P$_n$ and As$_n$ Ligands: A Novel Chapter in the Chemistry of Phosphorus and Arsenic

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Introduction

Even today, the most prominent phosphorus- and arsenic-containing complex ligands are of the 2e$^-$, 4e$^-$, and 6e$^-$ types R_3E, $R_2E(CH_2)_nER_2$, and $RC[(CH_2)_nER_2]_3$ (E = P, As). In 1969 and later, the groups of Dahl,[1] Ginsberg,[2] and Sacconi[3] reported on their pioneering work in the novel field of coordinatively stabilized, substituent-free ("naked") P$_n$ and As$_n$ ligands. These developments have been reviewed.[4]

Stimulated by these results, we examined the influence of substituted cyclopentadiene (Cp^R) ligands on the metal fragment with regard to the formation of acyclic and cyclic E$_n$ (E = P, As) building blocks. The successful coordinative stabilization of cyclo-E$_4$, cyclo-E$_5$$^-$, and cyclo-E$_6$ ligands—the all-phosphorus and all-arsenic analogues of cyclobutadiene C_4H_4, the cyclopentadienide ion $C_5H_5^-$, and benzene C_6H_6—as sandwich and triple-layer sandwich complexes represent a further impressive example of the diagonal relationship between carbon and phosphorus.[4,5]

C	N
Si	P

Furthermore, many of these compounds also are in accord with the concept of isolobal (HC $\longleftrightarrow$ P(As) $\longleftrightarrow$ NiCp^R) and isoelectronic fragments[6] as well as often fulfilling the electron-counting rules of Wade–Mingos.[7] Much new information about the remarkable parallels to polyphosphides (solid-state chemistry),[8] monocyclic and polycyclic phosphanes,[9] and the rich diversity of their reactivities has been obtained in the past decade. Typical examples are the oxidations to PX (X = O, S, Se, Te) ligands, ring cleavage and expansion reactions of E$_n$, and the activation of P$_4$ and P$_2$ at room temperature.

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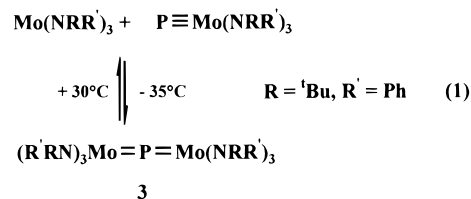
It is also worthy of note that complexes with P$_n$ and As$_n$ ligands are often thermally very stable, and some can even be handled in the air for short times.

The rapid developments in this field of phosphorus and arsenic chemistry were also influenced by the pioneering work of Huttner's group on phosphinidine, arsinidine, and starlike complexes [{L$_n$M}$_3$(E≡E)], where E = As, Sb, Bi.[10]
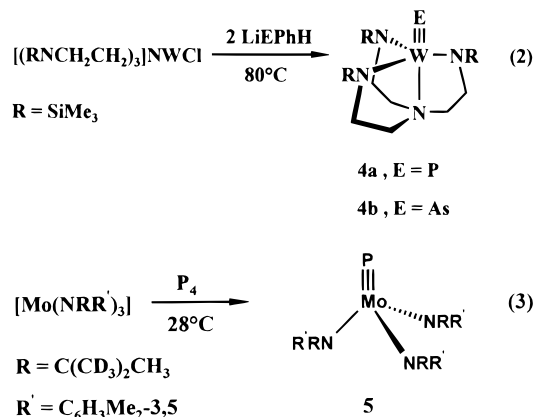
E$_1$ Ligands (E = P, As). Sources for the pnictogen E$_n$ ligands are, in particular, P$_4$ and As$_4$ as well as EX$_3$, E(SiMe$_3$)$_3$, cyclo-(AsR)$_n$, and E$_7$(SiMe$_3$)$_3$ or M$_3$E$_7$ (M = Li, Na, K, Rb; E = P, As). The L$_n$M fragments originate from mono- or dinuclear transition metal complexes with L$_n$ = CO and/or (mostly substituted) Cp^R.[4] The relevant coordination modes are shown schematically in Scheme 1.

The classical trivalent coordination of the phosphorus and arsenic atoms is achieved in structures **A** to **A'''**.

The complex [Cp*$_2$ZrPZrCp*$_2$] (**2**), formed by the reaction of [Cp*$_2$ZrCl$_2$] with KH and PH$_2$R (R = 2,4,6-^{t}Bu$_3$C$_6$H$_2$),[12] shows a striking parallel to the allene-like skeleton structure of [Cp^R(OC)$_2$Mn=E=Mn(CO)$_2$Cp^R]$^+$ (**1**; E = P, As; Cp^R = Cp*).[11] The X-ray crystallographic data for **2** are in harmony with the multiple bond character for the Zr–P bonds (2.54 Å); the Zr–P–Zr bond angle differs only slightly from linearity (167°). Similarly, a bond order of 2 has been proposed for the complex **3** (eq 1).[13]

$$Mo(NRR')_3 + \quad P≡Mo(NRR')_3$$

$$+ 30°C \Big\updownarrow - 35°C \qquad R = {}^tBu, R' = Ph \qquad (1)$$
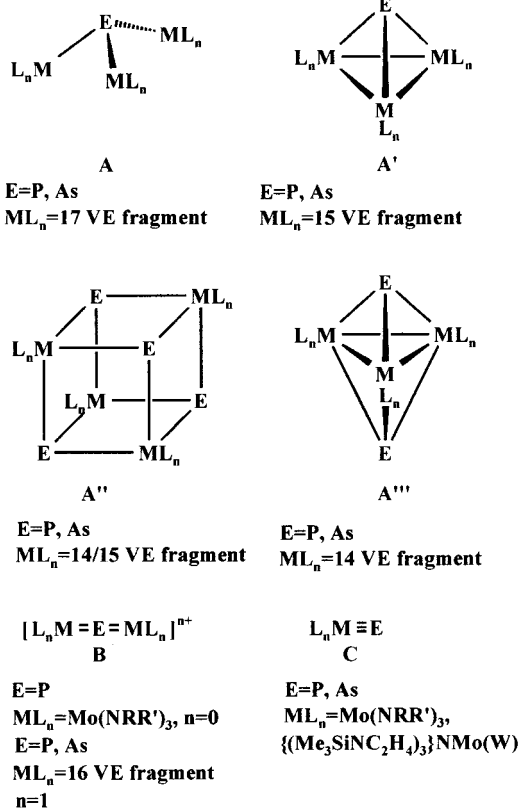
$$(R'RN)_3Mo=P=Mo(NRR')_3$$
$$\mathbf{3}$$

The long-sought and sometimes postulated complexes of the type **C** (Scheme 1), with a formal metal pnictogen triple bond, have now been verified in compounds **4** and **5** as shown in eqs 2 and 3.[14]

$$[(RNCH_2CH_2)_3]NWCl \xrightarrow[80°C]{2\ LiEPhH} \qquad (2)$$

R = SiMe$_3$

4a , E = P
4b , E = As

$$[Mo(NRR')_3] \xrightarrow[28°C]{P_4} \qquad (3)$$

R = C(CD$_3$)$_2$CH$_3$

R' = C$_6$H$_3$Me$_2$-3,5   **5**

The force constants for the triple bonds in **4a,b** parallel those for the bonds in HC≡E (E = N, P).[14] Moreover, unusual ^{31}P chemical shielding tensors have been found for **4a** and **5** in comparison with the isoelectronic molecules R–C≡P and [R–N≡P]$^+$.[14]

Scheme 1

A
E=P, As
ML_n=17 VE fragment

A'
E=P, As
ML_n=15 VE fragment

A''
E=P, As
ML_n=14/15 VE fragment

A'''
E=P, As
ML_n=14 VE fragment

$[L_nM=E=ML_n]^{n+}$
B
E=P
ML_n=Mo(NRR')$_3$, n=0
E=P, As
ML_n=16 VE fragment
n=1

$L_nM\equiv E$
C
E=P, As
ML_n=Mo(NRR')$_3$,
{(Me$_3$SiNC$_2$H$_4$)$_3$}NMo(W)

Complex **4a** reacts with [M(CO)$_5$(thf)] (M = Cr, W) to furnish (RNCH$_2$CH$_2$)$_3$NW$\equiv$P:$\rightarrow$M(CO)$_5$ (**6**), while the analogous complexes (^{t}BuO)$_3$W$\equiv$P:$\rightarrow$M(CO)$_5$ (**7**) have been characterized spectroscopically from the reaction of [M(CO)$_5$(thf)] (M = Cr, W) with ^{t}BuC$\equiv$P and [W$_2$(O^{t}Bu)$_6$].[14]

Compounds with a trigonal planar μ_3-E$_1$ atom (phosphinidine type) are known in addition to the complexes **A** to **A'''** (Scheme 1), with pyramidal E$_1$ atoms.[4,10] The five valence electrons of the E$_1$ atom are frequently involved in bonding to three L$_n$M fragments.

