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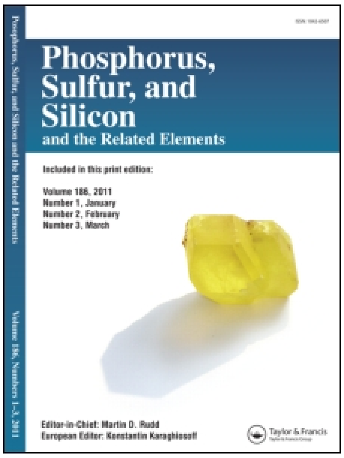

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DIFFERENT WAYS OF P_4 TRANSFORMATION IN THE COORDINATION SPHERE OF TRANSITION METALS

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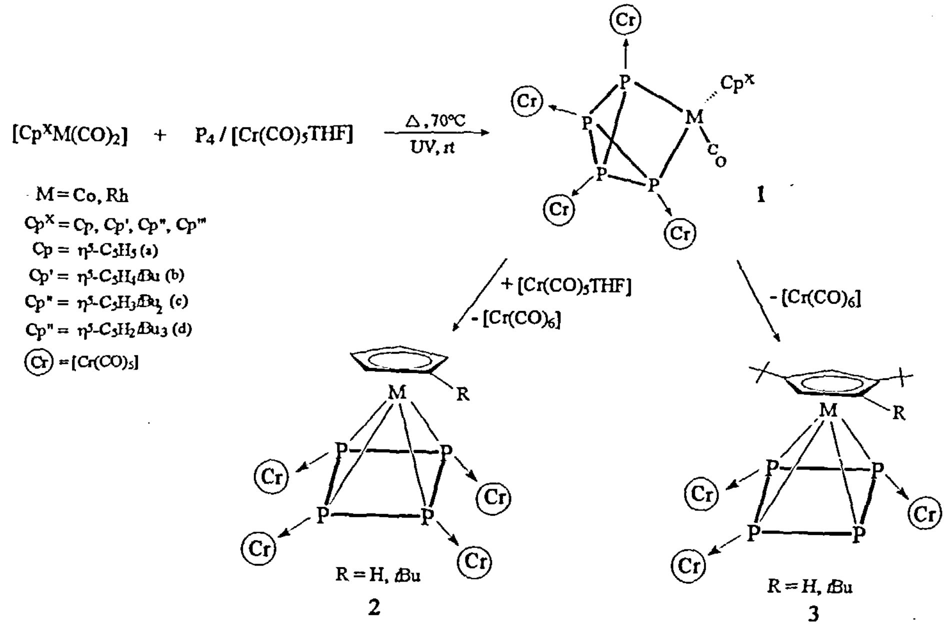
Abstract The transformation pathway of tetrahedral P_4 to the corresponding P_n ligands has been studied by the three-component-reaction are found to depend on the electron number of the complex fragments used. In the case of complexes forming fragments with an even number of valence electrons, a stepwise P-P bond cleavage is observed with a bicyclotetraphosphine intermediate to give a *cyclo*-P_4 containing product. Complexes with an odd number of valence electrons cause a P_1/P_3 fragmentation. A possible product of this reaction is a phosphido complex of the type $[L_nM{\equiv}P{\rightarrow}M'(CO)_5]$ (M' = Cr, W), which is self-stabilised by dimerisation. The phosphido complex $[(tBuO)_3W{\equiv}P{\rightarrow}M(CO)_5]$ (M = Cr, W) is formed via the reaction of $W_2(OtBu)_6$ with RC≡P in the presence of the Lewis acids $[M(CO)_5THF]$.

INTRODUCTION

Recently we studied the reaction of white phosphorus with transition metal carbonyl complexes, where *cyclo*-P_4 containing complexes are obtained.[1] To study the transformation pathway of the P_4 tetrahedron within the coordination sphere of transition metals we have developed the concept of the three-component-reaction. By adding simple metal carbonyls such as $[Cr(CO)_5THF]$ to the reaction mixture of P_4 and the corresponding coordination compound, the lone pairs of the first formed P_n ligands are able to coordinate to the carbonyl complexes. Thus intermediates may be stabilised along the reaction pathway.

RESULTS AND DISCUSSION

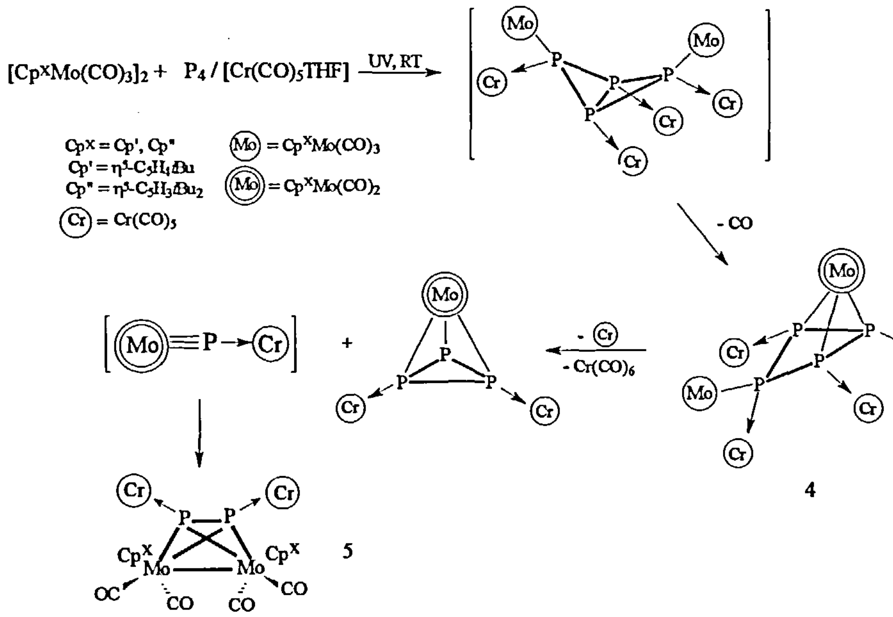
Coordination compounds forming fragments with an even number of valence electrons such as $[Cp^xM(CO)_2]$ (M = Co, Rh; $Cp^x = \eta^5\text{-}C_5H_{5-m}tBu_m$, m = 0, 1, 2, 3) react with P_4 in the presence of $[Cr(CO)_5THF]$[2-4] under either thermal or photochemical conditions to form the bicyclotetraphosphine derivatives **1** and the *cyclo*-P_4 ligand complexes **2** and **3**. All compounds are stabilised by chromium pentacarbonyl moieties.



