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Phosphorus, Sulfur, and Silicon and the Related Elements

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Unusual Phosphorus Ligands

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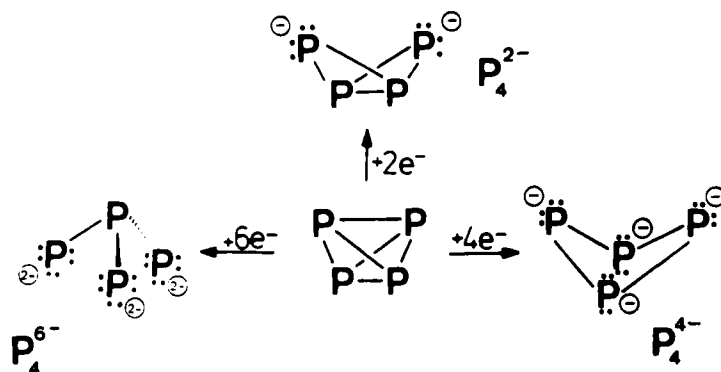
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UNUSUAL PHOSPHORUS LIGANDS

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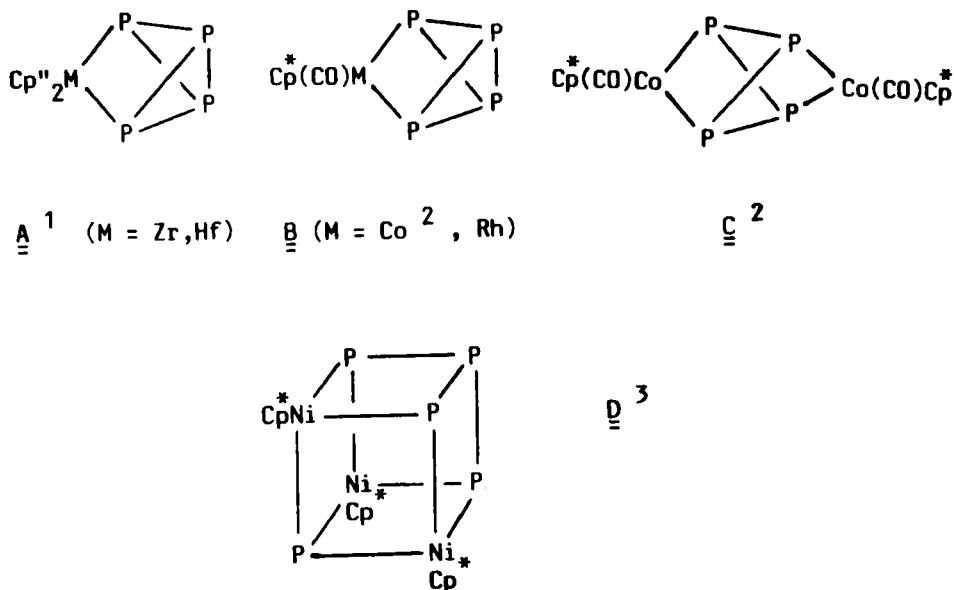
Abstract A variety of novel coordination complexes with cyclo-P₃, cyclo-P₄, cyclo-P₅, P₄²⁻, P₄⁴⁻ and P₄⁶⁻ as ligands will be described.

The two-, four- and six-electron reduction of white phosphorus, P₄, formally gives the polyphosphides P₄ⁿ⁻ (n = 2, 4, 6; Scheme 1).



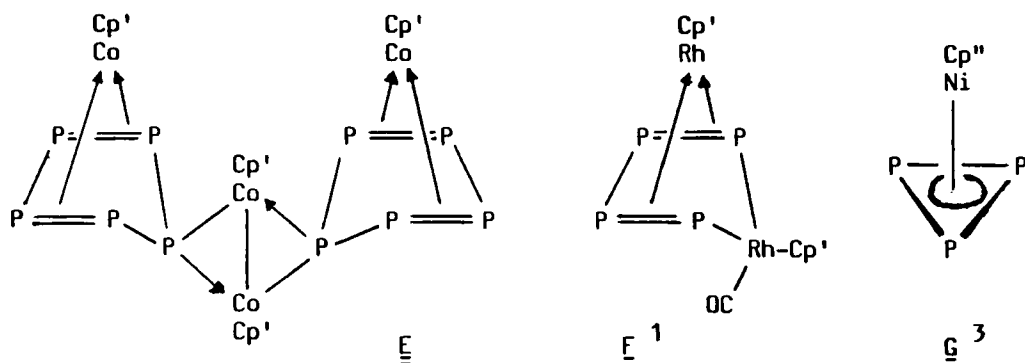
Scheme 1

The cothermolysis of [Cp^{''}₂M(CO)₂] (M = Zr, Hf) or [Cp^{*}M(μ-CO)]₂ (M = Co, Rh, Ni) and P₄ affords as oxidative addition products complexes A, the metallatetraphosphatricycloalkanes B, C and the nickelaphosphacubane D.



