

# P<sub>n</sub> and As<sub>n</sub> Ligands: A Novel Chapter in the Chemistry of Phosphorus and Arsenic

OTTO J. SCHERER

Fachbereich Chemie der Universität Kaiserslautern,  
Erwin-Schrödinger-Strasse, D-67663 Kaiserslautern,  
Germany

Received July 9, 1998

## Introduction

Even today, the most prominent phosphorus- and arsenic-containing complex ligands are of the 2e<sup>-</sup>, 4e<sup>-</sup>, and 6e<sup>-</sup> types R<sub>3</sub>E, R<sub>2</sub>E(CH<sub>2</sub>)<sub>n</sub>ER<sub>2</sub>, and RC[(CH<sub>2</sub>)<sub>n</sub>ER<sub>2</sub>]<sub>3</sub> (E = P, As). In 1969 and later, the groups of Dahl,<sup>1</sup> Ginsberg,<sup>2</sup> and Sacconi<sup>3</sup> reported on their pioneering work in the novel field of coordinatively stabilized, substituent-free (“naked”) P<sub>n</sub> and As<sub>n</sub> ligands. These developments have been reviewed.<sup>4</sup>

Stimulated by these results, we examined the influence of substituted cyclopentadiene (Cp<sup>R</sup>) ligands on the metal fragment with regard to the formation of acyclic and cyclic E<sub>n</sub> (E = P, As) building blocks. The successful coordinative stabilization of cyclo-E<sub>4</sub>, cyclo-E<sub>5</sub><sup>-</sup>, and cyclo-E<sub>6</sub> ligands—the all-phosphorus and all-arsenic analogues of cyclobutadiene C<sub>4</sub>H<sub>4</sub>, the cyclopentadienide ion C<sub>5</sub>H<sub>5</sub><sup>-</sup>, and benzene C<sub>6</sub>H<sub>6</sub>—as sandwich and triple-layer sandwich complexes represent a further impressive example of the diagonal relationship between carbon and phosphorus.<sup>4,5</sup>



Furthermore, many of these compounds also are in accord with the concept of isolobal (HC ↔ P(As) ↔ NiCp<sup>R</sup>) and isoelectronic fragments<sup>6</sup> as well as often fulfilling the electron-counting rules of Wade–Mingos.<sup>7</sup> Much new information about the remarkable parallels to polyphosphides (solid-state chemistry),<sup>8</sup> monocyclic and polycyclic phosphanes,<sup>9</sup> 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<sub>n</sub>, and the activation of P<sub>4</sub> and P<sub>2</sub> at room temperature.

Otto J. Scherer was born in Amberg (Bavaria) in 1933, and studied chemistry at the Universities of Aachen (TU) and Munich (LMU, Dr. rer. nat. 1962, supervisor Prof. Max Schmidt). He finished his Habilitation for Inorganic Chemistry in 1967 at the University of Würzburg. In 1970 he was appointed full Professor at the new University in Kaiserslautern. He received the Alfred-Stock-Gedächtnispreis of the German Chemical Society in 1994. His research interests are main-group chemistry as well as its combination with coordination chemistry.

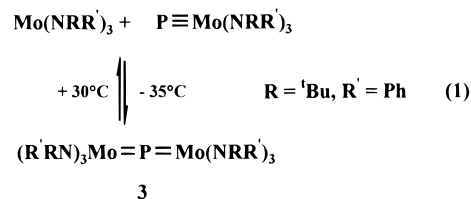
It is also worthy of note that complexes with P<sub>n</sub> and As<sub>n</sub> ligands are often thermally very stable, and some can even be handled in the air for short times.

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<sub>n</sub>M]<sub>3</sub>(E≡E), where E = As, Sb, Bi.<sup>10</sup>