The paramagnetic complex [{Cp$_2$Zr}$_2$(μ-Cl)(μ_3-P){ZrCp$_2$-Cl}] (**8**), containing one Zr(III) and two Zr(IV) centers, was recently prepared from H$_2$PR and Cp$_2$ZrCl$_2$; the three Zr atoms and the P atom are coplanar, with one short (2.51 Å) and two longer (2.59/2.60 Å) bonds.[15]

Not shown in Scheme 1 are the structurally highly diverse clusters containing semi-interstitial P and interstitial E atoms (E = P, As, Sb) incorporated in open or closed polyhedra as $\mu_{5,6,8,9,10,12}$-E$_1$ atoms.[4]

PX Ligands (X = O, S, Se, Te). The PO radical, the phosphorus analogue of the ubiquitous NO molecule and the most abundant phosphorus-containing species in interstellar clouds,[16] was coordinatively stabilized in complex **10** (eq 4) in 1991.[17a,18a]

Since then, the intriguing series of PO complexes **11–13**[14] (Scheme 2) has been prepared. The method of choice for the conversion of P to PO is air oxidation.[18a] An additional method is hydrolytic cleavage of the P–N bond in [{L$_3$M}$_4$(μ_3-PNR$_2$)] (**14**), the phosphinidine complex precursor of **11**.[17b]

[Cp$^R_2$Ni$_2$P$_2${W(CO)$_4$}]
9
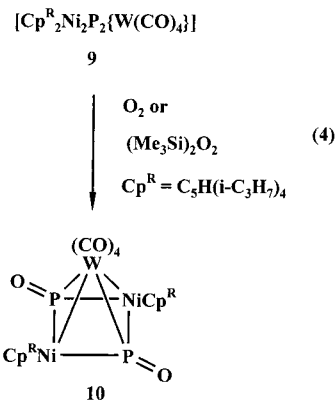
The as yet only known example of a complex with a terminal PO ligand, **13**, was prepared by oxidation of L$_3$Mo$\equiv$P with dimethyldioxirane.[14a] In complexes of these types, the IR $\tilde{\nu}$(PO) band is observed between 1050 and 1265 cm^{-1}, while the PO bond lengths range from 1.46 to 1.51 Å. Reactivity studies have shown that the P atom of the PO ligand is susceptible to nucleophilic attack.[14a]

Apart from the μ_3-PS derivatives of complex **10**[18a] and [{CpFe(CO)$_2$}$_3$(μ_3-PS)] (**15**),[18b] the sulfur analogue **13'** of **13** is, again, the only example of a complex with a terminal PS ligand.[14a] Crystallographic data for these complexes emphasize the importance of the following resonance structures: X–P$\equiv$Mo(NRR')$_3$ $\leftrightarrow$ X=P=Mo(NRR')$_3$ (**13**, X = O; **13'**, X = S).[14a] Complexes of these types are usually prepared by oxidation of the corresponding P$_1$ derivative with elemental sulfur, S$_8$.[14,18]
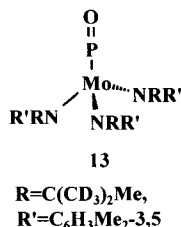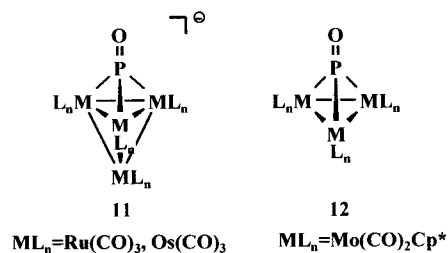
Compound **16** is an ideal starting material for the preparation of complexes containing one or two μ_3-PX (X = O, S, Se, Te) ligands (eq 5). The following trends in these
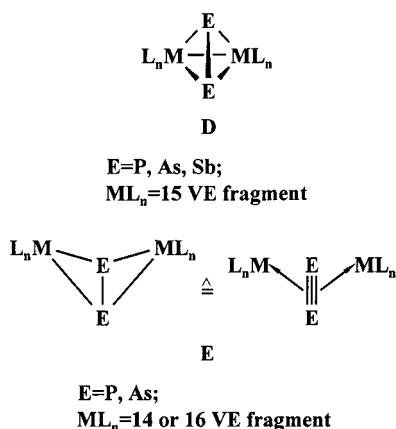

17a: X = Se   17b: X = Te

18a: X = O   18b: X = S   18c: X = Se
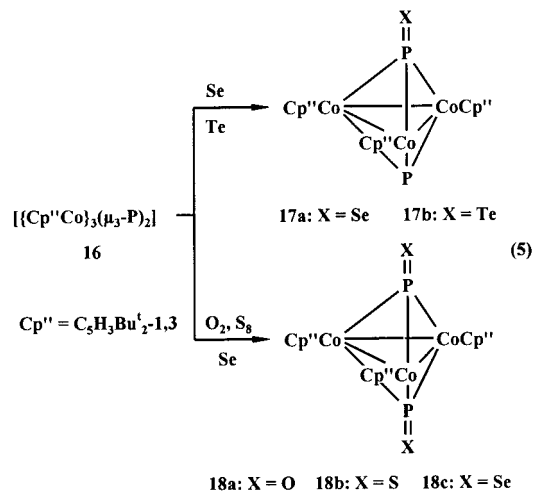
reactions are worthy of note. On reaction with O$_2$ or S$_8$, **16**[19a] furnishes exclusively the dioxidation products **18a,b**,[19c] whereas reaction with gray selenium affords both **17a**[19b] and **18c**.[19a] On reaction with tellurium, only one phosphorus atom of **16** is oxidized to yield **17b**.[19c]

The photochemical and thermal rearrangements of a μ_3-PS ligand to a side-on coordination mode are illustrated in eqs 6 and 7. Complex **21** represents the first example of a compound in which two chiral tetrahedranes, each
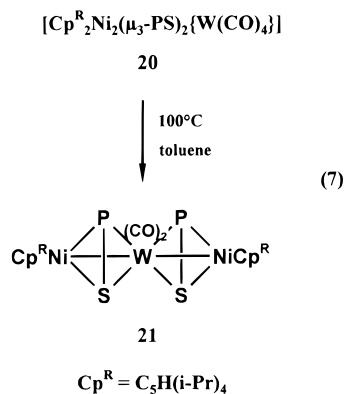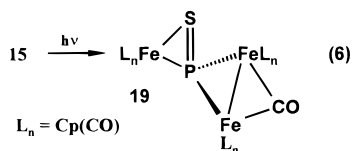
Scheme 2

11

ML$_n$=Ru(CO)$_3$, Os(CO)$_3$

12

ML$_n$=Mo(CO)$_2$Cp*

13

R=C(CD$_3$)$_2$Me,
R'=C$_6$H$_3$Me$_2$-3,5

Scheme 3

D

E=P, As, Sb;
ML$_n$=15 VE fragment

E

E=P, As;
ML$_n$=14 or 16 VE fragment

containing two main group atoms and two transition metal fragments, are joined by a common transition metal atom (W) vertex.[18a]

