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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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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>

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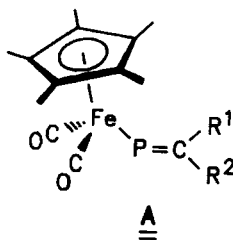
CYCLOADDITIONS WITH METALLO-PHOSPHAALKENES

LOTHAR WEBER^{*}, ANNETTE RÜHLICKE AND OLAF KAMINSKI

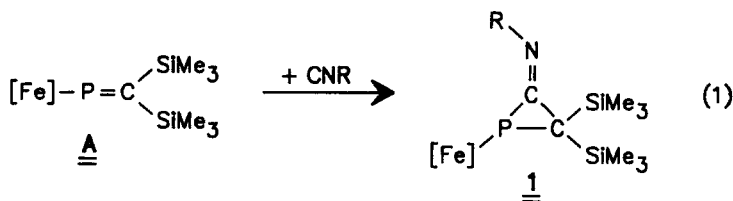
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Abstract Cycloadditions of metallo-phosphaalkenes such as $(C_5Me_5)(CO)_2Fe-P=CR^1R^2$ ($R^1 = R^2 = SiMe_3$, NMe_2 ; $R^1 = Ph$, $R^2 = SiMe_3$) are performed with isocyanides, electron-poor alkenes, alkynes and heteroalkenes.

Metallo-phosphaalkenes A¹ are polyfunctional molecules, which allow a number of interesting chemical transformations.

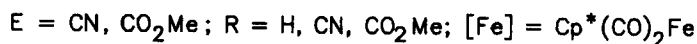
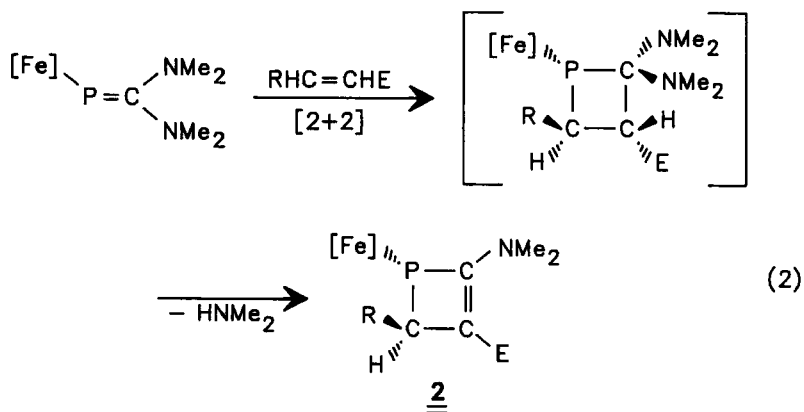


When metallo-phosphaalkenes A are exposed to equimolar amounts of isocyanides $[2 + 1]$ cycloadditions with the formation of 1-metallo-2-iminophosphiranes are observed (eq. 1)².

