The Chemistry of Inorganic Ring Systems, R. Steudel (Ed.)
Studies in Inorganic Chemistry, Vol. 14

Chapter 11

P_n and As_n UNITS AS BUILDING BLOCKS FOR METALLACYCLES, CAGES, SANDWICH AND TRIPLE-DECKER COMPLEXES

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

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.

1. INTRODUCTION

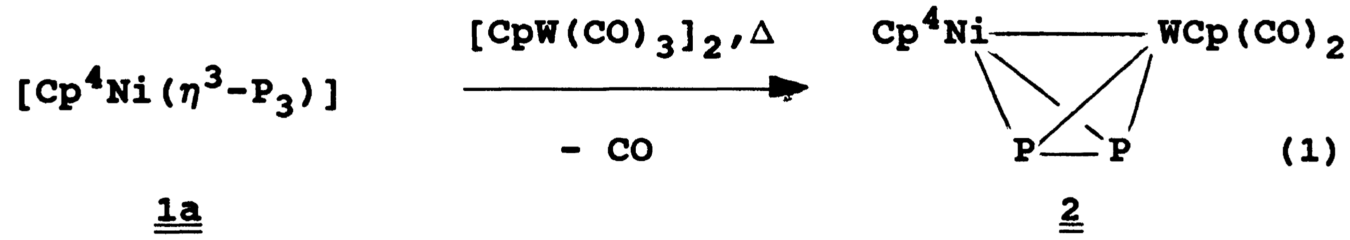
Within the last years many novel complexes with substituent-free acyclic and cyclic E_n units [1], E = P,As, Sb,Bi; n = 1-8, have been synthesized and characterized by IR, MS, NMR, and especially by X-ray analyses. Many of these compounds have forged bridges to organic chemistry (CH is isoelectronic 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 E_n units (E = P,As; n = 3,4,5,6 and 8)

2. RESULTS

2.1. E_2 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):

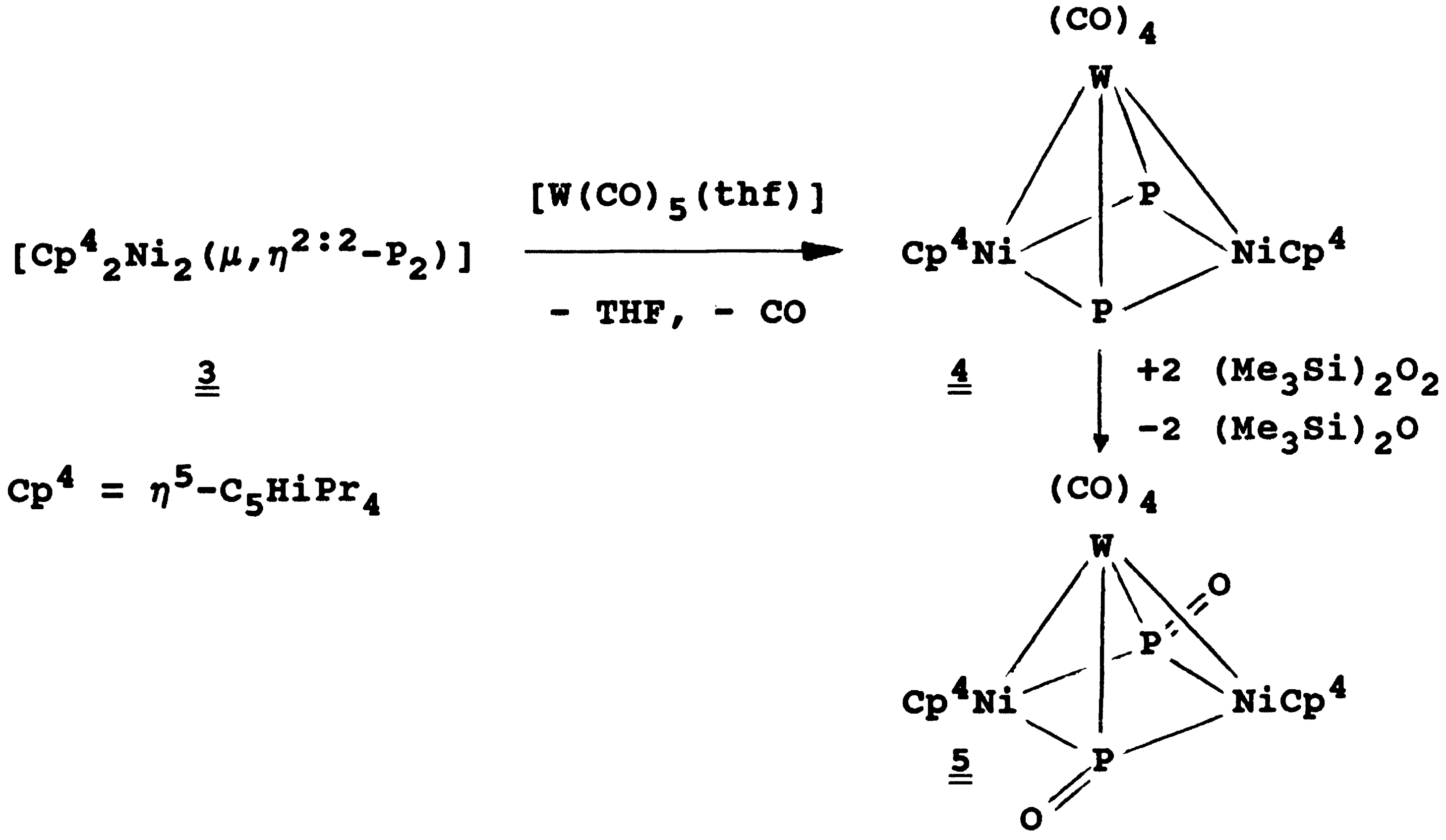


(1)

