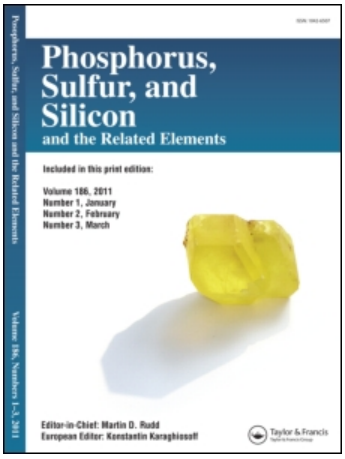

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[2 2] Cycloaddition Reactions of Phosphenium Complexes with Isocyanates and Isothiocyanates

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

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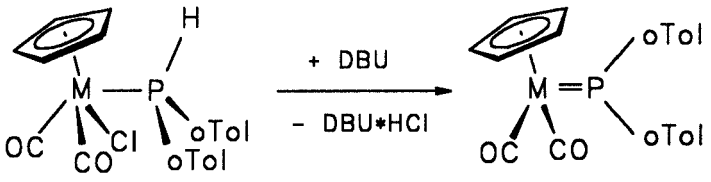
As a part of a systematic study concerning phosphenium complexes of the type $Cp(OC)_2M{=}PR_2$ (M = Mo, W; R = alkly, aryl) reactions with isocyanates and isothiocyanates were performed in order to get information with respect to regioselectivity.

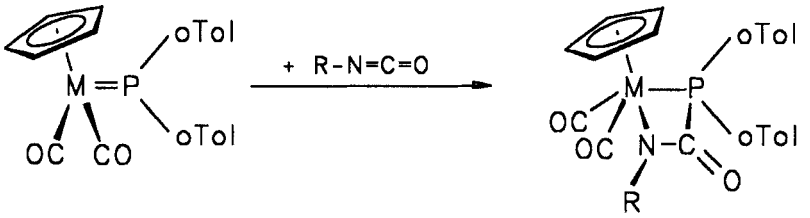
M=P - complexes can be obtained either via decarbonylation of the corresponding metallophosphane (a) or via base-assisted dehydrohalogenation of the bifunctional phosphane metal complexes $Cp(OC)_2(R_2(H)P)M\text{-}Cl$ (b).[1]

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



1a,b **a: M = Mo** **b: M = W** **2a ,b**

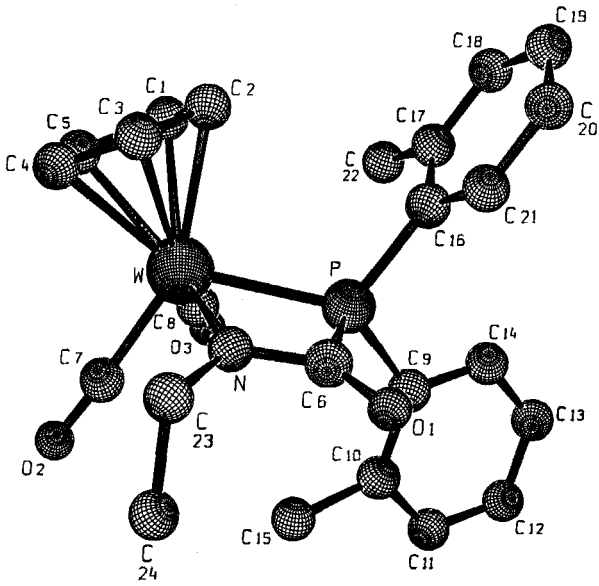
Isocyanates R-N=C=O (R = Et, Ph) exclusively add to the M=P-double bond via the N=C- unit to generate the four membered phospha-metalla-cycles **3a-d** containing an acyl function.



2	a	b
M	Mo	W

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

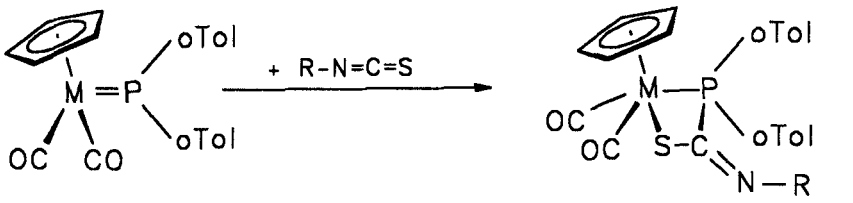
X-ray structure of **3c** :



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)

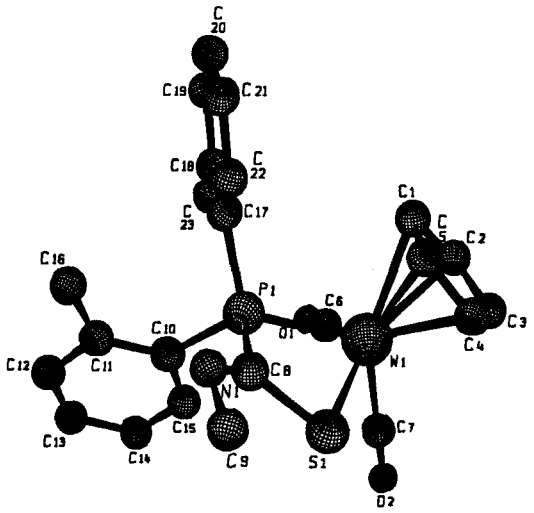
In contrast in the case of isothiocyanates R-N=C=S the C=S-unit is involved to form the metalla-cycles **4a-f** bearing an imino function. Variation of the metal and the bulkiness of R doesn't change the regioselectivity.



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)

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[1] a) W. Malisch, A.Meyer, K. Jörg, U. Hofmockel, M. Schmeußer, 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.