(6)

L$_n$ = Cp(CO)

[Cp$^R_2$Ni$_2$(μ_3-PS)$_2${W(CO)$_4$}]

20

(7)

21

Cp^R = C$_5$H(i-Pr)$_4$

The P=S bond lengths of the μ_3-PS ligands are in the range of 1.95−2.01 Å[18a,b] in **20** and, as expected, are

lengthened in **21** (2.09 Å, P−S single bond).[18a] The previously missing links in the PX ligand series, namely PSe and PTe, have been coordinatively stabilized in compounds **17a,b** and **18c** and partially characterized by X-ray crystallography [**17a**, d(P−Se) = 2.09 Å].[19b]

E$_2$ Ligands (E = P, As). A striking feature of molecules with this type of ligand is the dominating role of the E$_2$M$_2$ tetrahedrane skeleton (**D**; E = P, As, Sb; L$_n$M = 15 valence electron (VE) fragment; Scheme 3).[4] Molecules with the E$_2$M$_2$ butterfly skeleton (**E**; Scheme 3) almost exclusively contain 14 VE fragments [e.g., Ni(Pd)L$_2$; L = PR$_3$] at the wing tips, the only exception being [{Cp*(OC)$_2$Mn}$_2$(μ-η^2:η^2-As$_2$)] (**22**), with 16 VE ML$_n$ fragments.[20]

A remarkable mild activation of P$_4$ at room temperature has been realized according to eq 8.[21] In the diphosphini-

2 [{Cp*(OC)$_2$Re}$_2$] (Re≡Re)

(8)

23   **24**

[Re] = Re(CO)$_2$Cp*
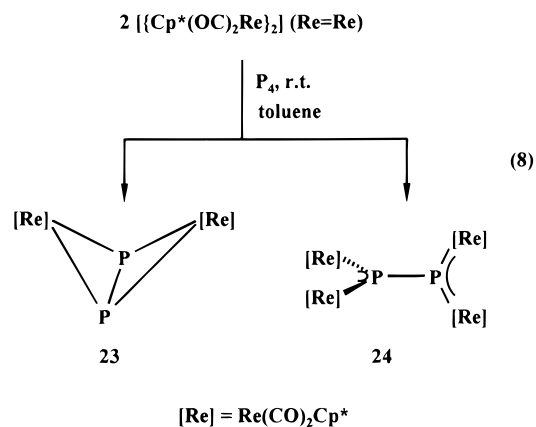
dine complex **24**, the unusual mesomeric $\overline{\text{P}}$−$\overline{\text{P}}$ structure of the P$_2$ molecule is stabilized as a formal 8 σ electron donor ligand. On going from **23** to **24**, d(P−P) increases from 2.04 to 2.23 Å.[21] The Re$_2$P planes in **24** are nearly orthogonal (91.1°), cf. [{Cp(OC)$_2$Mn}$_4$As$_2$] (**25**).[20b]

To date, [{Cp*(OC)$_2$Mo}$_2$(μ-η^2:η^2-Sb$_2$)] (**26**) is the only example of a compound with an Sb$_2$Mo$_2$ tetrahedrane structure. It is prepared by cothermolysis of [{Cp(OC)$_3$Mo}$_2$] with metallic antimony[22a] or with (^{t}BuSb)$_4$ as source of Sb$_2$.[22b] The Sb−Sb bond distance is in the range typical for double bonds.[22a]

Reactivity of P$_2$ Ligands. Promising perspectives with regard to activation of P$_2$ ligands were recently discovered (eqs 9 and 10). The P−P bond of the starting material **27** is cleaved during the two-step reaction leading to **28**[23a] (eq 9). Metalation of **28** with ^{t}BuLi followed by reaction

[{Cp(OC)$_2$Mo}$_2$(μ-η^2:η^2-P$_2$)]

27

1. OH$^-$
2. HBF$_4$

(9)

28
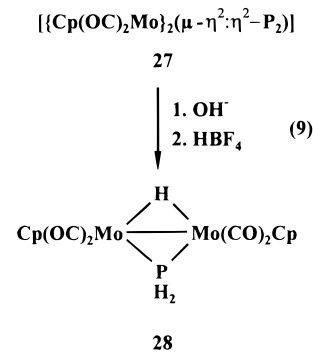
with ECl_3 (E = As, Sb) affords [{$Cp(OC)_2Mo$}$_2(\mu\text{-}\eta^2:\eta^2\text{-}PE)$], the first compounds containing PAs or PSb coordinatively stabilized in clusters having an Mo_2PE tetrahedrane skeleton.[23b] An extremely mild cleavage of the P_2 ligand possessing a formal P=P double bond (2.04 Å) is observed in the reaction of the butterfly-shaped **23** with excess [$W(CO)_5(thf)$] at room temperature. The phosphinidine complex **30**, with two planar 5e$^-$ donor P_1 ligands, is formed in addition to the chiral tetrahedrane **29** (eq 10).[21]


(10)

$[Re] = Re(CO)_2Cp*$
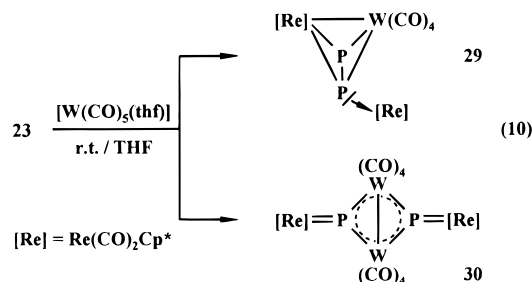
$(E_2)_n$ Ligands (E = P, As; n = 2, 3, 4). Some remarkable cluster and cagelike molecules with $(E_2)_n$ ligands have been prepared in the past few years. In addition to species of the [{L_nM}$_2(\mu\text{-}\eta^2:\eta^2\text{-}E_2)_2$] type,[4] the clusters **31** (eq 11), with triangulated dodecahedral Fe_4E_4 cores, have been obtained.[24] Interestingly, all the phosphorus atoms of


(11)

[Fe] = FeCp
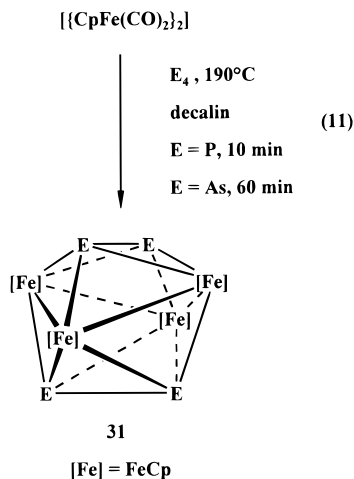
cluster **31** can be oxidized by S_8 or by gray selenium to afford the previously unknown XPPX ligands (X = S, Se).[24] On going from **31** (E = P) to [{$CpFe$}$_4(P_2S_2)_2$], the mean phosphorus–phosphorus bond length increases from 2.31 to 2.37 Å.[24]

Complexes with a Co_3E_6 skeleton are accessible as shown in eq 12. Although the E–E bond lengths in the Co_2E_2 butterfly subunits of **32a,b** are in the typical ranges for double bonds (P=P = 2.05 Å,[26a] As=As = 2.29 Å[25]), the other two E_2 ligands exhibit E–E and E···E bond lengths of 2.17/2.52 and 2.55 Å for E = P and 2.40/2.41/2.73 and 2.78 Å, respectively, for E = As. The reaction according to eq 12a also furnishes **33**, which can formally be regarded as an open-edged Dewar hexaarsabenzene (As···As = 3.55

(12)