1a **2**

$Cp^4 = \eta^5\text{-}C_5HiPr_4$, $Cp = \eta^5\text{-}C_5H_5$

Reaction of the dinickela-diphospha tetrahedrane **3** with $[W(CO)_5(thf)]$ leads to formation of the Ni_2WP_2-complex **4** which can be oxidized with bis(trimethylsilyl)peroxide to give **5**, the first complex with a PO ligand [6].

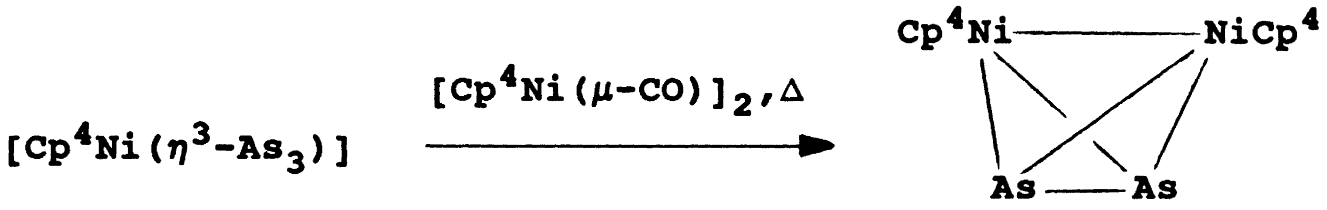


3 **4** **5**

$Cp^4 = \eta^5\text{-}C_5HiPr_4$

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 $[Cp^4Ni(\eta^3\text{-}As_3)]$ (1b) with $[Cp^4Ni(CO)]_2$ [7] affords in high yield complex 6 (d(As-As) = 2.277(6)Å) [8].

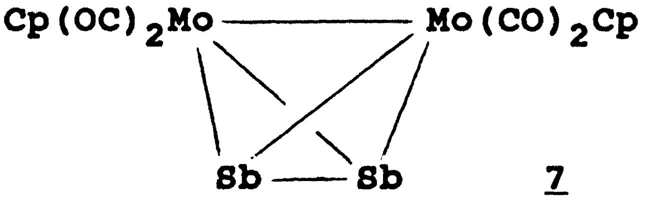


1b

6

$Cp^4 = \eta^5\text{-}C_5HiPr_4$

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].

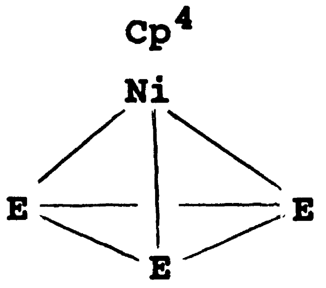


$Cp = \eta^5\text{-}C_5H_5$

7

2.2. E_3 Ligands (E = P,As)

The cothermolysis of $[Cp^4Ni(\mu\text{-}CO)]_2$ with an excess of E_4 (E = P,As) gives in about 60 % yield the nickelatripnictogena tetrahedranes 1 [8].



1a, E = P
1b, E = As

A side product of the reaction of $[(\eta^5\text{-}C_5Me_4R)Ru(CO)_2]_2$ with yellow arsenic, As_4, is the tetranuclear cluster $[\{(\eta^5\text{-}C_5Me_4R)Ru\}_3Ru(\eta^3\text{-}As_3)(\mu_3,\eta^3\text{-}As_3)(\mu_3\text{-}As)_3]$ (8 a,b; a:R = Me,b:R = Et), whose Ru_4As_9 skeleton is shown in Fig. 1 [10].

