Chapter 11

\textbf{P}_n \text{ and } \textbf{As}_n \text{ UNITS AS BUILDING BLOCKS FOR METALLACYCLES, CAGES, SANDWICH AND TRIPLE-DECKER COMPLEXES}

\textbf{O. J. Scherer, C. Blath, J. Braun, B. Höbel, K. Pfeiffer, B. Rink, H. Slodzyk, P. Walther, B. Werner and R. Winter}

Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Straße, W-6750 Kaiserslautern, Germany

\textbf{Abstract}

In the coordination sphere of substituted cyclopentadienyl transition-metal complex fragments PO, cyclo-P$_3^{3-}$, open-edged P$_6$ benzvalene and As$_6$ Dewar benzene, cyclo-As$_8$ as well as open-edged E$_{10}$ dihydrofulvalenes (E = P, As) have been stabilized for the first time. Source for the P$_n^{-}$ and As$_n^{-}$ units are white phosphorus, P$_4$, and yellow arsenic, As$_4$, respectively.

\textbf{1. \hspace{1em} INTRODUCTION}

Within the last years many novel complexes with substituent-free acyclic and cyclic E$_n$ units [1], E = P, As, Sb, Bi; $n = 1$-$8$, have been synthesized and characterized by IR, MS, NMR, and especially by X-ray analyses. Many of these compounds have forged bridges to organic chemistry (CH is isoelectronic and isolobal [2] to e.g. P and As), the solid-state chemistry of P$_n^X$-polyphosphides [3] and to acyclic and cyclic polyphosphanes [4]. This review mainly describes the newest developments on the reactivity of complexes with E$_n$.
ligands and the coordinative stabilization of cyclic, especially larger Eₙ units (E = P, As; n = 3, 4, 5, 6 and 8)

2. RESULTS

2.1. E₂ Ligands (E = P, As, Sb)

In the well-known series of dimetalla-diphospha tetrahedranes [1] derivative 2 [5] with two different metal atoms could be synthesized according to equation (1):

\[
\begin{align*}
[Cp^4Ni(\eta^3-P_3)] & \quad [CpW(CO)_3]_{2,\Delta} \quad \text{Cp}^4Ni \quad WCP(CO)_2 \\
& \quad \text{Cp}^4Ni \quad WP \quad \text{P} \quad \text{P} \quad \text{2} \quad \text{la}
\end{align*}
\]

\[
\begin{align*}
\text{la} \quad \text{Cp}^4 = \eta^5-C_5HiPr_4, \text{ Cp} = \eta^5-C_5H_5
\end{align*}
\]

Reaction of the dinickela-diphospha tetrahedrane 3 with \([W(CO)_5(thf)]\) leads to formation of the Ni₂WP₂-complex 4 which can be oxidized with bis(trimethylsilyl)peroxide to give 5, the first complex with a PO ligand [6].
For the tetragonal-pyramidally structured compounds 4 and 5 X-ray analyses show that 4 has a rather short P...P bond of 2.304(4) Å (2.624(5) Å in 5); the μ$_3$-PO ligands have P-O bond lengths of 1.46 and 1.48 Å (IR: ν(P=O)=1260 cm$^{-1}$) [6].

In analogy to the synthesis of 3 the interaction of [Cp$_4$Ni(η$^3$-As$_3$)] (1b) with [Cp$_4$Ni(CO)]$_2$ [7] affords in high yield complex 6 (d(As-As) = 2.277(6)Å) [8].

[Cp$_4$Ni(η$^3$-As$_3$)] → [Cp$_4$Ni(μ-CO)]$_2$,Δ

1b

Cp$_4$ = η$^5$-C$_5$HiPr$_4$

7 (d(Sb-Sb) = 2.678(1)Å) was obtained in ca. 4 % yield on heating (180°C) [CpMo(CO)$_3$]$_2$ and metallic antimony for five days [9].

2.2. E$_3$ Ligands (E = P,As)

The cothermolysis of [Cp$_4$Ni(μ-CO)]$_2$ with an excess of E$_4$ (E = P,As) gives in about 60 % yield the nickelatripnictogena tetrahedranes 1 [8].
A side product of the reaction of \([(\eta^5-C_5Me_4R)Ru(CO)_2]_2\) with yellow arsenic, \(As_4\), is the tetranuclear cluster \([(\eta^5-C_5Me_4R)Ru(\eta^3-As_3)(\mu_3,\eta^3-As_3)(\mu_3-As_3)]\) \((\text{a}, \text{b}; \text{a}:R = \text{Me}, \text{b}:R = \text{Et})\), whose \(Ru_4As_9\) skeleton is shown in Fig. 1 [10].