32a: E = As
32b: E = P
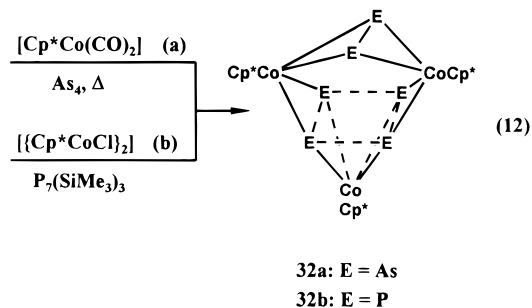
Å, As–As = 2.32–2.58 Å), capped by two Cp*Co fragments.[25]

33
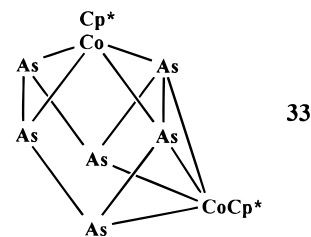
The reactions of $E_7(SiMe_3)_3$ with $FeCl_2$ and $LiCp*$ afford [{$Cp*Fe$}$_3E_6$]$^+$ (**32c**, E = P, Fe in place of Co;[26a] **32d**, E = As, Fe in place of Co[26c]) with four fewer electrons and an E_6 prismane unit in which one E–E bond has been cleaved (P–P = 2.27–2.39 Å;[26a] As–As = 2.51–2.71 Å[26c]). The corresponding Co_3As_6 framework of [{$Cp*Co$}$_3As_6$]$^{2+}$ consists of two cyclo-As_3 units [$\bar{d}(As–As)$ = 2.56 Å], forming an elongated As_6 prismane (As···As = 2.85 Å).[27]

Compounds of the type **32** have been examined by means of density functional calculations.[27] The complexes **32a** and **33** serve as versatile starting materials for cluster expansion reactions.[28] The skeleton of [$Pd_9As_8L_8$] (L = PPh_3), prepared by the reaction of [$PdCl_2L_2$] with $As(SiMe_3)_3$, is made up of a Pd-centered Pd_8 cube, capped by four As_2 units.[26d]
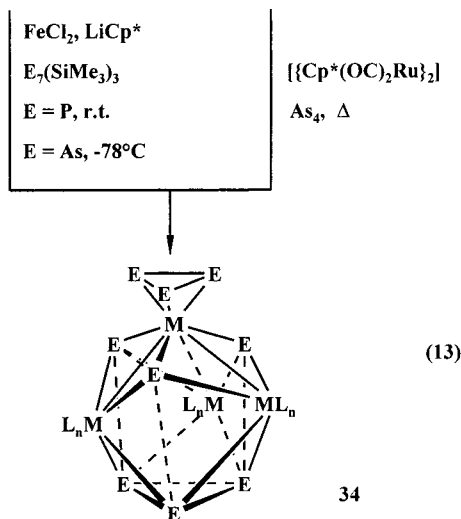
E_3 Ligands (E = P, As, Sb). In addition to the most important coordination modes[4] **F** and **G** (Scheme 4), other novel developments are the synthesis of [$Cp*(OC)_2Mo$-($\eta^3\text{-}Sb_3$)], containing a cyclo-Sb_3 ligand[22b] (cf. complex **26**), and reactivity studies on [(triphos)CoP_3].[29] Its cyclo-P_3 ligand remains intact on protonation[29a] with CF_3SO_3H and on reaction with RHg^+.[29b]

Further illustrative examples of the often unpredictable E_n and/or cluster-type complexes are the tetranuclear species **34** and **35**, with nine and six pnictogen atoms, respectively (eqs 13 and 14). A striking feature of **34** is the three different sets of E–E bond lengths: the ME_3 tetrahedrane subunit has P–P bond lengths of 2.11–2.12 Å,[26a] (As–As = 2.31–2.33 Å);[26b] longer distances are seen for the cyclo-E_3 parts of the ME_6 nortricyclane skeletons, while the E···E separations are even larger [2.33/2.42 Å for $\bar{d}(P–P)/(P···P)$ in **34a**; 2.57/2.73 Å for $\bar{d}(As–As)/(As···As)$ in **34b**]. The M_4P_6 skeleton of **35** consists of a distorted M_4P_4 cubane with one pair of opposing faces, each capped
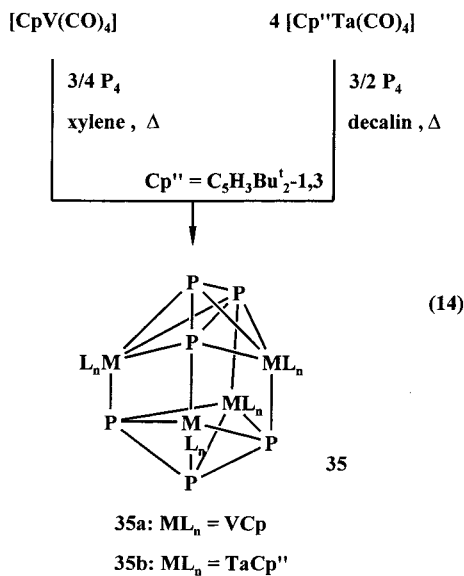
Scheme 4

F

E=P, As, Sb;
ML_n=15 VE fragment

G

E=P, As; ML_n=15/16 VE-
fragment, n=0,1,2
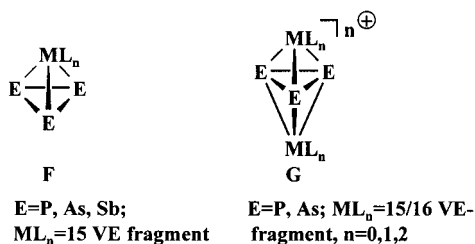
by one P atom from one of the two acyclic P_3 ligands (average P–P bond lengths, 2.18 Å in **35a**,[30a] 2.25 Å in **35b**[30b]).

(13)

34

34a: E = P, ML_n = FeCp*, M = Fe

34b: E = As, ML_n = RuCp*, M = Ru

34c: E = As, ML_n = FeCp*, M = Fe

[CpV(CO)$_4$]   4 [Cp''Ta(CO)$_4$]

3/4 P_4	3/2 P_4
xylene , Δ	decalin , Δ

Cp'' = $C_5H_3Bu^t_2$-1,3

(14)

**35**

35a: ML_n = VCp

35b: ML_n = TaCp''

The complex type **36** is formed by an unexpected and irreversible ring closure reaction (eq 15).[31]

E_4 Ligands (E = P, As). The most important coordination modes[4] are illustrated in Scheme 5. To date, no further examples of types **H** and **I** with terminal[3] or side-
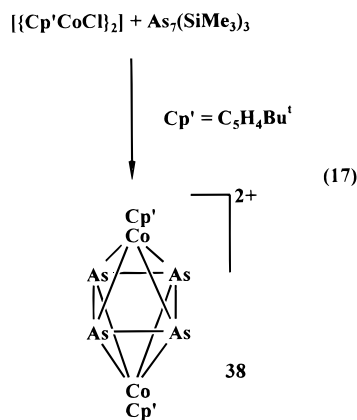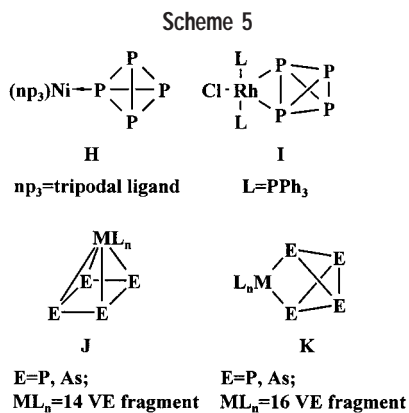

Cp' = $C_5H_4Bu^t$ | 0°C, r.t.
  - [Cr(CO)$_6$]
  - [{Cp'(CO)$_2$Mo}$_2$]

(15)

36
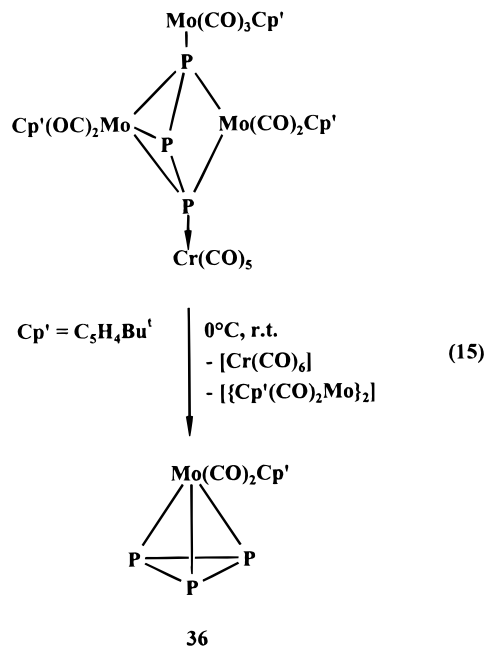
on[2] coordination of the P_4 tetrahedron have been reported. Photochemical[32a] or thermal reaction[32b] of P_4 with [W(CO)$_5$L] furnishes [{(OC)$_4$W}{PW(CO)$_5$}$_4$] (structure **J**, Scheme 5), in which cyclo-P_4 exists as a 12e$^-$ donor ligand.