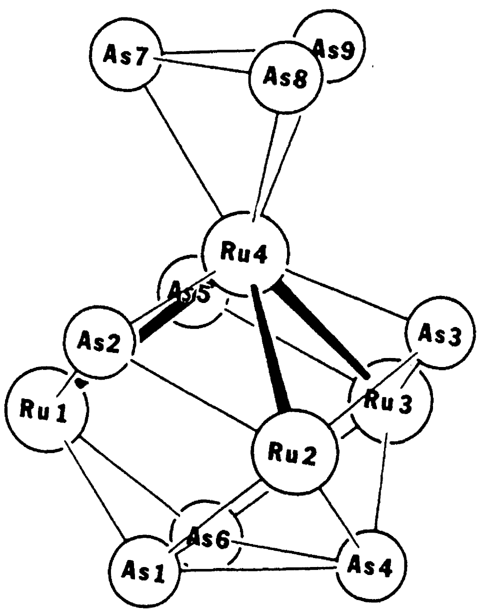
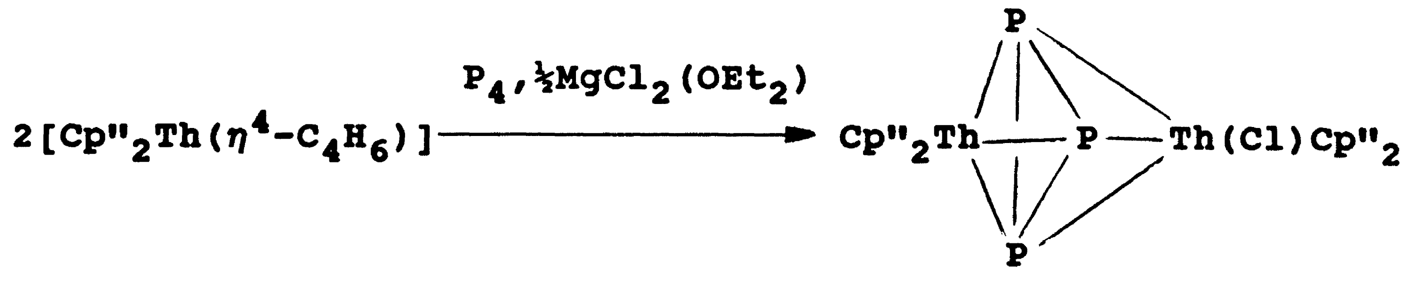


Fig. 1 (Cp'-ligands have been omitted)

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-As_3 ligands.

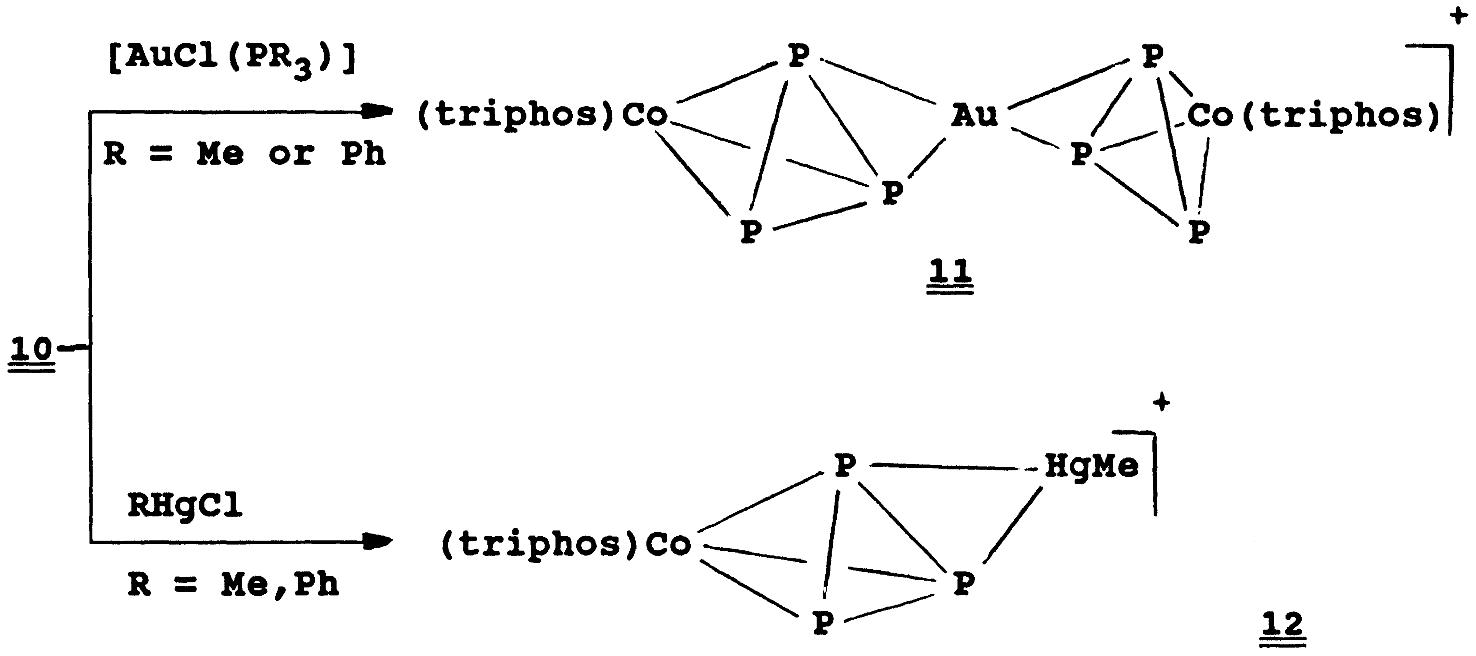
With respect to the oxidation state of IV, which is almost the only occurring state for thorium, the unsubstituted phosphorus ligand in 9 [11] is described as cyclo-P_3^{3-} (d(P-P) = 2.185 Å), a formulation isoelectronic with cyclo-S_3.



$Cp'' = \eta^5\text{-}1,3\text{-}tBu_2C_5H_3$

9

Treatment of a dichloromethane solution of $[(triphos)Co(\eta^3\text{-}P_3)]$(**10**) with $[AuCl(PR_3)]$ or RHgCl in the presence of $TlPF_6$ affords the complexes **11** [12] and **12** [13].