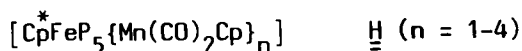
With LiR ($R = \text{Me, tBu}$) one PP bond of the "butterfly wings" of $\underline{\underline{A}}$ is cleaved with formation of $[\text{Cp}''_2\text{ZrP}(\text{Li})\text{PPP}(\text{R})]$. P...P distances of 2.606(1) and 2.560(2)|2.597(2) Å have been found crystallographically ² for the PCoP bridge(s) of the cobaltatetraphosphatetricycloalkanes $(\text{Cp}^*(\text{CO})\text{Co} \leftarrow \text{O} \rightarrow \text{CH}_2, \text{P} \leftarrow \text{O} \rightarrow \text{CH}) \underline{\underline{B}} \quad (M = \text{Co})$ and $\underline{\underline{C}} \quad \underline{\underline{D}} \quad (1 \times \text{P}_4^{6-}, 1 \times \text{P}^{3-}; d^6 \text{Ni})$ reveals an interesting parallel to the solid-state structure of $\text{La}_6\text{Ni}_6\text{P}_{17}$ ($4 \times \text{P}_4^{6-}, 1 \times \text{P}^{3-}$) ⁴.

The cothermolysis of $[\text{Cp}'\text{M}(\text{CO})_2]$ ($M = \text{Co, Rh}$) or $[\text{Cp}''\text{Ni}(\mu\text{-CO})]_2$ and P_4 gives the new P_x complexes $\underline{\underline{E}} - \underline{\underline{G}}$.

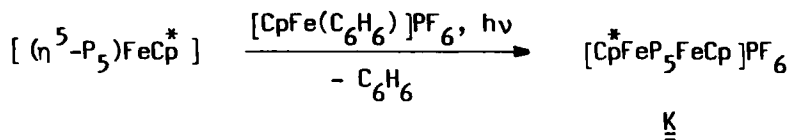


$\underline{\underline{E}}$ is the first example with the 7e-donor variant of the cyclo- P_5 ligand. $\underline{\underline{E}}$ can formally be regarded as a metallatetraphosphacyclopentadiene complex with η^4-P_4 ligand (P_4^{2-} isomer). If $\underline{\underline{E}}$ is heated for 60 minutes to 150°C (xylene) CO eliminates and one PP bond is cleaved with formation of $[Cp'Rh(P_2)_2RhCp']$.

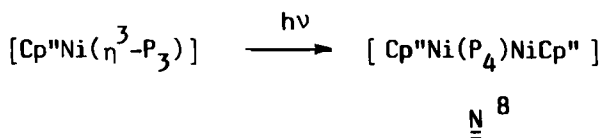
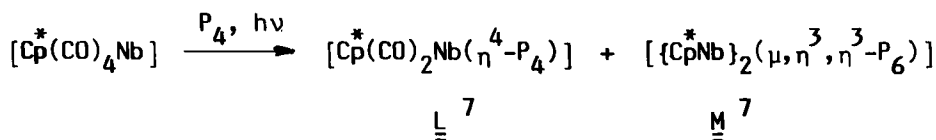
The P_5 ligand of the pentaphosphaferrocene $[(\eta^5-P_5)FeCp^*]$ shows interesting ligating properties. Its interaction with $[CpMn(CO)_2(thf)]$ affords the complexes $\underline{\underline{H}}$ in which until four of the five P_5 lone pairs are further coordinated to the $CpMn(CO)_2$ fragment.



According to the elegant triple-decker synthesis of Rybinskaya et al.⁵ $[(\eta^5-P_5)FeCp^*]$ forms the 30 VE triple decker $\underline{\underline{K}}$ with cyclo- P_5 middle deck $[d(Fe...Fe) = 3.043(2) \text{ \AA}, Cp' \text{ instead of } Cp^*]$ ⁶.



Tetraphosphacyclobutadiene, cyclo-P₄, can be synthesized photochemically and was stabilized according to the following equations:



Cp = $\eta^5\text{-C}_5\text{H}_5$, Cp* = $\eta^5\text{-C}_5\text{Me}_5$, Cp' = $\eta^5\text{-C}_5\text{Me}_4\text{Et}$, Cp'' = $\eta^5\text{-C}_5\text{H}_3(\text{tBu})_2$ -1,3, Cp''' = $\eta^5\text{-C}_5\text{H}(\text{i-C}_3\text{H}_7)_4$ -1,2,3,4

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