![Diagram of \(Ru_4As_9\) skeleton]

Fig. 1 (Cp'-ligands have been omitted)

Interesting to note are the different \(d(As-As)\) values of 2.32 Å (As7-9) and 2.57 Å (As1,4,6) for the two cyclo-As3 ligands.

With respect to the oxidation state of IV, which is almost the only occurring state for thorium, the unsubstituted phosphorus ligand in \(\text{c} [11]\) is described as cyclo-P3\(^{3-}\) \((d(P-P) = 2.185 \text{ Å})\), a formulation isoelectronic with cyclo-S3.
Treatment of a dichloromethane solution of \([(\text{triphos})\text{Co}(\eta^3-P_3)](\text{10})\) with [AuCl(PR₃)] or RHgCl in the presence of TlPF₆ affords the complexes 11 [12] and 12 [13].

X-ray structure analyses reveal that in 11 [12] the coordinated PP bond is lengthened to 2.30/2.31(2) Å; the same holds for 12(2.293(8) Å) [13].

2.3. \(E_4\) Ligands (\(E = P, As\))

In addition to \([\text{Cp}^*\text{(CO)}_2\text{Nb}(\eta^4-E_4)](\text{13a}: E=P [14], \text{13b}: E=As [15])\) 14, the tantalum analogue, can be synthesized photochemically according to equation (2) [16]:
The X-ray data of 14 (d(P-P) = 2.17 Å, 13a: 2.16 Å [14]) and 13a are nearly the same. 14 also shows a slight distortion of the planar P₄ base to a kite shape [16]. The Wade-Mingos electron counting rules [17] for the P₄Ta tetragonal pyramid in 14 lead to the necessary number of SEP (n+2 = 7 Skeletal Electron Pairs) for the nido structure.

Cyclo-P₄ as 12e donor ligand (four times W(CO)₅-terminal coordination) has been stabilized in complex 15 (d(P-P = 2.15 Å) which was made from P₄ and [W(CO)₅(thf)] [18].

Tight-binding band electronic structure calculations on a prototype skutterudite LaFe₄P₁₂ were performed in order to gain insight into the electronic properties of binary (i.e. CoAs₃) and ternary skutterudite compounds. The major contribution to the highest occupied band of LaFe₄P₁₂ comes
from the orbitals of the P$_4$ rings that form the phosphorus sublattice [19].

2.4. E$_5$ Ligands (E = P, As)

The first mixed carbonyl(pentaphosphacyclopentadienyl)-metal complex 16 (and further examples) was obtained by the following metathetic reaction [20]:

\[
\begin{align*}
\text{DMF, 155°C} & \\
\text{KP$_5$ + [Mn(CO)$_5$Br]} & \rightarrow [(\eta^5-P$_5$)Mn(CO)$_3$] \\
& - KBr, - 2CO
\end{align*}
\]

Starting with the sandwich complexes [Cp$^*$Fe(\eta$^5$-E$_5$)], E = P, As; Cp$^*$ = \eta$^5$-C$_5$Me$_5$, and [(OC)$_3$Mo(NCMe)$_3$] the 30 valence electron "triple deckers" 17 and 18 (Fig. 2) have been realized in a stacking reaction [21].
It is worthwhile to mention that in both dinuclear complexes d(Fe...Mo) is 3.44 Å (17: d(P-P) = 2.13 Å, 18: d(As-As) = 2.35 Å) [21]; for triple deckers with shorter metal-metal bonds, see reference [1]).

2.5. \( E_6 \) Ligands (\( E = P, As \))

In the triple-decker sandwich complex 19 with a rather distorted cyclo-P\(_6\) ligand [1] further terminal coordination to a phosphorus lone pair has been achieved for the first time [16].

\[
\begin{align*}
\text{Scheme 1} \\
&\xrightarrow{[\text{M(CO)}_5(\text{thf})]} \\
&\xrightarrow{[\text{[(Cp''Nb)}_2(\mu,\eta^3:3-P_6)]]} \\
&\xrightarrow{[(\text{Cp''Nb})_2(\mu,\eta^3:3-P_6)]} \\
&\text{Cp''} = \eta^5-1,3-\text{tBu}_2\text{C}_5\text{H}_3 \\
&\text{M} = \text{Cr, W} \\
&\text{A} \quad \text{B} \quad \text{C} \quad \text{D} \quad \text{E}
\end{align*}
\]

From the classical (CH)\(_6\)-valence isomers A-E of benzene intact or open-edged \( E_6 \) analogues, \( E = P, As \), have been stabilized in the coordination sphere of transition metal complex fragments.
The cothermolyses of \([\text{Cp}_2\text{"Th}(\eta^4-C_4H_6)]\) with \(P_4\) and \([\text{Cp}^*\text{Co(CO)}_2]\) with \(\text{As}_4\) give the di- and trinuclear complexes \(\text{19} [11], \text{20} [22]\) and \(\text{21} [22]\) (Fig. 3).