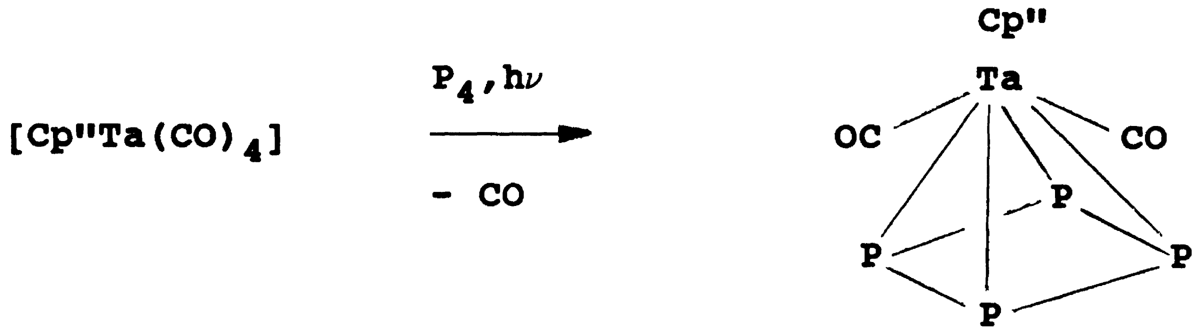
11

12

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 $[Cp^*(CO)_2Nb(\eta^4\text{-}E_4)]$ (**13a**: E=P [14], **b**: E=As [15]) **14**, the tantalum analogue, can be sythesized photochemically according to equation (2) [16]:



(2)

14

$Cp'' = \eta^5\text{-}1,3\text{-}tBu_2C_5H_3$

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 P_4 base to a kite shape [16]. The Wade-Mingos electron counting rules [17] for the P_4Ta tetragonal pyramid in 14 lead to the necessary number of SEP (n+2 = 7 Skeletal Electron Pairs) for the nido structure.

Cyclo-P_4 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 P_4 and $[W(CO)_5(thf)]$ [18].

$$[W(CO)_5(thf)] \xrightarrow{P_4,RT} [(OC)_4W(P_4)\{W(CO)_5\}_4]$$

15

Tight-binding band electronic structure calculations on a prototype skutterudite $LaFe_4P_{12}$ were performed in order to gain insight into the electronic properties of binary (i.e. $CoAs_3$) and ternary skutterudite compounds. The major contribution to the highest occupied band of $LaFe_4P_{12}$ comes from the orbitals of the P_4 rings that form the phosphorus sublattice [19].

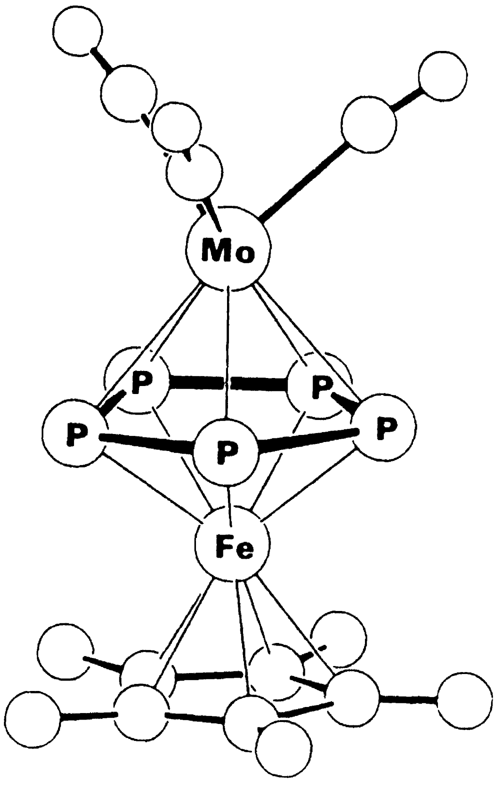
2.4. E_5 Ligands (E = P,As)

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

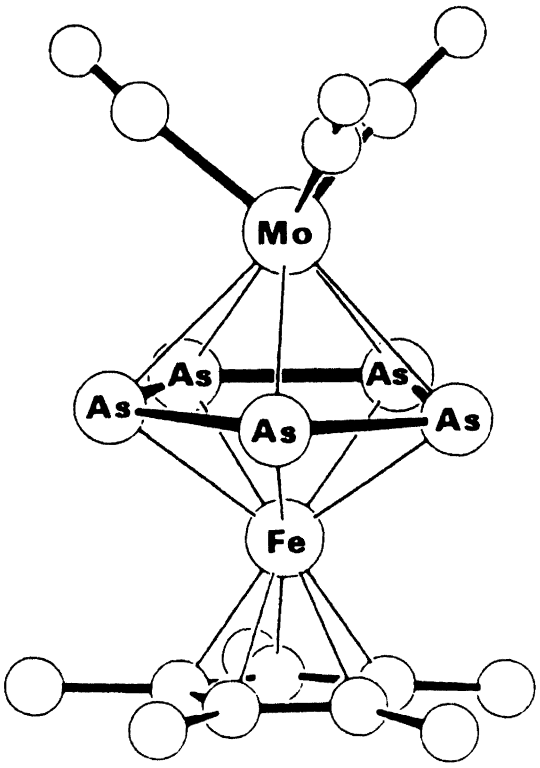
$$KP_5 + [Mn(CO)_5Br] \xrightarrow[-\ KBr,\ -\ 2CO]{DMF,\ 155°C} [(\eta^5\text{-}P_5)Mn(CO)_3]$$

<u>16</u>

Starting with the sandwich complexes $[Cp^*Fe(\eta^5\text{-}E_5)]$, E = P,As; $Cp^* = \eta^5\text{-}C_5Me_5$, and $[(OC)_3Mo(NCMe)_3]$ the 30 valence electron "triple deckers" <u>17</u> and <u>18</u> (Fig. 2) have been realized in a stacking reaction [21].



