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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 $Mes = Supermesity1$

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 amides¹ as well as with lithium supermesityl phosphide⁴. 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 known4 triphosphaallyllithium 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)

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

2
$$\xrightarrow{+\text{MeLi}}$$
 [MeP=PMes*] $\xrightarrow{+2\text{MeLi}}$ Me₃P + Mes*PLi₂ \downarrow +2 \downarrow -LiCp*

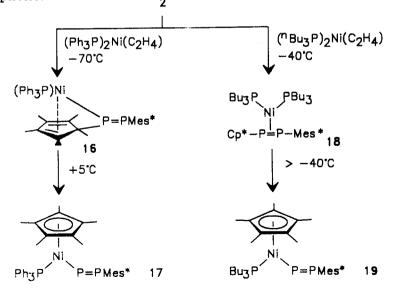
Homolytic Cp*El Bond Cleavage in [2 + 2]-Cycloaddition Products

Few examples of this type of reaction have already been ${\tt presented}^{\tt 5.6} \quad {\tt Four-membered} \quad {\tt ring} \quad {\tt compounds}, \quad {\tt formed}$ [2+2]cycloaddition of the double bond species 1, 4, 5, and 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 interminates 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 described9.10. 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 a substitution process, which leads to the substituted diphosphaselenacyclopropane 27.

25
$$\xrightarrow{+ \text{KFe(CO)}_2\text{Cp*}} \xrightarrow{\text{Se}} \text{Cp*P} \xrightarrow{-\text{P} \text{Fe(CO)}_2\text{Cp*}}$$

The 31 P-NMR data of the compounds 1 - 27 are of diagnostic value.

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