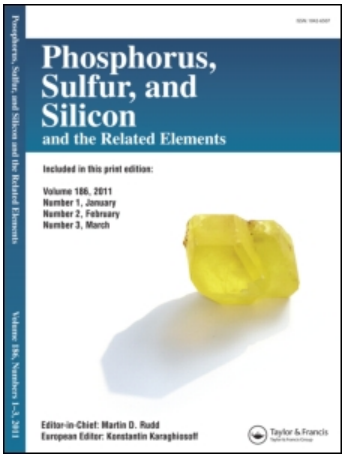


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Cycloadditions with Metauo-Phosphaalkenes

Lothar Weber[a]; Annette Rühlicke[a]; Olaf Kaminski[a]
[a] Faculty of Chemistry, Universitiit of Blelefeld, Bielefeld, Germany

To cite this Article Weber, Lothar , Rühlicke, Annette and Kaminski, Olaf(1994) 'Cycloadditions with Metauo-Phosphaalkenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 325 — 328
To link to this Article: DOI: 10.1080/10426509408021846
URL: http://dx.doi.org/10.1080/10426509408021846

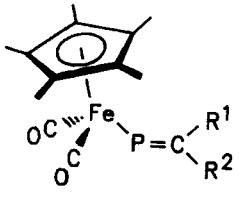
Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 325–328
Reprints available directly from the publisher
Photocopying permitted by license only

CYCLOADDITIONS WITH METALLO-PHOSPHAALKENES

LOTHAR WEBER*, ANNETTE RÜHLICKE AND OLAF KAMINSKI
Universität of Bielefeld, Faculty of Chemistry, D-33615 Bielefeld, Germany

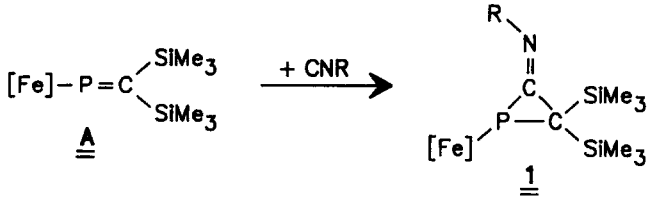
Abstract Cycloadditions of metallo-phosphaalkenes such as $(C_5Me_5)(CO)_2Fe$-$P=CR^1R^2$ ($R^1 = R^2 = SiMe_3$, NMe_2; R^1 = Ph, $R^2 = SiMe_3$) are performed with isocyanides, electron-poor alkenes, alkynes and heteroalkenes.

Metallo-phosphaalkenes **A**[1] are polyfunctional molecules, which allow a number of interesting chemical transformations.



A

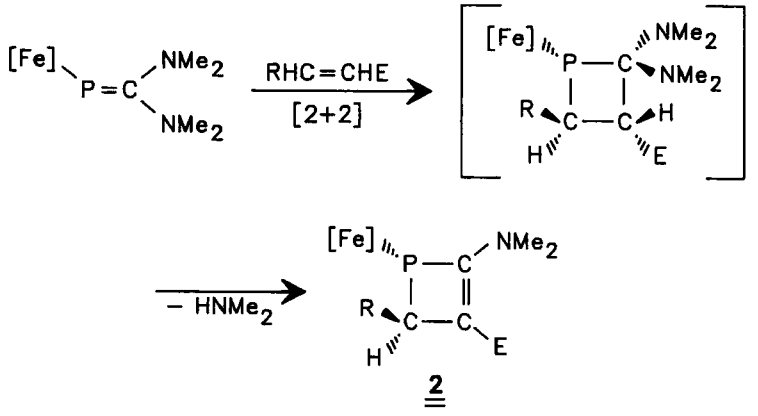
When metallo-phosphaalkenes **A** are exposed to equimolar amounts of isocyanides [2+1] cycloadditions with the formation of 1-metallo-2-iminophosphiranes are observed (eq. 1)[2].