<u>17</u>



<u>18</u>

Fig. 2

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]).

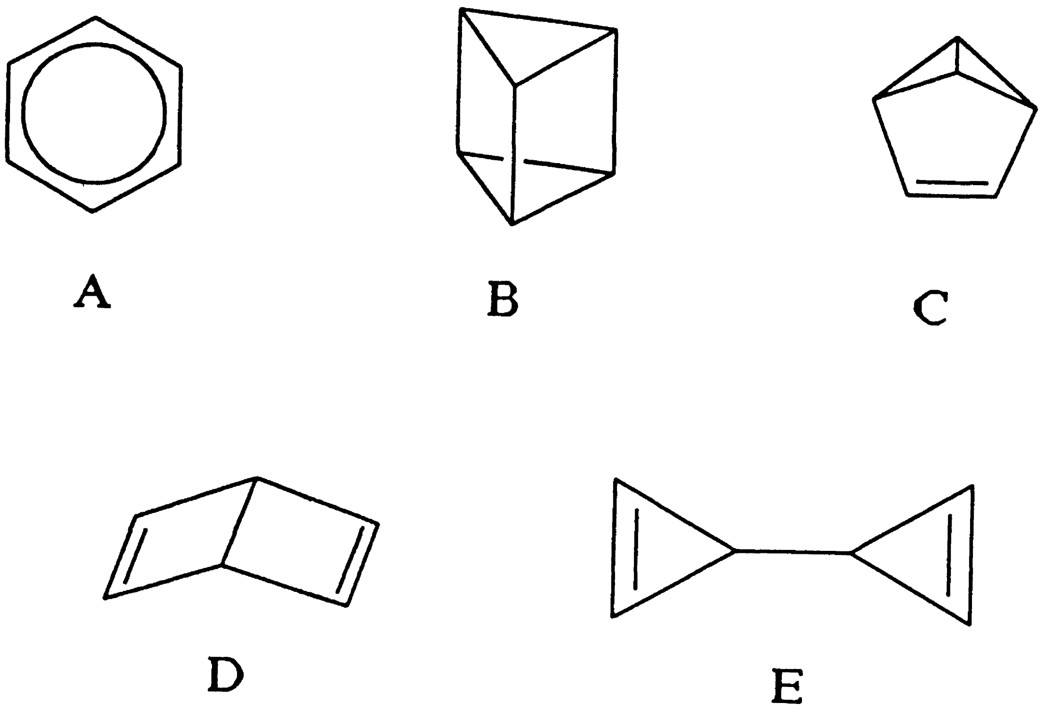
2.5. E_6 Ligands (E = P,As)

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].

$$\underset{\underline{\underline{19}}}{[(Cp''Nb)_2(\mu,\eta^{3:3}\text{-}P_6)]} \xrightarrow{[M(CO)_5(thf)]} \underset{\underline{\underline{20}}}{[(Cp''Nb)_2(P_6)\{M(CO)_5\}]}$$

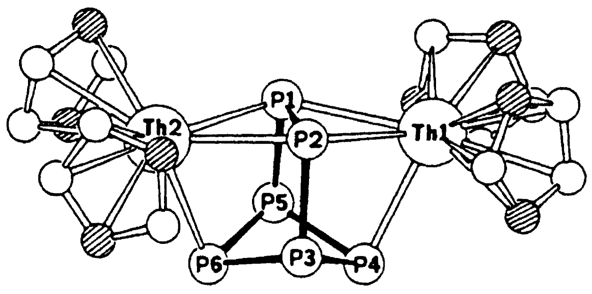
$Cp'' = \eta^5\text{-}1,3\text{-}tBu_2C_5H_3$ M = Cr,W

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.

