolated as violet crystalline powders.



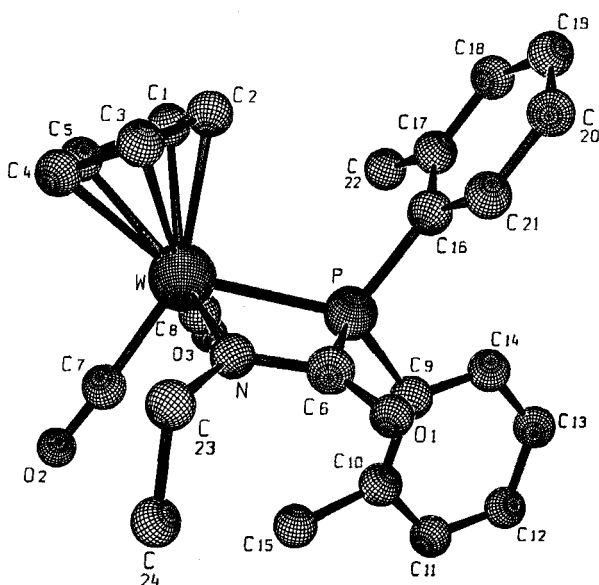
Isocyanates $R-N=C=O$ ($R = Et, Ph$) exclusively add to the $M=P$ -double bond via the $N=C$ - unit to generate the four membered phospho-metalla-cycles **3a-d** containing an acyl function.



2	a	b
M	Mo	W

3	a	b	c	d
M	Mo	Mo	W	W
R	Et	Ph	Et	Ph

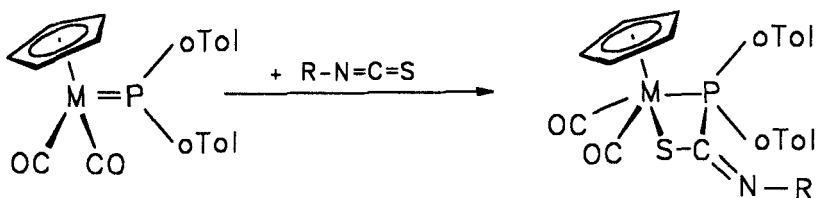
X-ray structure of **3c** :



Selected bond distances [pm] and bond angles [°]

W - N	218.8(5)	N - W - P	63.3(1)
W - P	247.4(1)	W - P - C6	84.7(2)
P - C6	188.1(6)	P - C6 - N	98.8(4)
N - C6	131.9(6)	W - S - C8	113.2(2)

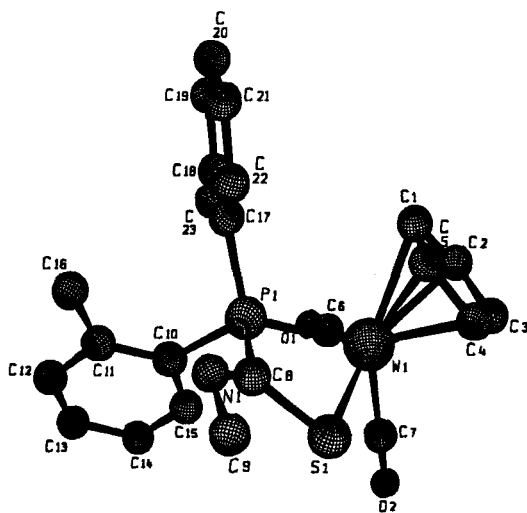
In contrast in the case of isothiocyanates $R-N=C=S$ the $C=S$ -unit is involved to form the metalla-cycles **4a-f** bearing an imino function. Variation of the metal and the bulkiness of R doesn't change the regioselectivity.



2	a	b
M	Mo	W

4	a	b	c	d	e	f
M	Mo	Mo	W	W	W	W
R	Me	Ph	Me	Ph	tBu	Allyl

X-ray structure of **4c**:



Selected bond distances [pm] and bond angles [°]

W - S	251.7(4)	S - W - P	67.0(1)
W - P	245.8(3)	W - P - C8	94.0(4)
P - C8	186 (1)	P - C8 - S	98.1(6)
S - C8	177 (1)	W - S - C8	94.3(4)

-
- 1 a) W. Malisch, A.Meyer, K. Jörg, U. Hofmockel, M. Schmeußner, R. Schemm, W.S. Sheldrick, *Phosphorus and Sulfur* **30** (1987) 205. - b) E. Groß, K. Jörg, K. Fiederling, A. Göttlein, W. Malisch, R. Boese, *Angew. Chem.* **96** (1984) 705; *Angew. Chem. Int. Ed. Engl.* **23** (1984) 738. - c) K. Jörg, W. Malisch, A. Meyer, W. Reich, U. Schubert, *Angew. Chem.* **98** (1986) 103; *Angew. Chem. Int. Ed. Engl.* **25** (1986) 92. - d) W.Malisch, M.Märkl, S.Amann, U.Hirth, M.Schmeusser, *Phosphorus and Sulfur* **49/50** (1990) 441.