(1)

R = Ph, o–Tol, 2,6–Xyl ; [Fe] = $Cp^*(CO)_2Fe$

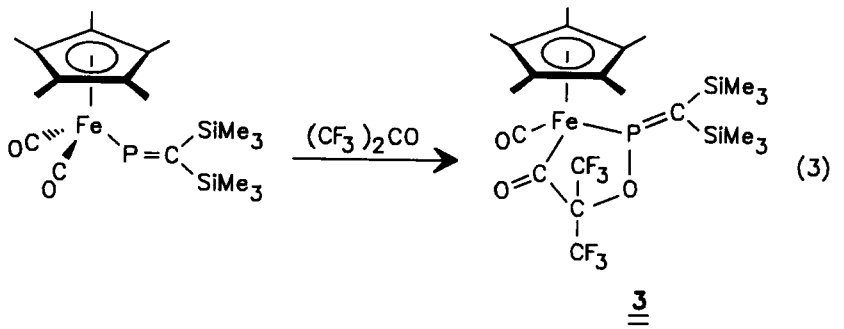
The reaction of $(C_5Me_5)(CO)_2Fe$-$P=C(NMe_2)_2$ with electron-poor alkenes such as methyl acrylate, dimethyl fumarate, and fumarodinitrile affords metal-functionalized 1,2-dihydrophosphetes **2**. Obviously the [2+2] cycloaddition of the components is followed by the rapid extrusion of dimethylamine[3].



(2)

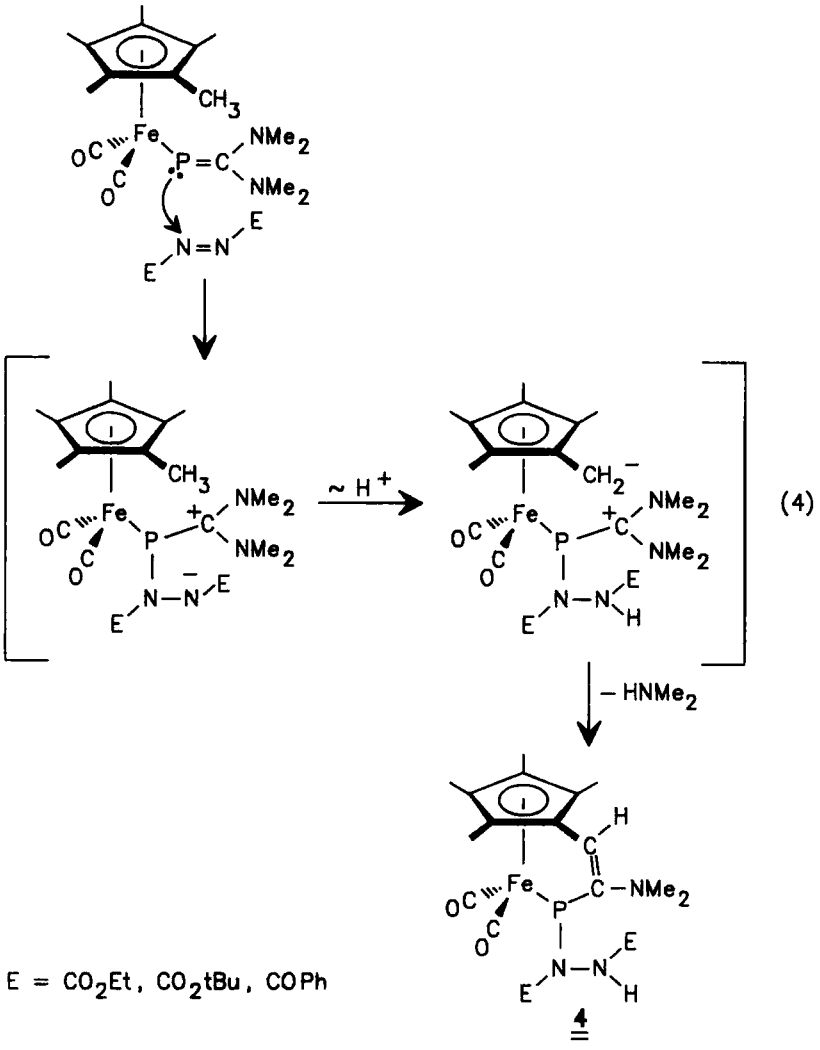
E = CN, CO_2Me; R = H, CN, CO_2Me; [Fe] = $Cp^*(CO)_2Fe$

The C=O bond in anhydrous hexafluoroacetone gives rise to a dipolar [3+2]-cycloaddition. Here the metalloheterocycle 3 is isolated (eq. 3).



