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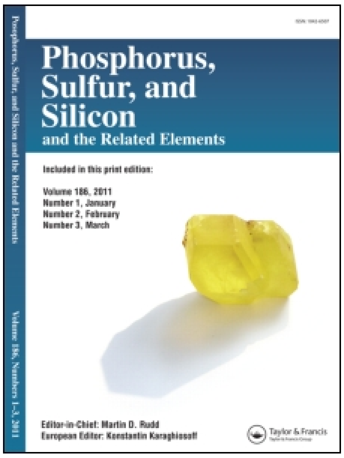

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Cyclo-P_4 Ligands with a Maximum of Electron-Donating Ability

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CYCLO-P_4 LIGANDS WITH A MAXIMUM OF ELECTRON-DONATING ABILITY

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Abstract The reactions of P_4 with metal carbonyls of chromium, tungsten and iron lead to square planar *cyclo*-P_4 ligand complexes and to a rectangular distorted P_4 ligand complex, respectively. Furthermore the study of the transformation pathway of tetrahedral P_4 to the corresponding P_x ligands reveals a stepwise (PP) bond cleavage with a bicyclotetraphosphine intermediate to give a *cyclo*-P_4 containing product.

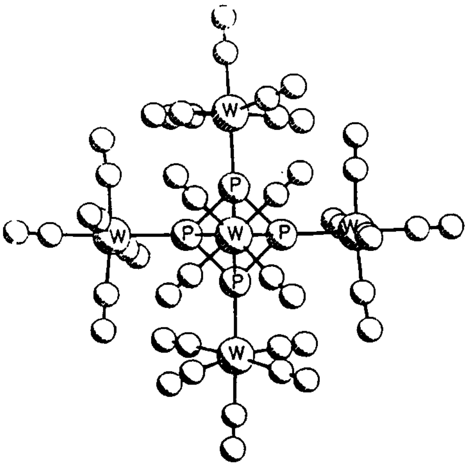
INTRODUCTION

The reactions of white phosphorus with cyclopentadienyl carbonyl complexes of various transition metals have been extensively studied, in contrast to the reaction of P_4 with carbonyl complexes.[1] In addition, only few studies concerning the transformation pathway of tetrahedral P_4 to the corresponding P_x ligands have been made. In the light of this, we have identified the following goals:

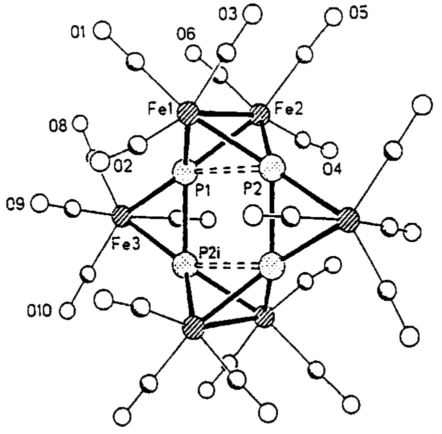
1. The reaction behavior of P_4 with tungsten, chromium and iron carbonyls.
2. The investigation of the transformation pathway of tetrahedral P_4 to the corresponding P_x ligands using the concept of three-component reactions.

RESULTS AND DISCUSSION

The reaction of white phosphorus with $[M(CO)_5THF]$ affords $[(CO)_4M(\eta^4\text{-}P_4\{M(CO)_5\}_4)]^2$ (1a: M = W, 1b: M = Cr) with a square planar *cyclo*-P_4 ligand serving as a 12-electron donor with all P atoms coordinated to the $[M(CO)_5]$ groups. The P-P distances in 1a are equal and, at 2.153 Å, shorter than those of the P-P single bonds. This structure also exists in solutions with non-coordinating solvents such as CH_2Cl_2 or n-pentane, whereas when a donor solvent such as THF or acetone is added, reversible changes to this structure are observed in the $^{31}P\{^1H\}$ NMR spectra.



