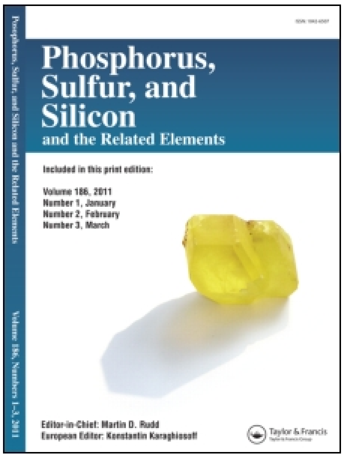

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Acyclic, Cyclic and Polycyclic P_n Ligands

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ACYCLIC, CYCLIC and POLYCYCLIC P_n LIGANDS

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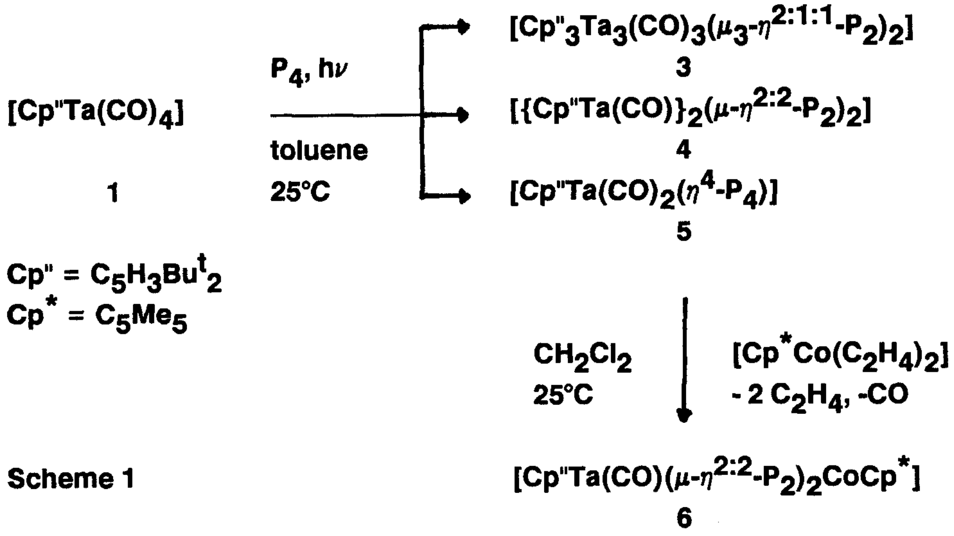
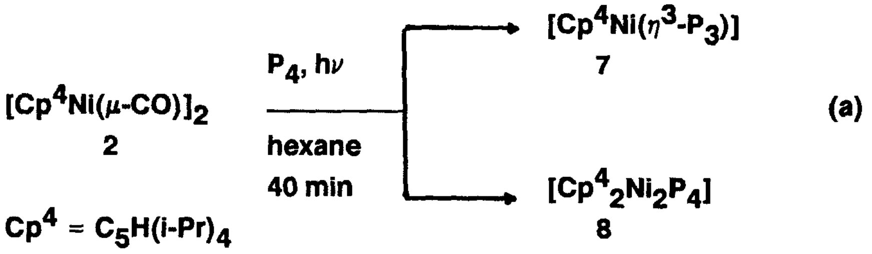
Abstract Within the coordination sphere of 10 and 12 to 16 electron L_nM transition-metal complex fragments P_2 to P_6, P_8, and P_{10} have been stabilized as acyclic, cyclic, and polycyclic P_n ligands.

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



Scheme 1



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

$$5 + 9 \xrightarrow[-CO]{h\nu,\ 25°C} \underset{10}{[\{Cp''Ta(CO)\}(\mu_3\text{-}\eta^{2:1:1}\text{-}P_2)_2Nb_2(CO)_2Cp^*{}_2]}$$

For 5 the crystal-structure analysis reveals a slightly distorted (kite-shaped) cyclo-P_4 unit while in 4 two separated P_2 ligands are found. The same holds for 6 in which two P-P bonds of the P_4 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) [2]. The novel 4e donor $\mu_3\text{-}\eta^{2:1:1}\text{-}P_2$ coordination mode [2] has been determined X-ray crystallographically in complex 10.

The X-ray crystal structure of **$[\{Cp^4Ni\}_2P_4\{W(CO)_5\}_2]$** (derivative of 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_2P_4 framework of 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].

$$\underset{12}{[Cp^*Fe(\mu\text{-}\eta^{5:5}\text{-}P_5)M(CO)_3],\ M = Cr,Mo}$$

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 [5].

$$\underset{\mathbf{11}}{[Cp^*Fe(\eta^5\text{-}P_5)]} \xrightarrow[\text{190°C, decalin, ca. 1 h}]{[Cp^*Ru(CO)_2]_2} \underset{\mathbf{13}}{[Cp^*Ru(\eta^5\text{-}P_5)]} \qquad \text{(b)}$$

The cothermolysis of $[Cp''Nb(CO)_4]$ with P_4 gives $\mathbf{[Cp''Nb(\mu\text{-}\eta^{6:6}\text{-}P_6)NbCp'']}$ (14), a triple decker with a severe bisallylic distortion of the planar P_6-middle deck, and $\mathbf{[\{Cp''Nb\}_3P_6]}$ (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 [2]. The dynamic behaviour of 15 will be discussed.

Open-edged P_6 benzvalene has been coordinated in the dinuclear thorium complex 16 [6].

$$[Cp''_2Th(\mu\text{-}\eta^{3:3}\text{-}P_6)ThCp''_2]$$

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 [7].

$$[\{Cp''Rh\}_2(P_5\text{-}P_5)\{RhCp''\}_2]$$

17

Replacement of the Cp" by the Cp"' ligand, Cp"' = $C_5H_2Bu^t_3$, gives for the former reaction instead of 17 the trinuclear complex **[{Cp"'M}$_3$P$_8$]**, M = Co, Rh, the structure of which will be discussed [8].

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