ACYCLIC, CYCLIC and POLYCYCLIC $P_n$ LIGANDS

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Abstract Within the coordination sphere of 10 and 12 to 16 electron $L_nM$ transition-metal complex fragments $P_2$ to $P_8$, $P_{10}$, and $P_{10}$ have been stabilized as acyclic, cyclic, and polycyclic $P_n$ ligands.

Besides some known ligating properties of $P_n$ ligands the main interest of this survey is focused on novel coordination modes and ring systems of such substituent-free $P_n$ units.

The photochemistry of 1 and 2 with $P_4$ gives according to Scheme 1 and equation (a) the complexes 3 - 8.

\[ \text{[Cp"Ta(CO)₄]} \xrightarrow{\text{P₄, hν}} \begin{cases} \text{[Cp"₃Ta₃(CO)₃(μ₃-η²:1:1-P₂)₂]} \\ \text{[{Cp"Ta(CO)}₂(μ-η²:2-P₂)₂]} \\ \text{[Cp"Ta(CO)₂(η⁴-P₄)]} \end{cases} \]

\[ \begin{array}{c} \text{Cp"} = C₅H₃Bu⁺₂ \\ \text{Cp*} = C₅Me₅ \end{array} \]

\[ \begin{array}{c} \text{C₂H₄Cl₂} \\ 25°C \end{array} \xrightarrow{\text{2C₂H₄, -CO}} \begin{cases} \text{[Cp⁺Co(C₂H₄)₂]} \\ \text{[Cp"₃Ta(CO)(μ-η²:2-P₂)₂CoCp*]} \end{cases} \]
Further reaction of \([\text{Cp}^\ast\text{Nb(CO)}_4]\) (9) with 8 affords besides \([\{\text{Cp}^\ast\text{Ta(CO)}\}\{\mu-\eta^{2:2}P_2\}_2\{\text{Nb(CO)}\text{Cp}^\ast\}]\) the trinuclear complex 10.

\[
\text{5} + \text{9} \xrightarrow{\text{hv}, \text{25°C}} \{\{\text{Cp}^\ast\text{Ta(CO)}\}\{\mu_3-\eta^{2:1:1}P_2\}_2\text{Nb}_2(\text{CO})_2\text{Cp}^\ast\}_2
\]

For 5 the crystal-structure analysis reveals a slightly distorted (kite-shaped) cyclo-P₄ unit while in 4 two separated P₂ ligands are found. The same holds for 6 in which two P-P bonds of the P₄ ring of 5 are cleaved with formation of a 18 valence electron (VE) Co atom (P-P = 2.079(6)Å, Ta...Co = 2.895(2)Å). The novel 4e donor \(\mu_3-\eta^{2:1:1}P_2\) coordination mode has been determined X-ray crystallographically in complex 10.

The X-ray crystal structure of \([\{\text{Cp}^4\text{Ni}\}_2\text{P}_4\{\text{W(CO)}_5\}_2]\) (derivative of 9) shows a rather distorted Ni₂P₄ prismane skeleton with three P-P bonds of ca. 2.22 Å, one P...P bond of 2.38 Å, and two terminal W(CO)₅ ligands.

\(^{31}\text{P}-\text{NMR spectroscopically dynamic behaviour of the Ni}_2\text{P}_4\) framework of 8 was observed; possible mechanistic aspects are discussed.

In a stacking reaction \([\text{Cp}^\ast\text{Fe(P}_5\)]\) (11) and \([\text{OC}_3\text{M(NCMe)}_3]\) yield the neutral 30 VE "triple-decker" complexes 12 with a Fe...Mo distance of 3.443(2) Å.

\([\text{Cp}^\ast\text{Fe(}\mu-\eta^{5:5}\text{P}_5\)M(\text{CO})_3], \ M = \text{Cr,Mo}\)
The cyclo-P$_5$ ligand of 11 can be transferred to the Cp*Ru fragment according to equation (b) with formation of 13 in about 30 % yield.

\[
\begin{align*}
\text{[Cp*Fe(\eta^5-P_5)]} & \rightarrow \text{[Cp*Ru(CO)$_2$]$_2$} \\
11 & 190^\circ C, \text{ decalin, ca. 1 h} & \text{[Cp*Ru(\eta^5-P_5)]} (b) & 13
\end{align*}
\]

The cothermolysis of [Cp"Nb(CO)$_4$] with P$_4$ gives [Cp"Nb(\mu-\eta^{6:6-P_6})NbCp"] (14), a triple decker with a severe bisallylic distortion of the planar P$_6$-middle deck, and [{Cp"Nb)$_3$P$_6$} (15), the spectroscopic data of which point to a Nb$_3$P$_6$-homocubene framework with a trigonal pyramidal P$_4$ and a P$_2$ phosphido-phosphinidene ligand. The dynamic behaviour of 15 will be discussed.

Open-edged P$_6$ benzvalene has been coordinated in the dinuclear thorium complex 16.

\[
\text{[Cp"$_2$Th(\mu-\eta^{3:3-P_6})ThCp"$_2$]}
\]

16

Starting with [Cp"Rh(CO)$_2$] and white phosphorus P$_{10}$, the all-phosphorus analogue of dihydrofulvalene (C$_{10}$H$_{10}$), has been coordinatively stabilized as the tetranuclear complex 17, the X-ray structure data of which show that in each five-membered ring one P-P bond is cleaved (2.624(2) Å). This ligand can formally be regarded as 16 electron-donor ligand.

\[
\text{[\{Cp"Rh)$_2$(P$_5$-P$_5$)\{RhCp"\}$_2$]}
\]

17
Replacement of the Cp" by the Cp" ligand, Cp" = C5H2Bu13, gives for the former reaction instead of 17 the trinuclear complex \(\{\text{Cp"}M\}_3\text{P}_8\), \(M = \text{Co, Rh}\), the structure of which will be discussed 8.

REFERENCES


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