1a



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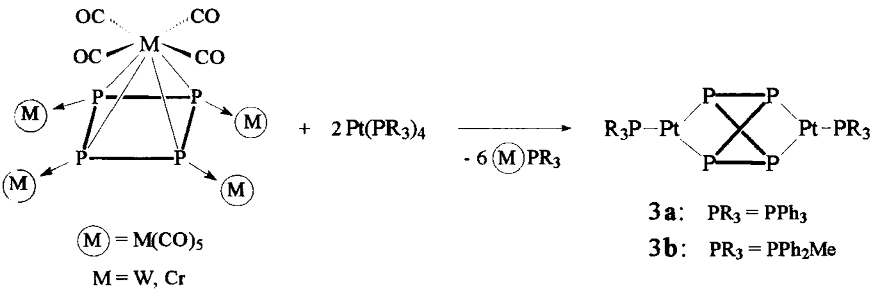
The reaction of P_4 with $Fe_2(CO)_9$ gives the highly symmetrical complex $[\{Fe(CO))_4(\eta^2\text{-}P_2)\}_2\{\mu\text{-}Fe_2(CO)_6\}_2]^3$ (2) which contains a distorted rectangular P_4 unit $((P_2)_2)$. The long P···P distance is, at 2.610 Å, too long to be described as a bonding interaction, but is bridged unusually, by $[Fe_2(CO)_6]$ fragments.

The reactivity of 1 was studied by the following reaction with tetrakis(triorganylphosphino)platinum(0) (Eq. (1)). The complexes 3a,b were formed, in which a tetraphosphorus ligand is fixed by two phosphinoplatinum fragments. The compounds were characterized by $^{31}P\{^1H\}$ NMR and ^{195}Pt NMR spectroscopy.

Furthermore the chlorination of 1a with C_2Cl_6 yields first a dichloroderivative 4 (Eq. (2)) which is rapidly transformed by traces of moisture to the more stable phosphahydroxy derivative 5. The X-ray structure of 5 reveals that the previously planar P_4 ring is bent. In 5 an allylic P_3 unit is capped by a $[W(CO)_2(CH_3CN)_2Cl]$ group.[4]



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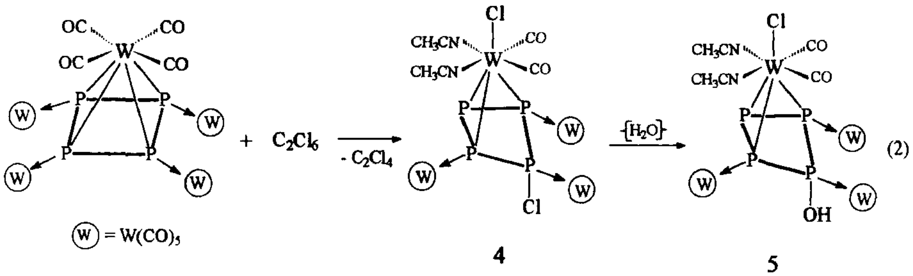
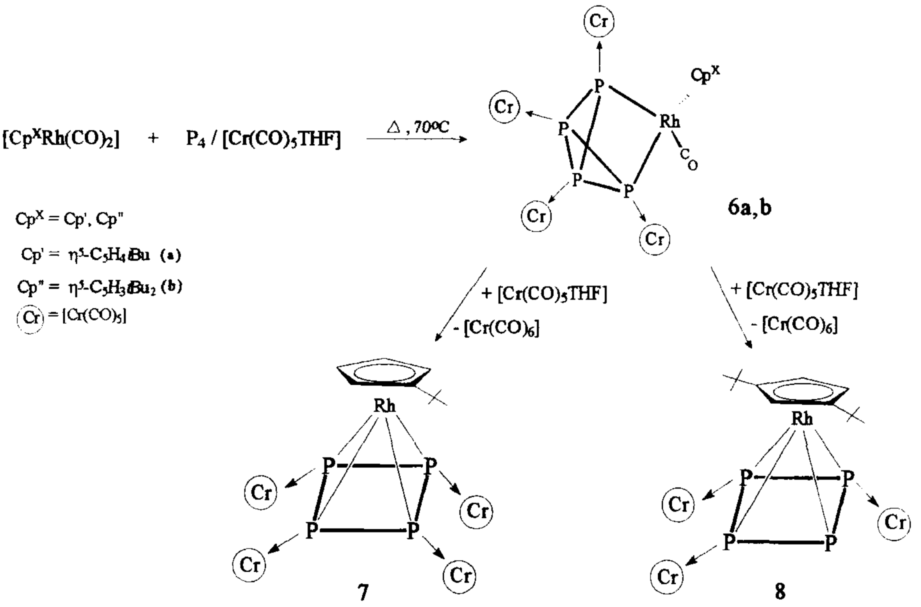