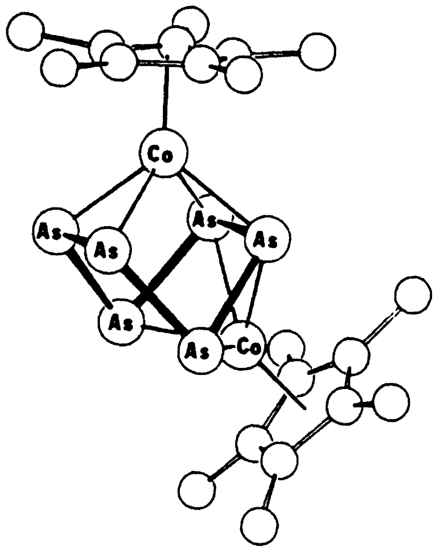


Scheme 1

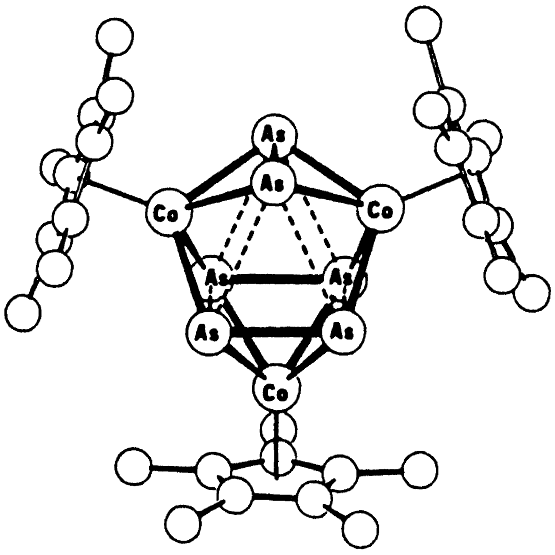
The cothermolyses of [Cp_2"Th(η^4-C_4H_6)] with P_4 and [$Cp^*Co(CO)_2$] with As_4 give the di- and trinuclear complexes 19 [11], 20 [22] and 21 [22] (Fig. 3).



19



20



21

Fig. 3.⊘=CBut

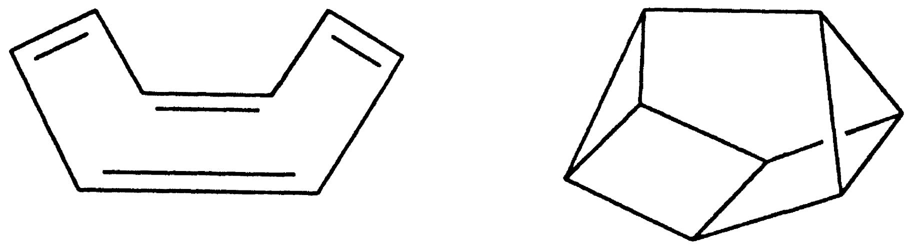
In [$Cp''_2Th(\mu,\eta^{3:3}$-$P_6)ThCp''_2$](19 [11], Cp"=η^5-1,3-t$Bu_2C_5H_3$) the bicyclic P_6 ligand can be formally regarded as P_6^{4-} and derived from P_6 benzvalene (cf. C, Scheme 1). The open-edged As_6 Dewar benzene (cf. D, Scheme 1) has been coordinatively stabilized in [$Cp^*_2Co_2(As_6)$] (20) [22]. Its As-As distances vary from 2.33 (π-bond coordination) to 2.44 (average) and 2.59 Å (π-and σ-bond coordination) [22]. Beside [$Cp^*Co(\mu$-$\eta^{2:2}As_2)]_2$(22) [22] one can also isolate [$Cp^*_3Co_3(As_2)_3$](21,

$Cp^{*}=\eta^5-C_5Me_5$), whose Co_3As_6 framework consists of three $Cp^{*}CoAs_2$ units formally forming a strongly distorted $Cp^{*}Co$ capped As_6 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 P_6 isomers are the benzvalene and prismane structure type [23].

2.6. E_8 Ligands (E = P,As)

Contrary to the many E_6 isomers only two complexes with an E_8 ligand have been synthesized so far.