The P_4 ligand in complex **37** (eq 16), which has also been examined with the help of EHT calculations, experiences a severe, kitelike distortion to afford a P_1 and a P_3 unit (P···P = 2.50 Å).[33]

[Cp''Co(CO)$_2$]
Cp'' = $C_5H_3Bu_2^t$-1,3

37   (16)
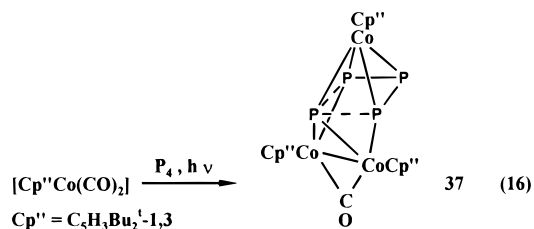
The 30 VE triple-decker cation **38** (closo type, $n + 1 = 7$ SEPs; eq 17) has a cyclo-As_4 unit as the middle layer and was further characterized by density functional calculations;[27] the As–As bond lengths are in the range 2.455–2.47 Å.

[{Cp'CoCl}$_2$] + As$_7$(SiMe$_3$)$_3$

Cp' = $C_5H_4Bu^t$

(17)

38

Scheme 5

H

np_3=tripodal ligand

I

L=PPh$_3$

J

E=P, As;
ML$_n$=14 VE fragment

K

E=P, As;
ML$_n$=16 VE fragment

Mechanistic Aspects. Mechanistic features of the reactions of E_4 tetrahedra with $Cp^RM(CO)_n$ fragments are summarized in Scheme 6A,B. Photolysis of [{Cp''Fe-(CO)$_2$}$_2$] with P$_4$ leads to the series of complexes **39–43**, possessing cyclic and acyclic P$_4$ ligands,[34a] by successive loss of CO ligands and cleavage of one to three P–P bonds in the P$_4$ subunit (Scheme 6A). Brief thermolysis of [{Cp'''Fe(CO)$_2$}$_2$] (Cp''' = 1,2,4-^{t}Bu$_3$C$_5$H$_2$) with P$_4$ proceeds with exclusive cleavage of one P–P bond to furnish *exo,exo*-[{Cp'''Fe(OC)$_2$FeP}$_2$P$_2$] (cf. **39**) in 75% yield, the butterfly structure of which has been confirmed by crystallography.[34b] Reaction of this product with diphenylacetylene leads to the sandwich complex [Cp'''Fe-(η^5-P$_3$C$_2$Ph$_2$)]. This is the first example in which the triphosphacyclopentadienide unit cyclo-(P$_3$C$_2$Ph$_2$)$^-$ has been formed directly from P$_4$ and an alkyne.[34c]
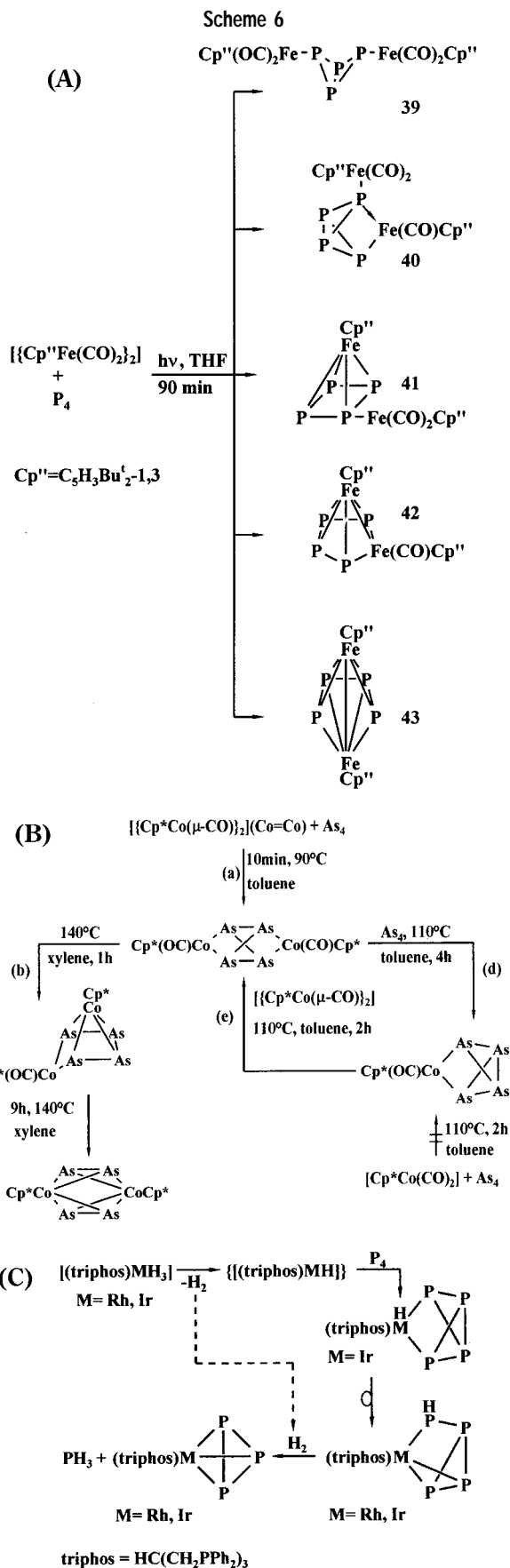
The CO elimination and As–As bond cleavage sequences a–e in Scheme 6B for the cothermolysis reaction of As$_4$ with [{Cp*Co(μ-CO)}$_2$] were deduced from ^{1}H NMR studies in comparison with known and structurally characterized cobalt complexes containing As$_4$ and (As$_2$)$_2$ ligands.[35]

Convincing evidence for the mechanism (Scheme 6C) postulated for the hydrogenation of P$_4$ with [(triphos)MH$_3$] (M = Rh, Ir) to give coordinated cyclo-P$_3$ and PH$_3$ has been presented.[36]

E$_5$ Ligands (E = P, As). On account of their surprising and manifold reactivities (Scheme 7), the most important members of this group are the sandwich complexes [Cp*Fe(η^5-E$_5$)] (**44**), conveniently prepared by thermolysis of [{Cp*Fe(CO)$_2$}$_2$] with E$_4$ (E = P, As).[4]

The E$_5$ unit remains intact in many reactions, e.g., in the cationic, 30 VE triple-decker complex **45**, reaction a.[37a] The corresponding Ru and Os analogues are obtained by transfer of the cyclo-E$_5$ unit, reaction b.[37b] The previously unknown η:$^5\eta^2$-cyclo-E$_5$ coordination mode is present in the complexes **47**, reaction c, in which the E–E bonds bearing the additional η^2-coordination are elongated to 2.36 Å for E = P and 2.50 Å for E = As.[37c]

