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Acyclic, Cyclic and Polycyclic P_ Ligands

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ACYCLIC, CYCLIC and POLYCYCLIC Pn 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_6 , P_8 , and P_{10} have been stabilized as acyclic, cyclic, and polycyclic P_n ligands.

Besides some known ligating properties of P_n ligands 1 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 $\underline{1}$ and $\underline{2}$ with P_4 gives according to Scheme 1 and equation (a) the complexes $\underline{3} - \underline{8}$.

$$[Cp^{4}Ni(\mu-CO)]_{2}$$

$$2$$

$$+exane$$

$$40 min$$

$$Cp^{4} = C_{5}H(i-Pr)_{4}$$

$$[Cp^{4}Ni(\eta^{3}-P_{3})]$$

$$7$$

$$[Cp^{4}Ni(\mu-CO)]_{2}$$

$$[Cp^{4}Ni(\eta^{3}-P_{3})]$$

$$7$$

$$[Cp^{4}Ni(\mu-CO)]_{2}$$

$$[Cp^{4}Ni(\eta^{3}-P_{3})]$$

$$[Cp^{4}Ni(\eta^{3}-P_{3})]$$

$$[Cp^{4}Ni(\eta^{3}-P_{3})]$$

$$[Cp^{4}Ni(\mu-CO)]_{2}$$

$$[Cp^{4}Ni(\eta^{3}-P_{3})]$$

$$[Cp^{4}Ni(\mu-CO)]_{2}$$

$$[Cp^{4}Ni(\eta^{3}-P_{3})]$$

$$[Cp^{4}Ni(\eta^{3}-P_{3})]$$

Further reaction of $[Cp^*Nb(CO)_4]$ (9) with 5 affords besides $[\{Cp^*Ta(CO)\}(\mu-\eta^{2:2}-P_2)_2\{Nb(CO)Cp^*\}]$ the trinuclear complex 10.

For $\underline{5}$ the crystal-structure analysis reveals a slightly distorted (kite-shaped) cyclo-P₄ unit while in $\underline{4}$ two separated P₂ ligands are found. The same holds for $\underline{6}$ in which two P-P bonds of the P₄ ring of $\underline{5}$ are cleaved with formation of a 18 valence electron (VE) Co atom (P-P = 2.079(6)Å, Ta...Co = 2.895(2)Å) 2 . The novel 4e donor μ_3 - η^2 :1:1-P₂ coordination mode 2 has been determined X-ray crystallographically in complex $\underline{10}$.

The X-ray crystal structure of $[\{Cp^4Ni\}_2P_4\{W(CO)_5\}_2]$ (derivative of $\underline{8}$) shows a rather distorted Ni_2P_4 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 3.

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

In a stacking reaction $[Cp^*Fe(P_5)]$ (11) and $[OC)_3M(NCMe)_3]$ yield the neutral 30 VE "triple-decker" complexes 12 with a Fe...Mo distance of 3.443(2) Å 4 .

$$[Cp^*Fe(\mu-\eta^{5:5}-P_5)M(CO)_3], M = Cr,Mo$$

The cyclo- P_5 ligand of $\underline{11}$ can be transferred to the Cp*Ru fragment according to equation (b) with formation of $\underline{13}$ in about 30 % yield $\underline{5}$.

[Cp*Ru(CO)₂]₂
[Cp*Fe(
$$\eta^5$$
-P₅)] — [Cp*Ru(η^5 -P₅)] (b)
11 190°C, decalin, ca. 1 h 13

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 $[\{Cp"Nb\}_3P_6]$ (15), the spectroscopic data of which point to a Nb_3P_6 -homocubene framework with a trigonal pyramidal P_4 and a P_2 phosphido-phosphinidene ligand P_4 . The dynamic behaviour of P_4 will be discussed.

Open-edged P_6 benzvalene has been coordinated in the dinuclear thorium complex $\underline{16}^{6}$.

[Cp"₂Th(
$$\mu$$
- η ^{3:3}-P₆)ThCp"₂]

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 $\underline{17}$, 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 7.

$$[{Cp"Rh}_2(P_5-P_5){RhCp"}_2]$$

Replacement of the Cp" by the Cp" ligand, $Cp^{III} = C_5H_2Bu^{t}_3$, gives for the former reaction instead of <u>17</u> the trinuclear complex [{Cp" M}₃P₈], M = Co, Rh, the structure of which will be discussed ⁸.

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