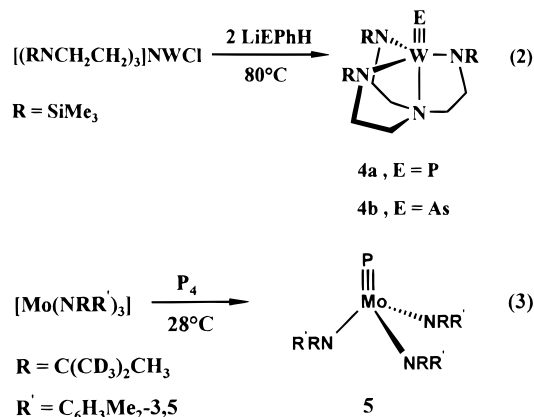
**E<sub>1</sub> Ligands (E = P, As).** Sources for the pnictogen E<sub>n</sub> ligands are, in particular, P<sub>4</sub> and As<sub>4</sub> as well as EX<sub>3</sub>, E(SiMe<sub>3</sub>)<sub>3</sub>, cyclo-(AsR)<sub>n</sub>, and E<sub>7</sub>(SiMe<sub>3</sub>)<sub>3</sub> or M<sub>3</sub>E<sub>7</sub> (M = Li, Na, K, Rb; E = P, As). The L<sub>n</sub>M fragments originate from mono- or dinuclear transition metal complexes with L<sub>n</sub> = CO and/or (mostly substituted) Cp<sup>R</sup>.<sup>4</sup> 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\*<sub>2</sub>ZrPZrCp\*<sub>2</sub>] (**2**), formed by the reaction of [Cp\*<sub>2</sub>ZrCl<sub>2</sub>] with KH and PH<sub>2</sub>R (R = 2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>),<sup>12</sup> shows a striking parallel to the allene-like skeleton structure of [Cp<sup>R</sup>(OC)<sub>2</sub>Mn=E=Mn(CO)<sub>2</sub>Cp<sup>R</sup>]<sup>+</sup> (**1**; E = P, As; Cp<sup>R</sup> = Cp\*).<sup>11</sup> 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).<sup>13</sup>

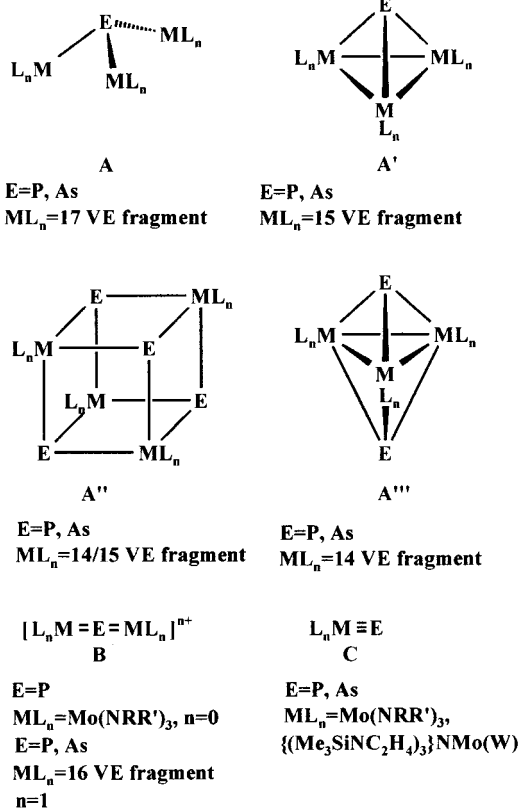


The long-sought and sometimes postulated complexes of the type **C** (Scheme 1), with a formal metal pnictogen triple bond, have now been verified in compounds **4** and **5** as shown in eqs 2 and 3.<sup>14</sup>



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

Scheme 1



Complex **4a** reacts with [M(CO)<sub>5</sub>(thf)] (M = Cr, W) to furnish (RNCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>NW≡P→M(CO)<sub>5</sub> (**6**), while the analogous complexes (tBuO)<sub>3</sub>W≡P→M(CO)<sub>5</sub> (**7**) have been characterized spectroscopically from the reaction of [M(CO)<sub>5</sub>(thf)] (M = Cr, W) with tBuC≡P and [W<sub>2</sub>(O<sup>t</sup>Bu)<sub>6</sub>].<sup>14</sup>

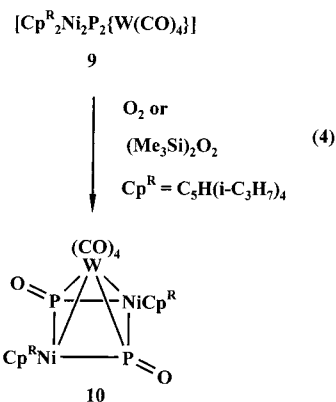
Compounds with a trigonal planar μ<sub>3</sub>-E<sub>1</sub> atom (phosphinidine type) are known in addition to the complexes **A** to **A'''** (Scheme 1), with pyramidal E<sub>1</sub> atoms.<sup>4,10</sup> The five valence electrons of the E<sub>1</sub> atom are frequently involved in bonding to three L<sub>n</sub>M fragments.