Although the P$_5$ ring in complex **48**, reaction d, has an envelope conformation,[37d] cisoid E$_5$ chain ligands are observed in complexes **51**, reaction e.[30b,37d] The system **49/50**, reaction e, involves an unusual equilibrium between two distorted cubanes with FeTa$_2$P$_5$ skeletons: the

Scheme 6

(A)

[{Cp''Fe(CO)$_2$}$_2$]
+
P$_4$

Cp''=C$_5$H$_3$Bu$^t_2$-1,3

hν, THF
90 min

Cp''(OC)$_2$Fe-P... P-Fe(CO)$_2$Cp''

39

Cp''Fe(CO)$_2$ ... Fe(CO)Cp''

40

41

42

43

(B)

[{Cp*Co(μ-CO)}$_2$](Co≡Co) + As$_4$

(a) 10min, 90°C
toluene

140°C
xylene, 1h

(b)

Cp*(OC)Co ... Co(CO)Cp*

As$_4$, 110°C
toluene, 4h

(d)

(e) [{Cp*Co(μ-CO)}$_2$]
110°C, toluene, 2h

9h, 140°C
xylene

Cp*(OC)Co

110°C, 2h
toluene

[Cp*Co(CO)$_2$] + As$_4$

Cp*Co ... CoCp*

(C)

[(triphos)MH$_3$]
M= Rh, Ir

$-$H$_2$

{(triphos)MH}}

P$_4$

(triphos)M
M= Ir

PH$_3$ + (triphos)M

H$_2$

(triphos)M

M= Rh, Ir

M= Rh, Ir

triphos = HC(CH$_2$PPh$_2$)$_3$

structure of **49** comprises an FeP$_5$ six-membered ring in the chair conformation, capped by two Cp''Ta fragments,

Scheme 7
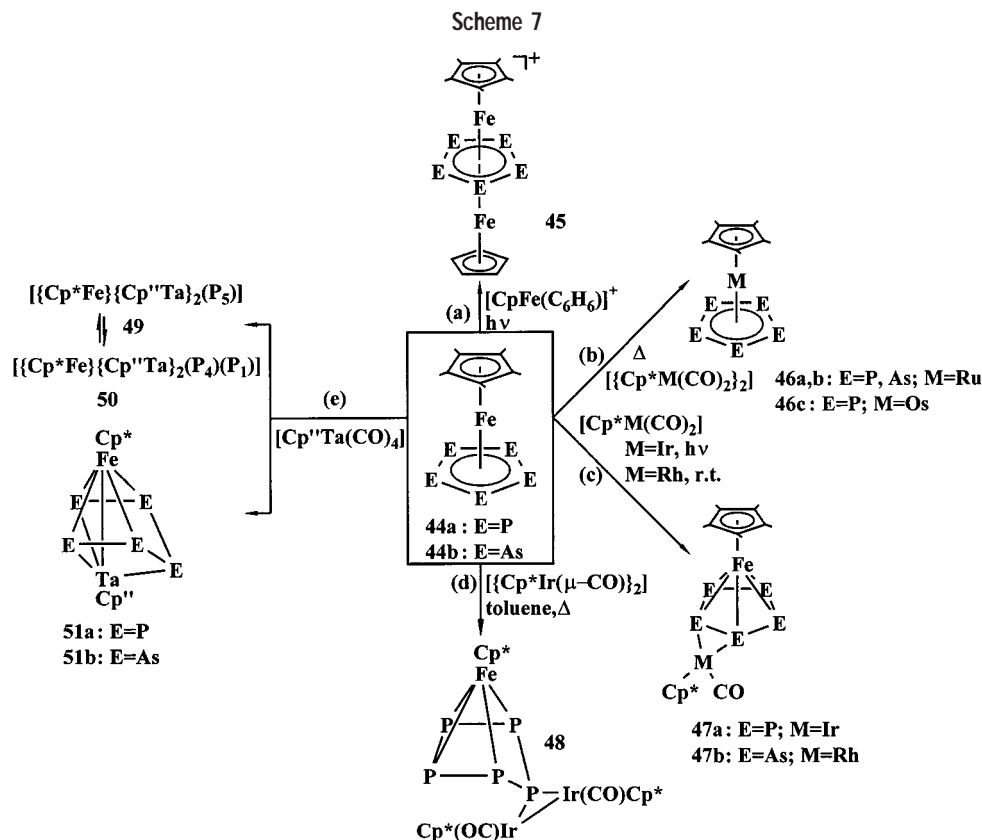
while the P_5 ligand in **50** is split into a P_1 unit and a trigonal pyramidal P_4 unit.[30b]

A broad palette of Cp^RCo complexes containing "naked" P_n ligands is obtained from the reactions of **44a** with $[Cp^RCo(CO)_2]$ species (eq 18).[19a]
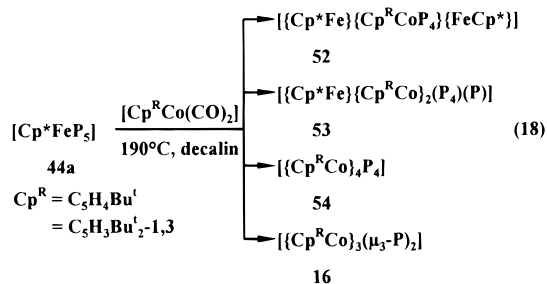
The "triple-decker" complex **52** (eq 18), with a planar CoP_4 five-membered ring as the middle layer, is worthy of special mention. Replacement of the mononuclear starting material $[Cp^RCo(CO)_2]$ in this reaction by the dinuclear species $[\{Cp^RCo(\mu\text{-}CO)_2\}_2]$ in eq 19 provides access to complex **55**.[19a]

The X-ray crystallographic data for **55** reveal that two of the P–P bonds (each 2.35 Å, compared with an average of 2.13 Å for the other three bonds) are also involved in side-on ($\eta^2{:}\eta^2$) coordination to the $Co_2Cp^R_2(\mu\text{-}CO)$ fragment.[19a]

A novel synthetic approach to P_5 sandwich complexes has been verified for $[Cp''Fe(\eta^5\text{-}P_5)]$ (**44c**) by the reaction of $K[Fe(CO)_2Cp'']$ ($Cp'' = 1{,}3\text{-}^tBu_2C_5H_3$) with $[(OC)_5Cr\text{-}(PCl_3)]$.[31] The cyclo-$P_5$ sandwich complexes of the type **44**
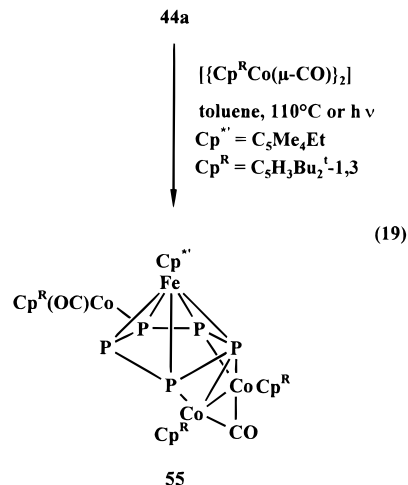
mentioned above show ^{31}P NMR chemical shifts in the range 153–167 ppm.

It is interesting to note that gray arsenic was used as staring material for the triple-decker sandwich $[\{CpCr\}_2\text{-}(\mu\text{-}\eta^5{:}\eta^5\text{-}As_5)]$.[38] Magnetic susceptibility studies on the related P_5 species $[\{Cp^*Cr\}_2(\mu\text{-}\eta^5{:}\eta^5\text{-}P_5)]^+$ revealed spin crossovers at 33 and 23 K.[39]

E_6 Ligands (E = P, As). Of the all-pnictogen analogues of the $(CH)_6$ valence isomers (Scheme 8), cyclo-E_6 (**L**) has been coordinatively stabilized as the middle layer of 28 VE triple-decker complexes.[4] The 26 VE triple-decker complex $[\{Cp''Nb\}_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)]$ experiences severe bis-allylic distortions which have been explained by means of extended Hückel calculations.[40] The formal E_6 prismane

Scheme 8

$E = CH, P, As$
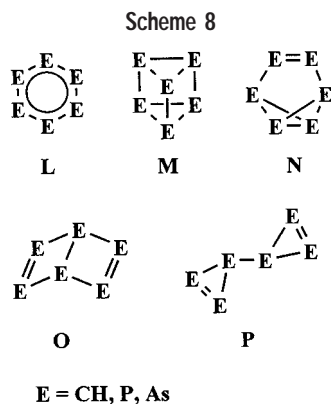
structure (**M**) is present as a subunit in nine-atom clusters of the $[\{Cp^*M\}_3E_6]^{n+}$ type (see above).