These results suggest the following reaction pathway: (i) First a P-P edge of the P_4 tetrahedron is opened by the metal complex making the lone pairs of all the phosphorus atoms in the newly formed tetraphosphabicyclobutane chemically active for coordination to $[Cr(CO)_5]$ groups thus forming complex 1. (ii) The attack of a second $[Cp^xM(CO)]$ fragment at a P-P edge is prevented by the $[Cr(CO)_5]$ groups and therefore CO abstraction from the coordinated metal complex triggers the opening of another P-P bond in 1 and the formation of complexes 2 and 3 with square planar *cyclo*-P_4 moieties. The substitution pattern of the *cyclo*-P_4 ring depends on the steric influence of the Cp^x ligands. In the case of the CpM or Cp'M complexes all four P atoms coordinate to $[Cr(CO)_5]$ groups. An additional tBu-group in the case of Cp"M complexes 3 results in only three of the phosphorus atoms bonding to a $[Cr(CO)_5]$ moiety. Adding a third *t*Bu-group also yields complexes of type 3, but in solution there is a strong tendency for conversion into species with two or one Cr-carbonyls

Our attempts to examine parallel reactions with $[Cp^*Ir(CO)_2]$ led to bicyclotetraphosphine derivatives where only three of the P atoms coordinate to Cr-carbonyls. In one of these bicyclotetraphosphines a CO molecule has inserted into an Ir-P bond.

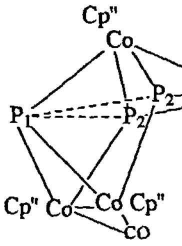
For coordination compounds forming fragments containing an odd number of valence electrons a P_1/P_3-fragmentation of the P_4 tetrahedron is observed. The scheme shown below gives an overview of preliminary results of the reaction of $[Cp^xMo(CO)_3]_2$ with P_4 in the presence of $[Cr(CO)_5THF]$.



The reaction proceeds with the formation of a bicyclotetraphosphine intermediate anchored by two Mo complex fragments. One of the Mo units subsequently adopts a capping position. We have structural evidence for a fragmented species of 4, obtained after chromatographic workup. The P_3/P_1-fragmentation results in a *cyclo*-P_3-ligand compound and a complex where a terminal phosphido ligand coordinates to a $Cr(CO)_5$ group. Such species are not stable as monomers and a dimerisation readily occurs. The tetrahedral P_2Mo_2 complex 5 was structurally characterised.

Additional evidence for a P_1/P_3 fragmentation was obtained with the isolation of complex 6, formed by the two component reaction between $Cp''Co(CO)_2$ and P_4 under photochemical conditions.[5] Complex 6 shows a new type of a kite-like distorted planar P_4 ligand capped by a Cp"Co moiety. A $[(Cp''Co)_2(CO)]$ dimer coordinates to three of the phosphorus atoms. The most remarkable feature of the structure is the long P···P distance between P(1) and P(2) of 2.503 Å. EHMO calculations suggest that it can be considered as a weak P···P contact and is therefore on the borderline between a P-P bonding interaction and a Van der Waals contact.

Two other synthetic approaches to phosphido ligand complexes containing a metal phosphorus triple bond are also possible. The phosphinidenes $[\{M(CO)_5\}_2PCl]$ (M = Cr, W) react with $[Cp^*NiCO]^-$ to give Ni_2P_2-tetrahedral complexes. There are two indications of a phosphido complex as an intermediate.



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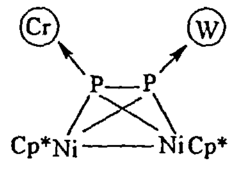
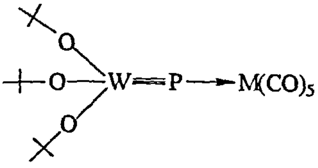


Ⓜ = $M(CO)_5$; M = Cr, W

7



M = Cr (a), W (b)

8

Firstly, the reaction of the phosphinidene with $[Cp^XMo(CO)_3]^-$ leads to a compound where a CO molecule is inserted into a P-P bond. Secondly, the reaction of $[Cp^*NiCO]^-$ with an equimolar mixture of the phosphinidenes of chromium and tungsten reveals, in addition to the homonuclear chromium and tungsten complexes, a statistically mixed substituted tetrahedral compound 7.

Another approach to phosphido complexes was observed by the reaction of $[W_2(OtBu)_6]$ with RC≡P in the presence of the Lewis acids $[M(CO)_5THF]$ (M = Cr, W).[6] The formation of the alkylidyne $[(tBuO)_3W{\equiv}CtBu]$ and the phosphido complexes 8a,b occurs. An additional reaction between the first formed phosphido complex and phosphaalkynes is not completely hindered and four membered ring compounds are also formed. Finally a 1,3-OtBu shift results to give phosphaalkoxy derivatives. By fractional crystallisation we were able to enrich a solution with the desired phosphido complexes 8a,b. The monomeric nature of these products is supported by two separate experiments.

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