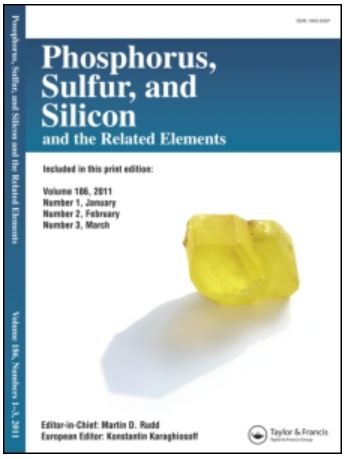

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P. Jutzi[a]; N. Brusdeilins[a]; U. Meyer[a]; S. Opiela[a]
[a] Faculty of Chemistry, University of Bielefeld, Bielefeld, FRG

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THE PENTAMETHYLCYCLOPENTADIENYL LIGAND AT PHOSPHORUS OR ARSENIC - EFFECT ON SMALL-MEMBERED RINGS AND DOUBLE-BOND SPECIES

P. JUTZI, N. BRUSDEILINS, U. MEYER, AND S. OPIELA
Faculty of Chemistry, University of Bielefeld,
4800 Bielefeld, FRG.

Abstract The versatility of the pentamethylcyclopentadienyl(Cp^*) ligand is based on its ability for kinetic stabilization and on its potential application as a leaving group[1,2,3]. Here we report new results from the chemistry of diphosphenes and arsaphosphenes as well as of three- and four-membered ring systems. Concerning the Cp^* reactivity, we have studied: I) nucleophilic substitution reactions, II) homolytic Cp^*-El bond cleavages, and III) Cp^* migration to Transition Metals.

DIPHOSPHENES AND ARSAPHOSPHENES

Following classical routes, the double bond species **1** - **5** have been synthesized.

$Cp^*P = PCp^*$ **1** $Cp^*P = PMes^*$ **2** $Mes^*P = AsCp^*$ **3**
$Cp^*P = AsMes^*$ **4** $Cp^*P = AsCp^*$ **5** Mes = Supermesityl

Beside the chemistry expected for P=P or P=As systems, we have observed:

Nucleophilic Substitution of the Cp* Ligand

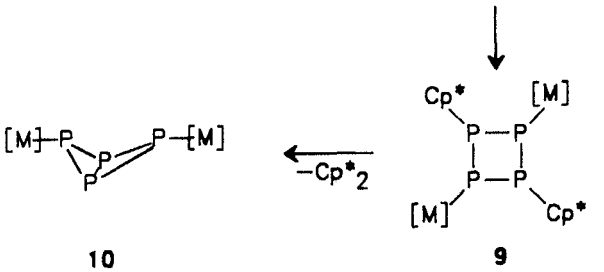
We have already reported on the substitution with bulky lithium alkyls and amides[1] as well as with lithium supermesityl phosphide[4]. Reaction of **2**, **3**, and **5** with sodium pentamethylcyclopentadienyl(dicarbonyl)ferrate leads

to the iron substituted double-bond systems **6**, **7**, and **8**, resp.. In a multistep synthesis, the known[4] triphospha-allyllithium species **11** is formed from **2** and methyllithium.

2 + $NaFe(CO)_2Cp^*$ ---> $Cp^*(CO)_2FeP = PMes^*$ (**6**)

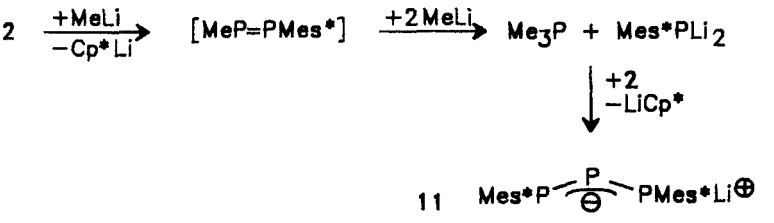
3 + $NaFe(CO)_2Cp^*$ ---> $Cp^*(CO)_2FeAs = PMes^*$ (**7**)

1 + $NaFe(CO)_2Cp^*$ ---> $Cp^*(CO)_2FeP = PCp^*$ (**8**)