The open-edge E_6 benzfulvalene structure (**N**, Scheme 8) has been stabilized in the complexes **56** (eq 20). [41]
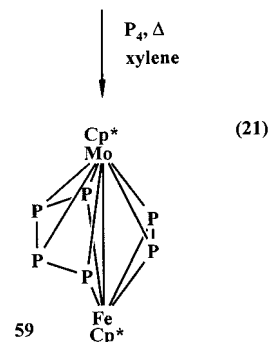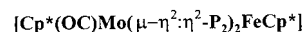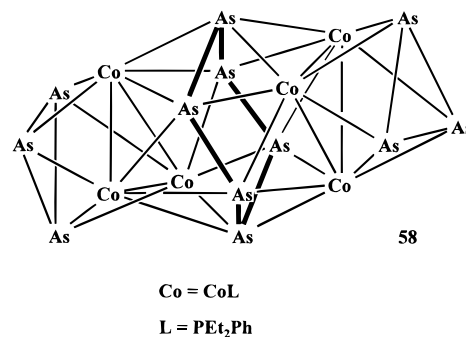

$E = P, As$
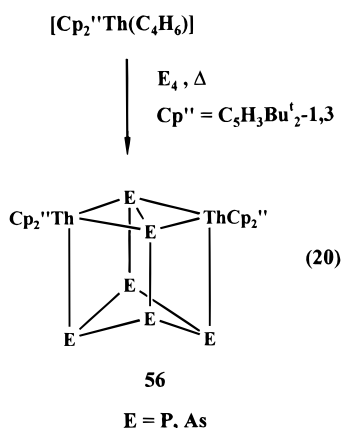
Although the E_6 bicyclopropenyl analogue **P** is still unknown, a part of this structure has been observed in the P_8 ligand of $[\{Cp''Co\}_3(P_3-P_5)]$ (**62**, see below).[42] The complex **57**, prepared from $[Cp^*_2Ti(CO)_2]$ and P_4,[4] contains
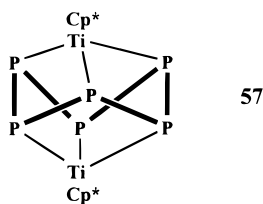

a cyclo-P_6 ligand in the chair conformation—which can formally be regarded as $[cyclo\text{-}P_6]^{6-}$ ($\triangleq cyclo\text{-}S_6$)—as part of its Ti_2P_6 cubane-like skeleton. In contrast, cyclo-As_6 is a subunit in the cluster $[(LCo)_6As_{12}]$ (**58**), generated in the reaction of $[CoCl_2L_2]$ with "K_3As_7".[26a] The unusual Co_6As_{12} skeleton of **58** is built up of a Co_6As_6 icosahedron, in which the cobalt atoms are capped by cyclo-As_3 ligands to form two face-sharing Co_3As_3 octahedra. The remaining As_6 ring adopts the chair conformation.[26a]

In addition to the mentioned complexes with cleaved "E_6" ligands ("E_6" = 2 × E_3, 3 × E_2), compound **59**, containing a "P_6" ligand (P_4/P_2), has been prepared as shown in eq 21.[43] The X-ray crystallographic data for **59** can best be interpreted in terms of two polyhedra (pentagonal $MoFeP_4$ pyramid and $MoFeP_2$ tetrahedrane) shar-


58

$Co = CoL$

$L = PEt_2Ph$

$[Cp^*(OC)Mo(\mu-\eta^2:\eta^2\text{-}P_2)_2FeCp^*]$

(21)

59

ing a common edge. The 54 cluster electrons are in accord with the electron-counting rules of Wade−Mingos.[7]

E_7 and E_8 Ligands (E = P, As, Sb). The currently known molecular E_7 building blocks in coordination chemistry have the nortricyclane- and norbornadiene-like skeletons of types **Q** and **R**. Structure **Q** has been realized in the
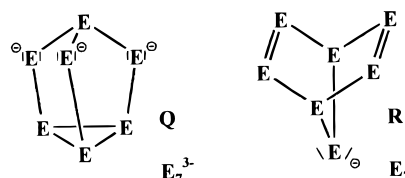
complex $[P_7\{Fe(CO)_2Cp\}_3]$,[26a] while complexes with the ligand **R** constitute by far the most intensively studied coordination mode.

Syntheses of the anionic complexes **60** (eq 22) by the groups of Eichhorn[45] and Tremel[46] opened up an intriguing chapter in the chemistry of Zintl ions[44] and provided a further bridge to solid-state chemistry.[4] Complexes **60**
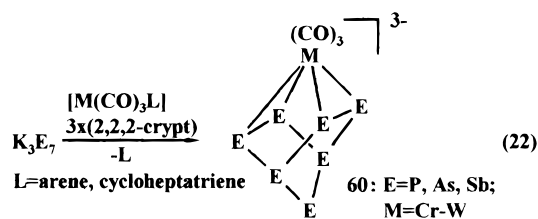
react with R_4N^+ salts (R = Me, Et, ^nBu) in ethylenediamine solution to furnish $[\{\eta^4\text{-}RP_7\}\{W(CO)_3\}]^{2-}$, in which R is bonded to the divalent P atom of **60**.[45] Many of these complexes exhibit fluxional behavior in solution.[45] The X-ray crystallographic data for the series $[\{\eta^4\text{-}E_7\}\{M(CO)_3\}]^{3-}$ (**60**) reveal the following features:[45,46] (i) four

short E−E bonds (2 × η^2 and 2 × to the divalent E atom) as well as (ii) two nonbonding E···E separations for the trapezoidally arranged "E$_2$" subunits coordinated to M(CO)$_3$ (E = P, As, M = Cr;[45] E = Sb, M = Mo[46]).

This class of compounds has also been studied by EH[46] and Fenske−Hall MO calculations.[45]

To date, neither cubic or square antiprismatic nor triangulated dodecahedral structures of E$_8$ have been stabilized coordinatively. However, the open-edge P$_8$-cuneane structure—a structural motif of Hittorf's phosphorus—is found in complex **61**, prepared as shown in eq 23 starting from P$_4$. The P−P bond lengths of the "P$_2$" bridges in **64** are 2.24 Å (cf. ref 47b).[47a]
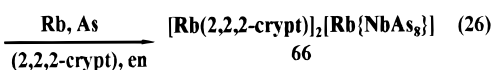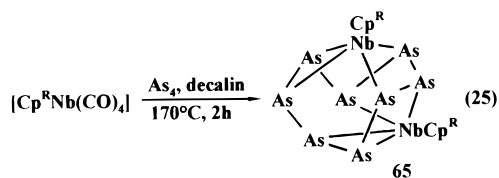
(23)
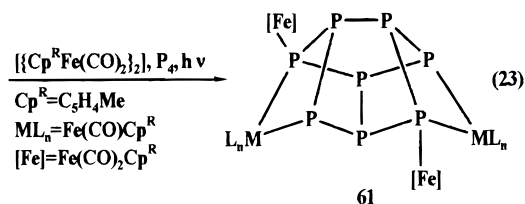
Cluster **62**, formed together with [{Cp'''Co}$_2$(P$_2$)$_2$] (**63**) and [{Cp'''Co}$_3$(P$_{12}$)] (**64**) according to eq 24,[42] contains an unusual P$_8$ ligand composed of a P$_5$−P$_3$ framework.

