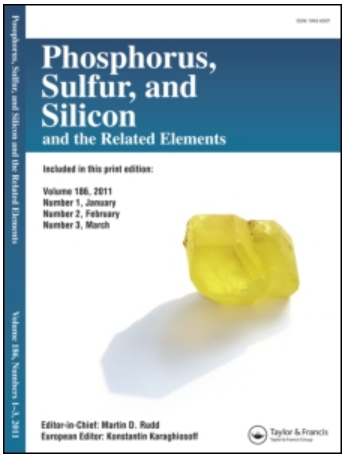


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# $P_n$-COMPLEX LIGANDS: an INTERIM REPORT

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**Abstract** The thermal or photochemical reaction of white phosphorus, $P_4$, with mono- and dinuclear Cp substituted carbonyl metal complexes affords a wide variety of coordinatively stabilized $P_n$ ligands. E.g.: $P_1$,$P_2$, acyclic and cyclic $P_3$, $P_4$ and $P_5$ as well as $P_8$($P_5$-$P_3$) and $P_{12}$($P_5$-$P_7$). Mechanistic aspects of P-P bond cleavage in white phosphorus are discussed.

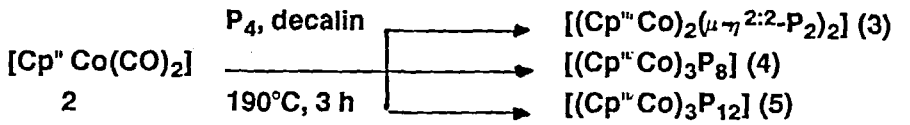


Within the last decade we and others could show [1] that the formation of $P_n$ ligands is strongly influenced by the substituent pattern of the Cp ligand on the transition metal.

In the case of $^4$Cp ($^4$Cp = (i-Pr)$_4$C$_5$H) the hitherto unknown PO ligand could be stabilized in the trinuclear complex **1** [2].

$$[(^4CpNi)_2(\mu_3\text{-}PO)_2\{W(CO)_4\}]\ (1)$$

The rather bulky Cp‴ ligand (Cp‴ = 1,2,4-t$Bu_3C_5H_2$), incorporated into [Cp‴Co(CO)$_2$] (**2**), is necessary for the formation of **3**, **4**, and **5** on the cothermolysis of **2** and $P_4$ [3].

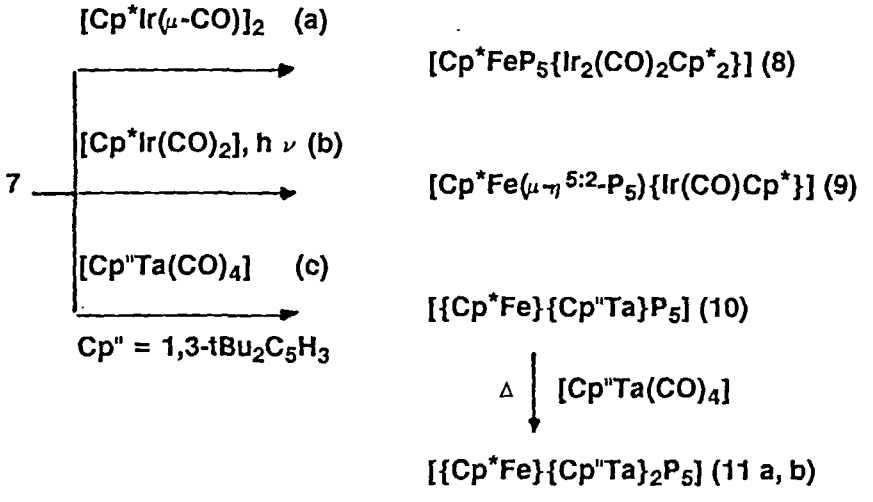



The $P_8$ and $P_{12}$ skeletons in **4** and **5** consist of $P_5$-$P_3$ (open edged $P_8$ dihydrocalicene) and $P_5$-$P_7$ ($P_7$ norbornadiene and open edged $P_5$) building blocks. $P_8$, $P_{10}$ and $P_{12}$ can formally be derived [3] from Hittorf phosphorus.

Further coordination of **3** with $[W(CO)_5(thf)]$ affords with coupling of two $P_2$ units an acyclic $P_4$ ligand [4].

*Starting with the sandwich complex* $[Cp" Ni(\eta^3\text{-}P_3)]$ *and* $[Cp^*Co(CO)_2]$, $Cp^* = C_5Me_5$, besides known compounds also $[Cp" NiP_3Co_2(\mu\text{-}CO)Cp^*_2]$ (**6**) is formed, the $NiCo_2P_3$ skeleton of which forms a strongly distorted prismane [5].

Of special interest are the ligating properties of the sandwich complex $[Cp^*Fe(\eta^5\text{-}P_5)]$ (**7**) [6].



The spirocyclic complex **8** (equation (a)), which possibly is formed in a [2+1] cycloaddition, contains an intact cyclo-$P_5$ ligand with envelope conformation. The photochemical reaction of **7** with $[Cp^*Ir(CO)_2]_2$ gives **9** (equation (b)), where for the first time the $\mu$-$\eta^{5:2}$-cyclo-$P_5$-coordination mode has been realized [6b]. According to equation (c) **10** is synthesized, a cluster with a $TaP_5$ Dewar-benzene skeleton capped by $Cp^*Fe$ [6a]. Its further reaction with $[Cp''Ta(CO)_4]$ leads under cage enlargement to the cubane-like compounds **11 a, b**. One isomer consists of an $FeP_5$ chair with two Cp"Ta capes; the $P_5$ ligand of the other one is a trigonal pyramidal $P_4$ and a $P_1$ unit.

A new coordination type of $P_2$ as well as the novel ligands $P_2S_2$ and $P_2Se_2$ have been realized with the "naked" Cp ligand [7].

$$[CpFe(CO)_2]_2 \xrightarrow[190°C,\ 10\ min]{P_4} \underset{12}{[(CpFe)_4(P_2)_2]} \xrightarrow[grey\ Se]{4/8S_8} \underset{13\ (X = S,Se)}{[(CpFe)_4(P_2X_2)_2]}$$

In **12** and **13** the $Fe_4P_4$ framework belongs to the class of triangulated dodecahedra.

Mechanistic inside in the cleavage of $P_4$ could be reached by the following reaction [8]:

$$[Cp''Fe(CO)_2]_2 \xrightarrow[THF,\ 25°C]{P_4,\ h\nu} \underset{14}{[(Cp''Fe(CO)_2P)_2P_2]} + \underset{15}{[(Cp''Fe(P_4)\text{-}Fe(CO)_2Cp'']}$$

$$[Cp''FeP_4\{Fe(CO)Cp''\}] \underset{16}{} + \underset{17}{[Cp''FeP_4FeCp'']}$$

The successive cleavage of one (complex **14** with $P_4$ butterfly), two (complex **15** with cyclo-$P_4$), and three (complexes **16**, a $P_4$ "ferrole", and **17** with trapezoidally arranged acyclic $P_4$) P-P bonds in $P_4$ (six P-P bonds), followed by stepwise CO elimination, affords compounds **14-17**.

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