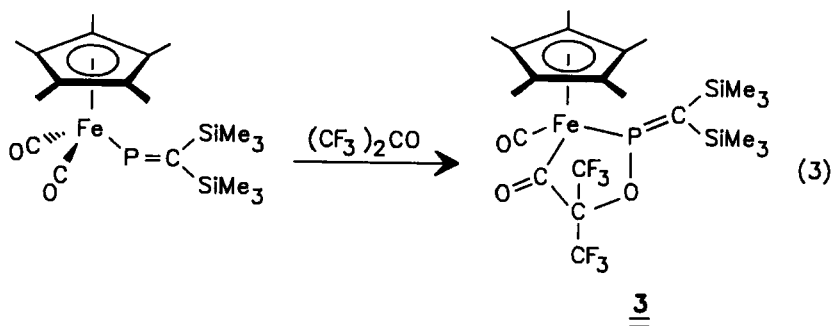


$R = Ph, o-Tol, 2,6-Xyl$; $[Fe] = Cp^*(CO)_2Fe$

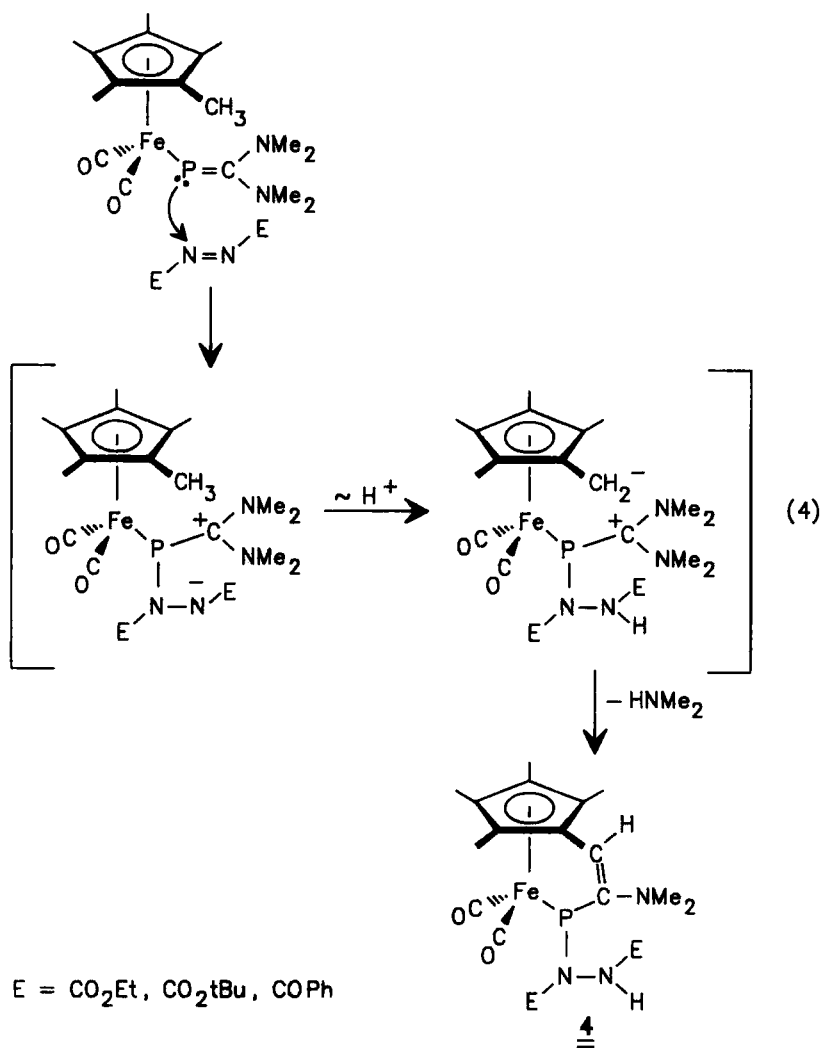
The reaction of $(C_5Me_5)(CO)_2Fe-P=C(NMe_2)_2$ with electron-poor alkenes such as methyl acrylate, dimethyl fumarate, and fumarodinitrile affords metal-functionalized 1,2-dihydrophosphetes 2. Obviously the $[2 + 2]$ cycloaddition of the components is followed by the rapid extrusion of dimethylamine³.



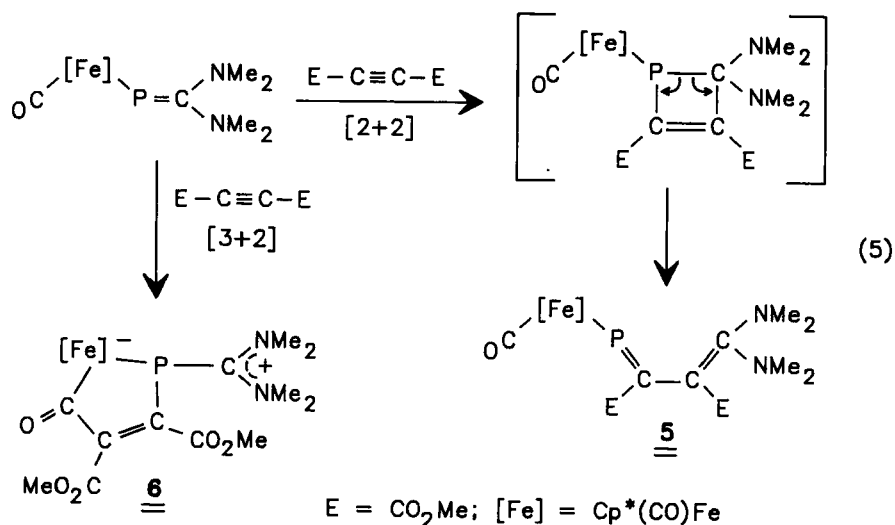
The C=O bond in anhydrous hexafluoroacetone gives rise to a dipolar [3+2]-cycloaddition. Here the metallocycle 3 is isolated (eq. 3).



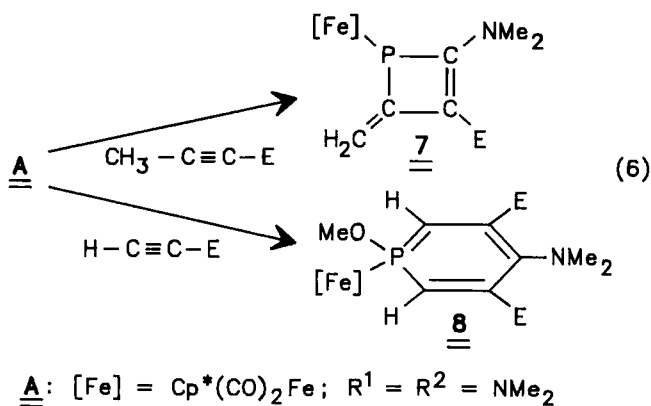
A quite different behavior is encountered when the amino-functionalized metallo-phosphaalkene is treated with azo compounds. This reaction results in the condensation of a ring methyl substituent with the bis(dimethylamino)methylene group to give compound 4 (eq. 4).



The same metallo-phosphaalkene and dimethyl acetylenedicarboxylate undergo reaction to give the metallated 1-phosphabutadiene 5 and the metallocycle 6 in a 2:1 ratio⁴.



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-butyrate 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-λ⁵-phosphinine 8, respectively (eq. 6).



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