(24)
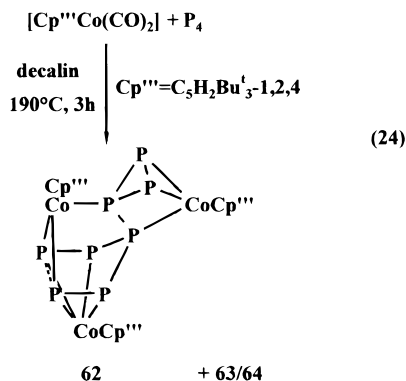
X-ray crystallography of MNiP$_8$ (M = Mo, W) revealed a "cube" structure of the P$_8$ unit (formally [P$_8$]$^{6-}$) in which 3 (shown by broken lines) of the 12 edges have been cleaved.[48a] Electronic band−structure calculations are indicative of a relevant covalent character in MoNiP$_8$.[48b]
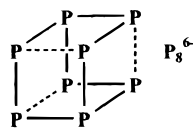
Two unique cyclo-As$_8$ ligands, forming parts of Nb clusters, have been prepared according to eqs 25 and 26.

(25)

$$[Cp^R Nb(CO)_4] \xrightarrow[170°C, 2h]{As_4,\ decalin}$$

$$\xrightarrow[\text{(2,2,2-crypt), en}]{Rb,\ As} [Rb(2,2,2\text{-crypt})]_2[Rb\{NbAs_8\}] \quad (26)$$

66

While the cyclo-As$_8$ ligand in **65**[49] (eq 25) exists as a highly distorted eight-membered ring, which can formally be considered as the all-arsenic analogue of cyclooctatetraene, the $_\infty^1$[Rb{NbAs$_8$}]$^{2-}$ anion of **66**[4,44] (eq 26) contains a crownlike [cyclo-As$_8$]$^{8-}$ unit that is isoelectronic and isostructural with cyclo-S$_8$.

E$_n$ Ligands (E = P, As; n > 8). In contrast to the polyphosphides,[8] pnictogen-rich complexes with "naked" P$_n$ and As$_n$ ligands are relatively rare. The all-pnictogen analogue E$_{10}$ (E = P, As) of dihydrofulvalene (C$_{10}$H$_{10}$) exists in complex **67** as a P$_5$−P$_5$, 16e$^-$ donor ligand with a P···P separation of 2.62 Å.[50]

67: M=Rh; Cp^R=C$_5$H$_3$Bu$^t_2$-1,3
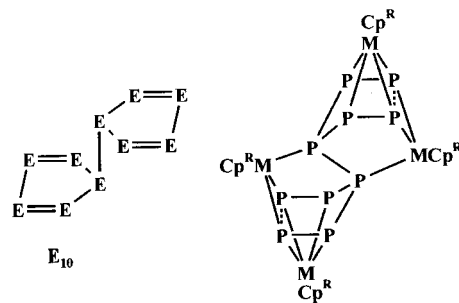
The P$_{10}$ ligand in the paramagnetic complex [{CpCr-(CO)$_2$}$_5$P$_{10}$] (**68**), presumably formed via a radical mechanism, can be regarded as a P$_7$ norbornane unit with a P$_2$ bridge and one terminal P atom.[51]

A number of interesting parallels can be drawn on comparing **62** (eq 24) and other P$_n$ ligands with polycyclic phosphanes,[9] polyphosphides,[8] and the results of theoretical calculations.[52]

The P$_7$−P$_5$ structure for the P$_{12}$ ligand of **64** was deduced from extensive ^{31}P NMR investigations.[42] The

64

Cp'''=C$_5$H$_2$Bu$^t_3$-1,2,4
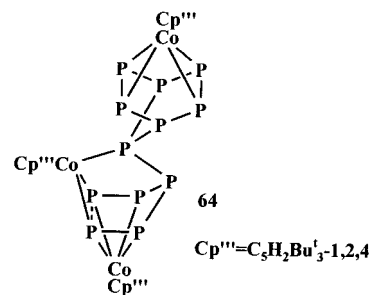
norbornadiene-like P$_7$ part of the P$_{12}$ ligand (12e$^-$ donor) corresponds to the P$_7$ skeleton of **60** (eq 22),[45,46] while the P$_5$ part should be equivalent to those in the P$_{10}$ complex **67**.[50] Formally, the P$_{12}$ ligand can be considered as the cycloaddition product of P$_{10}$ with P$_2$.[42]

Further Links. Interesting agreements between theoretical calculations and experimental results were found for the complex (CuI)$_3$P$_{12}$ (**68**).[53] Its P$_{12}$ skeleton consists of the theoretically predicted[52] $_\infty^1${[P$_{10}$]P$_2$[}$^\circ$ phosphorus strands. Alternatively, the strands may be considered to consist of linked P$_7$ norbornane units.[53] Another example of impressive agreements between theory and experiment is (CuI)$_2$P$_{14}$ (**69**).[54] This novel, polymeric phosphorus allotrope with the translational unit [P$_{14}^{\pm 0}$] consists of [P$_{12}$]

units linked by $[P_2]$ fragments[54] in harmony with the theoretically derived $^1_\infty\{[P_{10}]P_2[]\}^\circ$ system.[52]

The complex $[\{L_2Ni\}_4P_{14}]$ (**70**)[26a] was prepared in a straightforward reaction according to eq 27. X-ray crystallographic data show that the P_{14} ligand of **70** consists of two linked P_7 cages with norbornadiene-like structure.[26a]
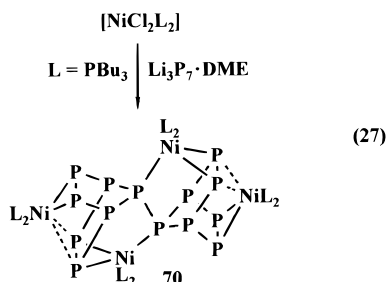
From the elegant works of Baudler,[9] von Schnering,[8] and Häser,[52] it is known that five-membered phosphorus rings as well as P_7-norbornane-like (bicyclic P_5 rings) structures are important structural motifs (cf. Hittorf's phosphorus) in phosphorus chemistry. The remarkable parallels described above add a new dimension to this topic.

Theoretical Aspects. As a supplement to the earlier theoretical studies,[4] an important recent result is that [cyclo-P_5]$^-$ is almost as aromatic as its carbon analogue $[C_5H_5]^-$.[55] The results of laser photoelectron detachment measurements in $[P_n]^-$ ($n = 1-9$) and $[P_8]^{2-}$ were compared with those of density functional calculations under simulated annealing.[56] The most stable forms are the butterfly isomer for $[P_4]^-$, D_{5h} symmetry for $[P_5]^-$, and a cuneane-like structure for $[P_8]^-$. The $[P_8]^{2-}$ system is analogous to the planar, isoelectronic 10 π system $[(CH)_8]^{2-}$, while the situations in $[P_7]^-$ and $[P_9]^-$ are less clear.[56] Häser and Böcker have performed by far the most comprehensive ab initio calculations on covalent P_n structures, including red phosphorus.[52] Their results have had and will continue to have an important and stimulating impact on investigations of complexes with "naked" P_n ligands. Density functional studies on As_n clusters ($n = 2-11$) produce structures analogous to those for the P_n isomers but expanded by about 9%.[57]

Concluding Remarks

The developments in the field of P_n and As_n ligands mentioned above have impressively demonstrated that the concept of the diagonal relationship between carbon and phosphorus is still capable of expansion and that many of these coordinatively stabilized, substituent-free P_n and As_n molecules serve as relevant bridges between main group, transition metal, or solid-state chemistry on one hand and organic or theoretical chemistry on the other. Further studies on the role of Cp^R ligands and the reactivity of the obtained products will certainly be rewarding. More information on mechanistic aspects is urgently required, and the potential scope of application for these new classes of complexes with "naked" P_n and As_n ligands is still unknown.

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