(3)

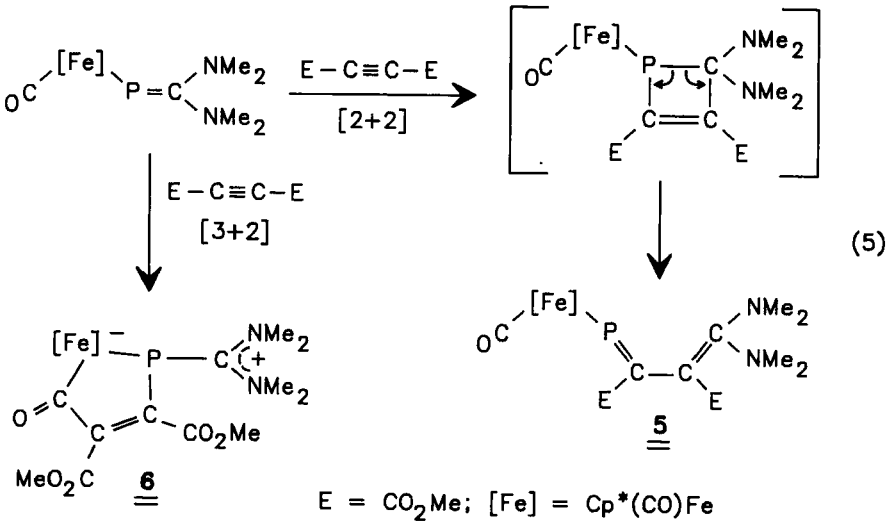
A quite different behavior is encountered when the amino-functionalized metallophosphaalkene is treated with azo compounds. This reaction results in the condensation of a ring methyl substituent with the bis(dimethylamino)methylene group to give compound 4 (eq. 4).



(4)

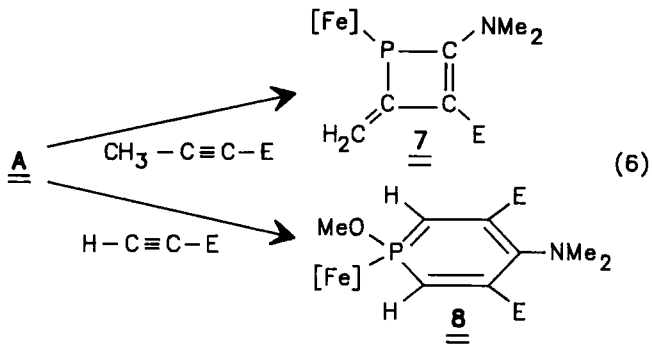
4

The same metallo-phosphaalkene and dimethyl acetylenedicarboxylate undergo reaction to give the metallated 1-phosphabutadiene 5 and the metalloheterocycle 6 in a 2:1 ratio[4].



(5)

A series of [3+2] and [2+2] cycloadditions including a [2+2] cycloreversion are invoked to explain the course of this transformation. In contrast to this methyl 2-butynoate and methyl propiolate give rise to the conversion of the metallo-phosphaalkene into the 1-metallo-2-methylene-1,2-dihydrophosphete 7 and the P-metallo-λ^5-phosphinine 8, respectively (eq. 6).



(6)

REFERENCES

1. E. Niecke, H.-J. Metternich, M. Nieger, D. Gudat, P. Wenderoth, W. Malisch, C. Hahner, and W. Reich, Chem. Ber., 126, 1299 (1993).
2. L. Weber, A. Rühlicke, H.-G. Stammler, and B. Neumann, Organometallics, 12, 4653 (1993).
3. L. Weber, O. Kaminski, H.-G. Stammler, B. Neumann, and V.D. Romanenko, Z. Naturforsch., 48b, 1784 (1993).
4. L. Weber, O. Kaminski, R. Boese, H.-G. Stammler, and B. Neumann, Z. Naturforsch., manuscript submitted.