Our second field of interest concerns the study of the transformation of tetrahedral P_4 into the corresponding P_x ligands. In order to trap intermediates along the reaction pathway we have used the simple concept of binding the lone pairs of the phosphorus atoms by addition of $[Cr(CO)_5THF]$ to the reaction mixture of P_4 and the coordination compound (three-component reaction). E.g. the thermal reaction of $[Cp^xRh(CO)_2]$ ($Cp^x = \eta^5\text{-}C_5H_{5\text{-}n}{}^tBu_n$, n = 1, 2) with P_4 in the presence of $[Cr(CO)_5THF]$ [5] leads to the bicyclotetraphosphine derivative $[Cp^xRh(CO)\{\eta^2\text{-}P_4(Cr(CO)_5)_4\}]$ 6a,b and the *cyclo*-P_4 ligand complexes $[Cp^xRh\{\eta^4\text{-}P_4(Cr(CO)_5)_n\}]$ (7: Cp^x = Cp', n = 4; 8: Cp^x = Cp", n = 3). All compounds are stabilized by the chromium pentacarbonyl moieties.



First a P-P edge of the P_4 tetrahedron is opened by the Rh complex making the lone pairs of all the phosphorus atoms in the newly formed tetraphosphabicyclobutane chemically active for the coordination to $[Cr(CO)_5]$ groups. 6a,b are formed. The attack of a second $[Cp^xRh(CO)]$ fragment at a P-P edge is prevented by $[Cr(CO)_5]$

groups. Therefore CO abstraction from the coordinated Rh complex triggers the opening of another P-P bond in 6 and the complexes 7 and 8 with square planar *cyclo*-P_4 moieties are formed. The coordination pattern of the *cyclo*-P_4 ring depends on the steric influence of the Cp^x ligands. In the case of the Cp'Rh complex 7 all four P atoms coordinate to $[Cr(CO)_5]$ groups. However, there is an angle between the Cp' ring and the P_4 plane of 7 due to the steric hindrance caused by the t-Bu group of the Cp' ligand to one $[Cr(CO)_5]$ moiety. In the Cp"Rh product 8 only three of the P atoms are able to use their lone pairs to bind $[Cr(CO)_5]$ units. The three-component reaction is also possible under UV conditions allowing less reactive carbonyls to be involved in these reactions.

$[Cr(CO)_5]$ moieties serve two functions in these reactions. Firstly they act as strong Lewis-acids by binding the lone pairs of the P atoms and stabilizing intermediates along the reaction pathway. Secondly they activate the first reaction component by promoting the lost of CO. No reaction is observed between e.g. $[Cp^xRh(CO)_2]$ and P_4 up to 110 C, but in the presence of $[Cr(CO)_5THF]$ the reaction proceeds at temperatures as low as 70 C.

This transformation pathway is valid for complexes forming fragments with an even number of valence electrons. In the case of fragments containing odd numbers of valence electrons usually the fragmentation of the P_4 tetrahedron into P_1- and *cyclo*-P_3 complexes is observed in two component reactions.[6,7] Our recent research concerns the three component reaction of those systems. In particular, the reaction of $[Cp^xMo(CO)_3]_2$ with P_4 in the presence of $[Cr(CO)_5THF]$ has been investigated.

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