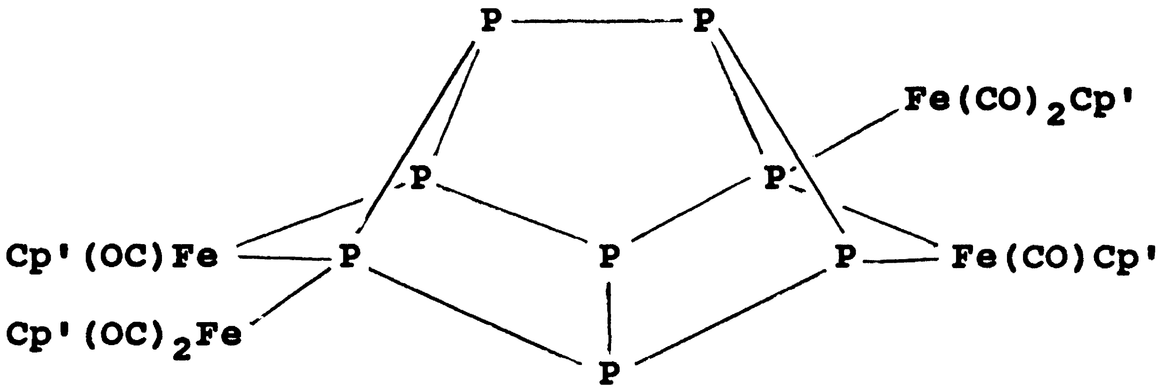


F G

Scheme 2

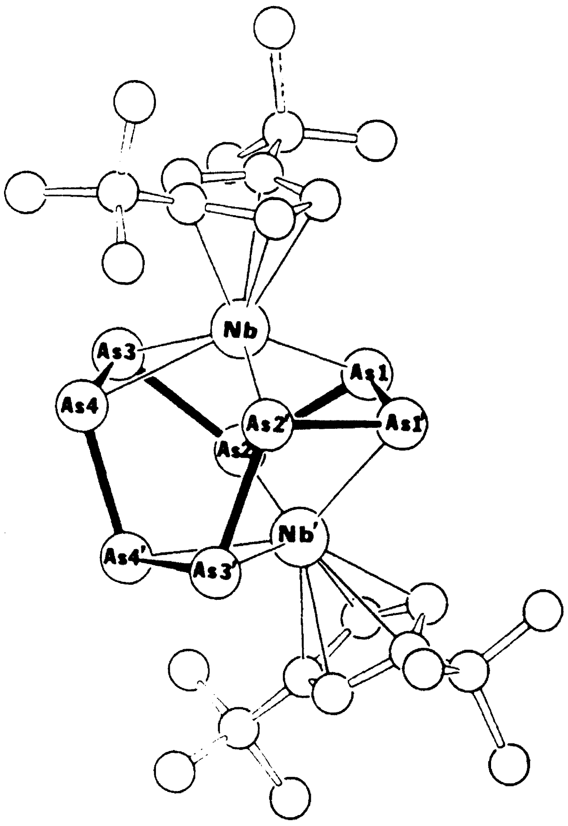
On the one hand, the photolysis of a $P_4/[Cp'Fe(CO)_2]_2$ -

toluene solution affords $[Cp'_4Fe_4(CO)_6(P_8)]$(23) [24], whose P_8 cage can be formally derived from the open-edged $(CH)_8$ isomer cuneane [24] (see G in Scheme 2).



23 [24]

$Cp' = \eta^5\text{-}C_5H_4Me$



24 [25]

$Cp'' = \eta^5\text{-}1,3\text{-}tBu_2C_5H_3$

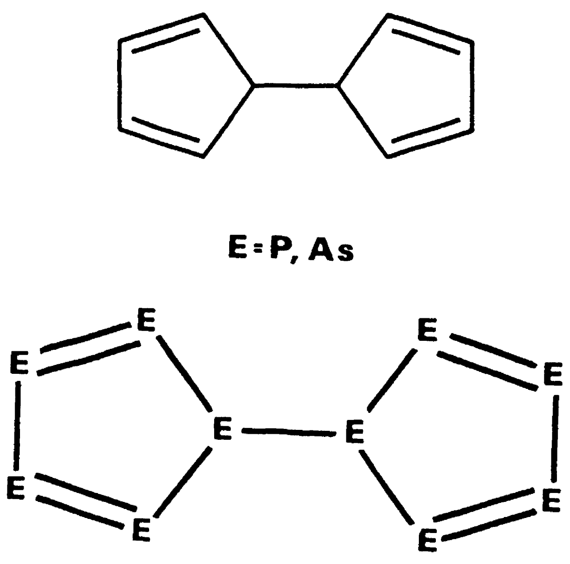
X-ray crystallographically P-P distances from 2.185(4) to 2.254(4) Å have been found for 23 [24]

On the other hand, in $[(Cp''Nb)_2(\mu,\eta^{4:4}\text{-}As_8)]$(24) [25], synthesized from $[Cp''Nb(CO)_4]$ and As_4 in decalin (170°C,2h), the As_8 analogue of cyclooctatetraene (see 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.

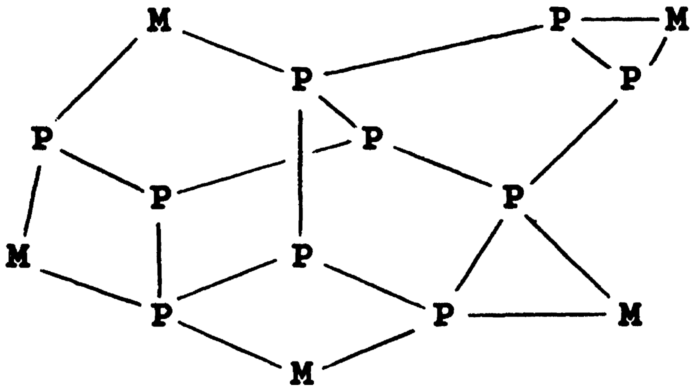
2.7. E_{10} Ligands (E = P,As)