10 **9**

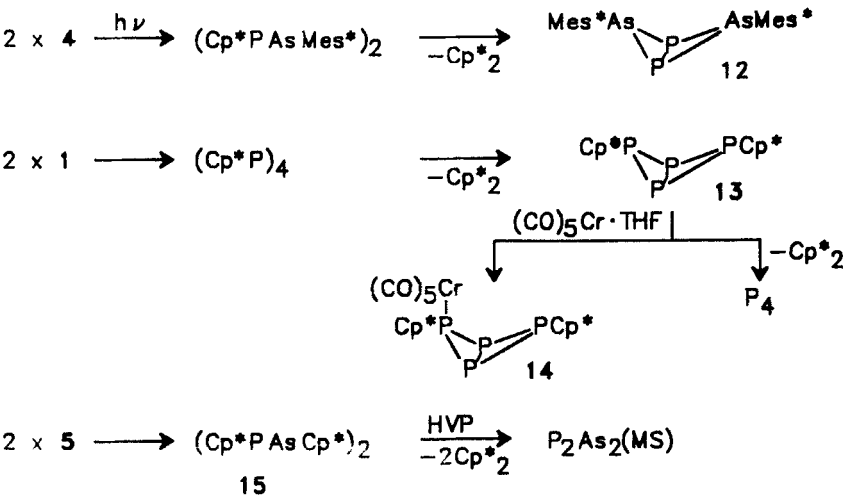
[M] = $Fe(CO)_2Cp^*$



Homolytic Cp*El Bond Cleavage in [2 + 2]-Cycloaddition Products

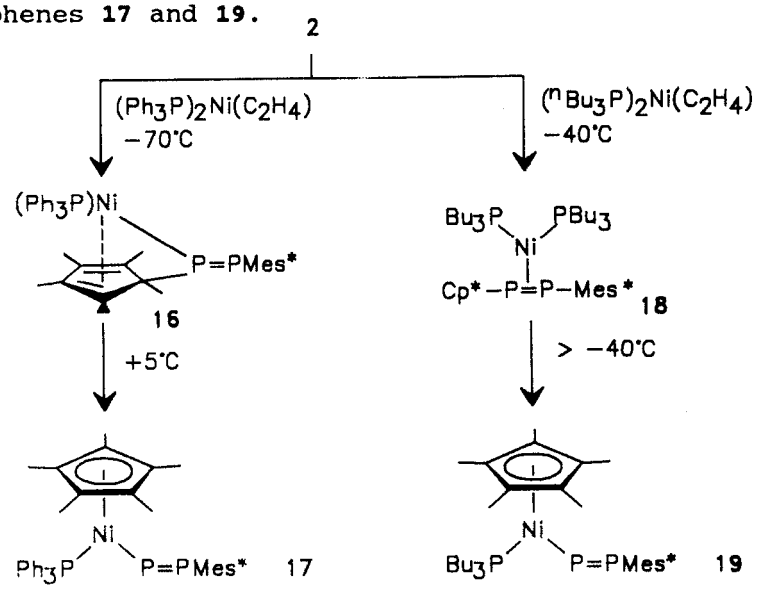
Few examples of this type of reaction have already been presented[5,6] Four-membered ring compounds, formed by [2+2]cycloaddition of the double bond species **1**, **4**, **5**, and **8**, show easy cleavage of Cp^*-El bonds, which leads to butterfly systems, such as **13**, **12**, **15**, and **10**, resp., and furtheron to P_4 and As_2P_2, resp..

The reactive intermediate **13** can be trapped via complexation (formation of **14**)



Cp*-Migration to a Transition Metal

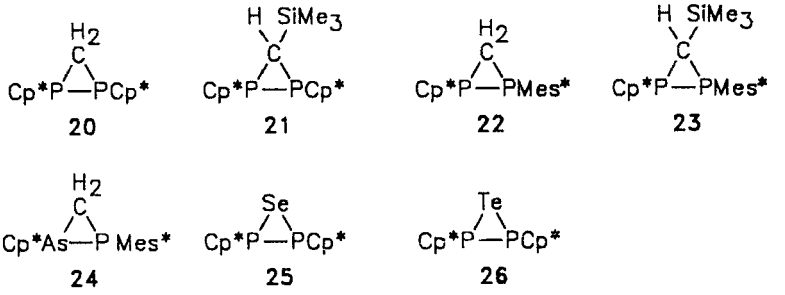
Some examples for this useful synthetic method have already been described[7,8]. Here we present results from our studies in nickel chemistry. Compounds of the type **16** und **18** are intermediates in the reaction of **2** with zero-valent nickel, which finally leads to the labile nickel-substituted diphosphenes **17** and **19**.



THREE-MEMBERED RING-SYSTEMS

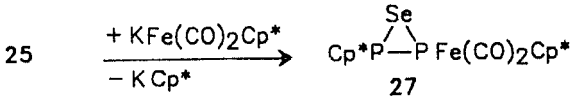
Synthesis and some reactions of the cyclotri-

phosphane $(Cp^*P)_3$ have already been described[9,10]. Treatment of **1**, **2**, and **3** with the corresponding diazomethanes leads to the ring compounds **20** - **24**; with selenium and tellurium, the addition products **25** and **26** are formed.



Nucleophilic Substitution of the Cp* Ligand

The Cp^* ligand in **25** can be replaced by the $Cp^*(CO)_2Fe$-unit in a substitution process, which leads to the iron-substituted diphosphaselenacyclopropane **27**.



The ^{31}P-NMR data of the compounds **1** - **27** are of diagnostic value.

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