In \([\text{Cp}^\prime\text{Th(\mu,}\eta^3:3\text{-P}_6)\text{ThCp}^\prime\text{]19 [11], Cp}^\prime=\eta^5-1,3\text{-tBu}_2\text{C}_5\text{H}_3\) the bicyclic \(\text{P}_6\) ligand can be formally regarded as \(\text{P}_6{}^{4-}\) and derived from \(\text{P}_6\) benzvalene (cf. \(\text{C}\), Scheme 1). The open-edged \(\text{As}_6\) Dewar benzene (cf. \(\text{D}\), Scheme 1) has been coordinatively stabilized in \([\text{Cp}^*\text{Co}_2(\text{As}_6)]\) \(\text{20} [22]\). Its As-As distances vary from 2.33 (\(\pi\)-bond coordination) to 2.44 (average) and 2.59 \(\AA\) (\(\pi\)-and \(\sigma\)-bond coordination) \(\text{[22]}\). Beside \([\text{Cp}^*\text{Co(\mu-}\eta^2:2\text{As}_2)]_2\) \(\text{22} [22]\) one can also isolate \([\text{Cp}^*\text{Co}_3(\text{As}_2)_3]\) \(\text{21},\)
Cp*=η⁵-C⁵Me₅), whose Co₃As₆ framework consists of three Cp*CoAs₂ units formally forming a strongly distorted Cp*Co capped As₆ prismane with As-As bond lengths between 2.29 and 3.05 Å [22].

The molecular dynamics/density functional (MD/DF) approach [23] shows that the most stable P₆ isomers are the benzvalene and prismane structure type [23].

2.6. E₈ Ligands (E = P, As)

Contrary to the many E₆ isomers only two complexes with an E₈ ligand have been synthesized so far.

On the one hand, the photolysis of a P₄/[Cp'Fe(CO)₂]₂ -
toluene solution affords \([\text{Cp'}_4\text{Fe}_4(\text{CO})_6(\text{P}_8)]\) [23] [24], whose P\(_8\) cage can be formally derived from the open-edged \((\text{CH})_8\) isomer cuneane [24] (see \(\text{G}\) in Scheme 2).

\[
\begin{align*}
\text{Cp'} & = \eta^5\text{-C}_5\text{H}_4\text{Me} \\
\text{Cp''} & = \eta^5\text{-1,3-tBu}_2\text{C}_5\text{H}_3
\end{align*}
\]
X-ray crystallographically P-P distances from 2.185(4) to 2.254(4) Å have been found for \[23\] [24].

On the other hand, in \([(\text{Cp}''\text{Nb})_2(\mu,\eta^{4:4}-\text{As}_8)](24)\) [25], synthesized from [Cp''Nb(CO)_4] and As_4 in decalin (170°C, 2h), the As_8 analogue of cyclooctatetraene (see \(\text{F}\) in Scheme 2) has been coordinatively stabilized as a puckered, strongly distorted eight-membered ring, whose As-As bond lengths vary between 2.355(3) and 2.530(3) Å [25].

Theoretical studies [23] have shown that, contrary to widespread belief, the most stable isomer of P_8 is not cubic, but the "wedge" or "cradle" structure ("cuneane") found as a structural motif in Hittorf phosphorus.

2.7. \(E_{10}\) Ligands (\(E = P, As\))

Up to now the largest \(E_n\) units that have been coordinated to transition-metal complex fragments are P_{10} and As_{10}.

![Diagram](attachment:image.png)

Scheme 3
Whereas $P_{10}$, synthesized by cothermolysis of $[\text{CpCr(CO)}_3]_2$, $\text{Cp}=\eta^5-\text{C}_5\text{H}_5$, and $P_4$, in the paramagnetic complex 25 [26] forms a polycyclic $\text{Cr}_5P_{10}$ skeleton (cf. Baudler's polycyclic phosphanes [4]) $E_{10}$ ($E = P, \text{As}$) can be formally derived from (CH)$_{10}$ dihydrofulvalene (see Scheme 3). Treatment of $[\text{Cp}''\text{Rh(CO)}_2]$ with $E_4$ at elevated temperature affords the tetranuclear complexes 26 (a: $M = P$, b: $M = \text{As}$) [27].

\[ M = \text{CpCr(CO)}_2 \]
X-ray structure analyses show that in 25 the mean value of the P-P distances is 2.22 Å [26]. For 26a P-P-bond lengths between 2.14 and 2.19 Å are found. It is of interest to note that in 26a and 26b (its X-ray structure is until now of low quality) the E-E bond at the "end" of both five-membered rings adds oxidatively (d(P...P)=2.62 Å) [27] with formation of d⁶ rhodium.

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