

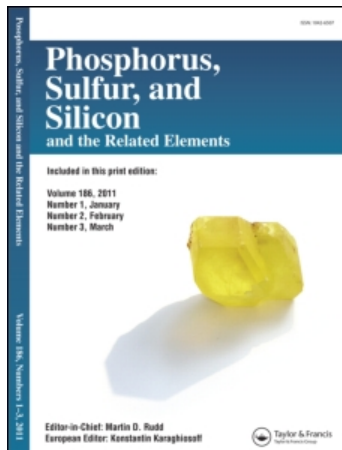
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The Reaction Behavior of White Phosphorus with Metal Complexes of Cobalt and Molybdenum

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THE REACTION BEHAVIOR OF WHITE PHOSPHORUS WITH METAL COMPLEXES OF COBALT AND MOLYBDENUM

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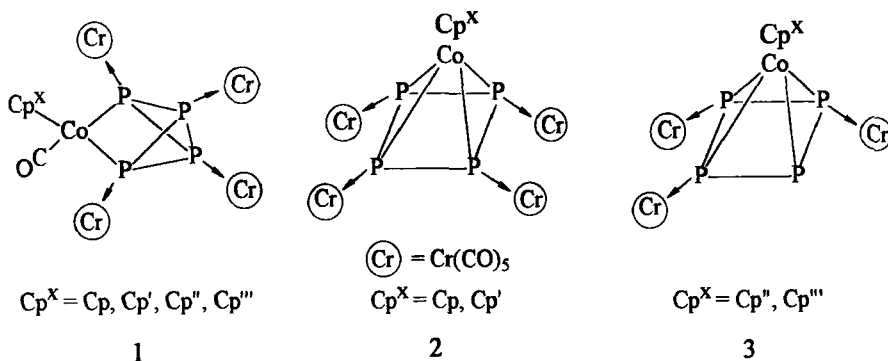
Abstract Studies of the reaction pathway of tetrahedral P_4 with cobalt- and molybdenum coordination compounds lead to novel complexes containing P_x -ligands ($x = 2, 4$) in unusual binding modes.

INTRODUCTION

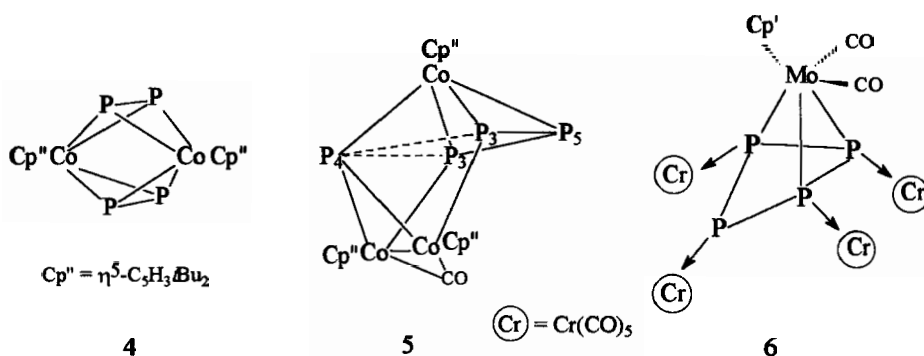
The reaction of white phosphorus with coordination compounds has been studied extensively.¹ However, little attention has been paid to the investigation of the reaction pathways of the tetrahedral P_4 to the corresponding P_x -ligands.

RESULTS AND DISCUSSION

The three-component reaction of $[Cp^xCo(CO)_2]$ ($Cp^x = Cp, Cp', Cp'', Cp'''$; $Cp' = \eta^5-C_5H_4tBu$, $Cp'' = \eta^5-C_5H_3tBu_2$, $Cp''' = \eta^5-C_5H_2tBu_3$) with P_4 in the presence of $[Cr(CO)_5THF]$ under UV conditions provides an explanation of the reaction pathway in the case of complexes forming fragments with an even number of valence electrons. The reaction proceeds via a bicycletetraphosphine derivative 1 to give the cyclotetraphosphine complexes 2 and 3 as the final products.²



The comparison of the reaction described above with the analogous photochemical two component reaction of P_4 with $[Cp''Co(CO)_2]$ affords besides $[Cp''Co(\mu, \eta^2-P_2)]_2$ (**4**)³ the major product $[(Cp''Co)_3(P_4)(CO)]$ (**5**).⁴ **5** 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(3) and P(4) of 2.503 Å, which can be considered as a borderline case between a still bonding P-P bond and a Van der Waals contact.



$[Cp^XMo(CO)_2]_2$ ($Cp^X = Cp', Cp''$), which forms fragments with an odd number of valence electrons, reacts with P_4 in the presence of $[Cr(CO)_5THF]$ under photochemical conditions to give at least three different P_X ligand containing products.⁵ **6** is one of the products. In **6** the $[Cp^XMo(CO)]$ fragment binds to three P-atoms of the non planar P_4 ring. The P(4)-atom lies out of the plane of the other P-atoms. **5** as well as **6** could be intermediates in the reaction to P_1 - and P_3 -ligand complexes.

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