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Recent Advances in the Chemistry of Complexes with P_n Ligands

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Starting with $[Cp^*FeP_5]$ and mono as well as dinuclear $Cp^R(CO)Co$ -complexes novel cobalt complexes with P_5 , P_4 , P_2 and P_1 ligands are formed. Room temperature P_4 activation with $[(Cp^*(OC)_2Re)_2]$ ($Re=Re$) is described.

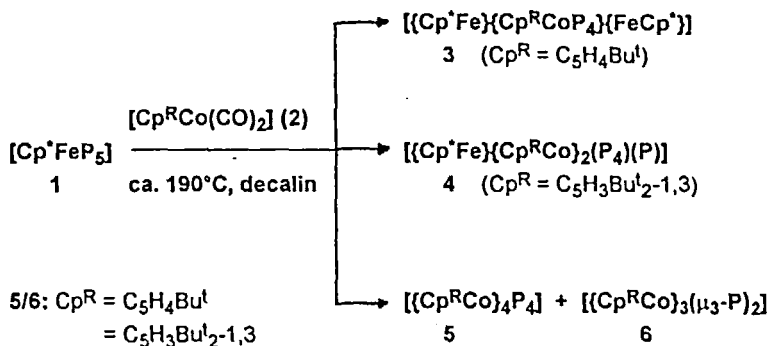
Keywords: P_n ligands; P_4 activation; iron; cobalt; rhenium complexes; PX ligands

INTRODUCTION

With the synthesis ¹ of the sandwich complex $[Cp^*FeP_5]$ (**1**) a new chapter on compounds with substituent-free („naked“) P_n ligands was discovered. Stacking, ring-transfer, ring-opening, and P_5 ring-cleavage reactions can be realized. On the other hand, for some complexes oxidation of P_1 to μ_3 - PX ligands ($X = O, S$) was achieved by air or S_8 . ² The photolysis of $[(Cp^R(OC)_2Fe)_2]$ ($Fe-Fe$) and P_4 affords some insight into mechanistic aspects of such reactions. ³

RESULTS

The cothermolysis of **1** and **2** affords the following series of P_n complexes:



1 forms with the dinuclear cobalt compound $[(\text{Cp}^R\text{Co}(\mu\text{-CO}))_2]$ molecule **7**,

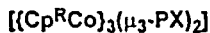


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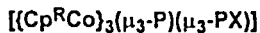
a sandwich complex with additional $\eta^2\text{:}\eta^2\text{-cyclo-P}_5$ coordination to $\{\text{Co}_2\text{Cp}^R_2(\mu\text{-CO})\}$. ⁴

The X-ray crystal structure of **3** reveals a „triple-decker“ with a five-membered CoP_4 „middle deck“.

The oxidation of **6** with O_2 , S_8 , and $\text{Se}_{(\text{grey})}$ gives access to the classes **8** and **9** with $(\mu_3\text{-PX})$ ligands in the axial position of the trigonal bipyramids.

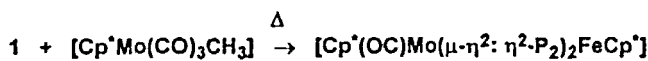


8: X = O, S, Se

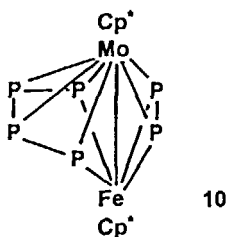


9: X = Se

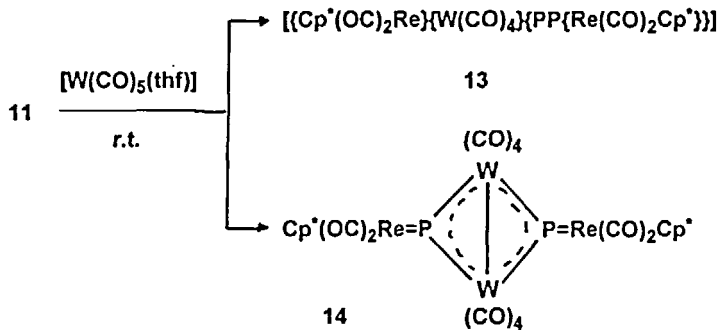
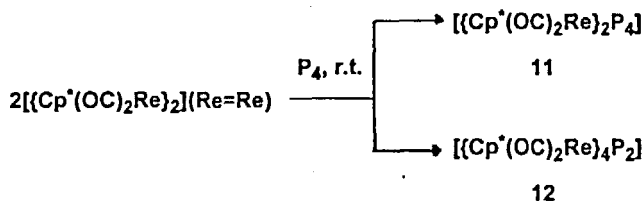
A novel type of „ P_6 “ ligand has been realized for complex **10**. ⁵



$\downarrow \text{P}_4, \Delta$



The room-temperature activation of P_4 and P_2 has been studied for the following reactions: ⁶



The skeleton of **11** consists of a butterfly-type molecule with $\text{Re}(\text{CO})_2\text{Cp}^*$ at the wing tips. The P_2 ligand ($d(\text{P}-\text{P}) = 2.23 \text{ \AA}$) of the diphosphinidene complex **12** can formally be regarded as $8e^-$ donor $\text{P}=\text{P}$.

Treatment of **11** with excess $[\text{W}(\text{CO})_5(\text{thf})]$ leads to **13**, a cluster with a chiral ReWP_2 tetrahedrane framework, and **14** where P_2 is cleaved at room temperature into two P_1 -phosphinidene ligands. X-ray crystallographically a planar arrangement of the $\text{Re}_2\text{W}_2\text{P}_2$ core was determined.

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