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



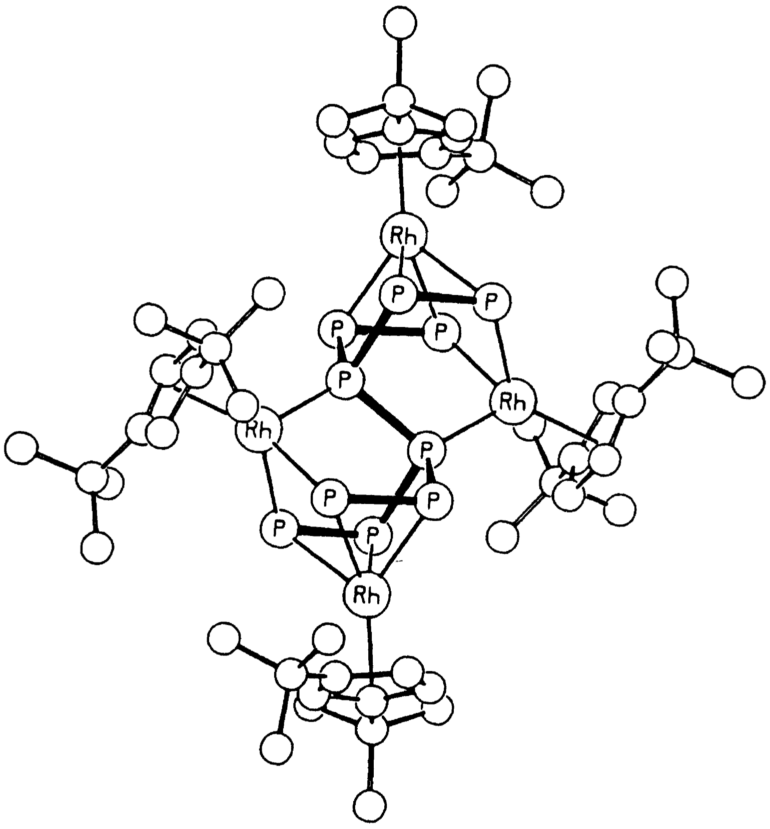
Scheme 3

Whereas P_{10}, synthesized by cothermolysis of $[CpCr(CO)_3]_2$, $Cp=\eta^5-C_5H_5$, and P_4, in the paramagnetic complex 25 [26] forms a polycyclic Cr_5P_{10} skeleton (cf. Baudler's polyclic phosphanes [4]) E_{10} (E = P, As) can be formally derived from $(CH)_{10}$ dihydrofulvalene (see Scheme 3). Treatment of $[Cp''Rh(CO)_2]$ with E_4 at elevated temperature affords the tetranuclear complexes 26 (a: M = P, b: M = As) [27].



25 [26]

M = $CpCr(CO)_2$



26a [27]

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 d^6 rhodium.

Acknowledgement. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support as well as Johnson Matthey for a generous loan of $RhCl_3$.

3. REFERENCES

1 O.J. Scherer, Angew. Chem. 102(1990) 1137; Angew. Chem. Int. Ed. Engl. 29 (1990) 1104.

2 R. Hoffmann, Angew. Chem. 94 (1982) 725; Angew. Chem. Int. Ed. Engl. 21 (1982) 711.

3 H.G. von Schnering and W. Hönle, Chem. Rev. 88 (1988) 243.

4 M. Baudler, Angew. Chem. 94 (1982) 520; Angew. Chem. Int. Ed. Engl. 21 (1982) 492; ibid. 97 429 and 26 (1987) 419.

5 H.Slodzyk, unpublished results.

6 O.J. Scherer, J. Braun, P. Walther, G. Heckmann and G. Wolmershäuser, Angew. Chem. 103 (1991) 861; Angew. Chem. Int. Ed. Engl. 30 (1991) 852.

7 H. Sitzmann, unpublished results.

8 J. Braun, Thesis, University of Kaiserslautern, 1990.

9 J. R. Harper and A. L. Rheingold, J. Organomet. Chem. 390 (1990) C 36.

10 O.J. Scherer, C. Blath, G. Heckmann and G. Wolmershäuser, J. Organomet. Chem. 409 (1991) C 15.

11 O.J. Scherer, B. Werner, G. Heckmann and G. Wolmershäuser, Angew. Chem. 103 (1991) 562; Angew. Chem. Int. Ed. Engl. 30 (1991) 553.

12 M. Di Vaira, P. Stoppioni and M. Peruzzini, J. Chem. Soc. Dalton Trans. 1990, 109.

13 M. Di Vaira, D. Rovai and P. Stoppioni, Polyhedron 9 (1990) 2477.

14 O. J. Scherer, J. Vondung and G. Wolmershäuser, Angew. Chem.101 (1989) 1395; Angew. Chem. Int. Ed. Engl. 28 (1989) 1355.

15 O. J. Scherer, J. Vondung and G. Wolmershäuser, J. Organomet. Chem. 376 (1989) C 35.

16 O. J. Scherer, R. Winter, G. Heckmann and G. Wolmershäuser, to be published.

17 For example: K. Wade, Adv. Inorg. Chem. Radiochem. 18 (1976) 1; D. M. P. Mingos, Acc. Chem. Res. 17 (1984) 311.

18 M. Scheer, E. Herrmann, J. Sieler and M. Oehme, Angew. Chem. 103 (1991) 1023.

19 D. Jung, M.-H. Whangbo and S. Alvarez, Inorg. Chem. 29 (1990) 2252.

20 M. Baudler and T. Etzbach, Angew. Chem. 103 (1991) 590; Angew. Chem. Int. Ed. Engl. 30 (1991) 580.

21 B. Rink, O. J. Scherer, G. Heckmann and G. Wolmershäuser, to be published.

22 O. J. Scherer, K. Pfeiffer, G. Heckmann and G. Wolmershäuser, J. Organomet. Chem., in press.

23 R. O. Jones and D. Hohl, J. Chem. Phys. 92 (1990) 6710.

24 M. E. Barr, B. R. Adams, R. R. Weller and L. F. Dahl, J. Am. Chem. Soc. 113 (1991) 3052.

25 O. J. Scherer, R. Winter, G. Heckmann and G. Wolmershäuser, Angew. Chem. 103 (1991) 860; Angew. Chem. Int. Ed. Engl. 30 (1991) 850.

26 L. Y. Goh, R. C. S. Wong and E. Sinn, J. Chem. Soc. Chem. Commun. 1990, 1484.

27 O. J. Scherer, B. Höbel, G. Heckmann and G. Wolmershäuser, to be published.