The paramagnetic complex [{Cp<sub>2</sub>Zr}<sub>2</sub>(μ-Cl)(μ<sub>3</sub>-P){ZrCp<sub>2</sub>-Cl}] (**8**), containing one Zr(III) and two Zr(IV) centers, was recently prepared from H<sub>2</sub>PR and Cp<sub>2</sub>ZrCl<sub>2</sub>; 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.<sup>15</sup>

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 μ<sub>5,6,8,9,10,12</sub>-E<sub>1</sub> atoms.<sup>4</sup>

**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,<sup>16</sup> was coordinatively stabilized in complex **10** (eq 4) in 1991.<sup>17a,18a</sup>

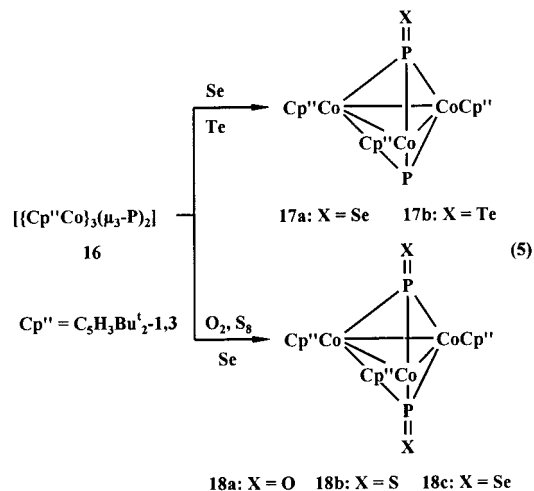
Since then, the intriguing series of PO complexes **11**–**13**<sup>14</sup> (Scheme 2) has been prepared. The method of choice for the conversion of P to PO is air oxidation.<sup>18a</sup> An additional method is hydrolytic cleavage of the P–N bond in [{L<sub>3</sub>M}<sub>4</sub>(μ<sub>3</sub>-PNR<sub>2</sub>)] (**14**), the phosphinidine complex precursor of **11**.<sup>17b</sup>



The as yet only known example of a complex with a terminal PO ligand, **13**, was prepared by oxidation of L<sub>3</sub>Mo≡P with dimethyldioxirane.<sup>14a</sup> In complexes of these types, the IR ν̄(PO) band is observed between 1050 and 1265 cm<sup>-1</sup>, 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.<sup>14a</sup>

Apart from the μ<sub>3</sub>-PS derivatives of complex **10**<sup>18a</sup> and [(CpFe(CO)<sub>2</sub>]<sub>3</sub>(μ<sub>3</sub>-PS)] (**15**),<sup>18b</sup> the sulfur analogue **13'** of **13** is, again, the only example of a complex with a terminal PS ligand.<sup>14a</sup> Crystallographic data for these complexes emphasize the importance of the following resonance structures: X–P≡Mo(NRR')<sub>3</sub> ↔ X=P=Mo(NRR')<sub>3</sub> (**13**, X = O; **13'**, X = S).<sup>14a</sup> Complexes of these types are usually prepared by oxidation of the corresponding P<sub>1</sub> derivative with elemental sulfur, S<sub>8</sub>.<sup>14,18</sup>

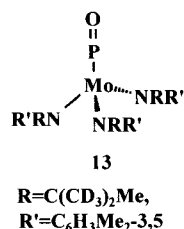
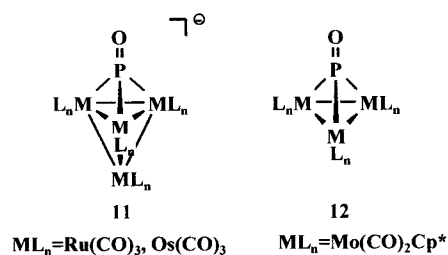
Compound **16** is an ideal starting material for the preparation of complexes containing one or two μ<sub>3</sub>-PX (X = O, S, Se, Te) ligands (eq 5). The following trends in these



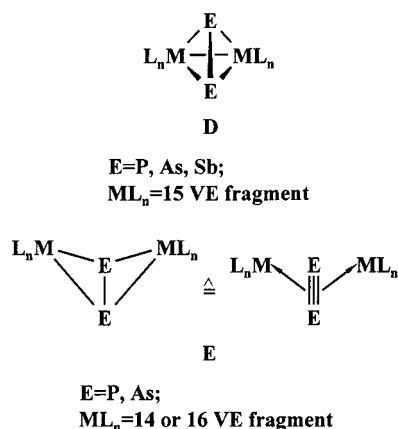
reactions are worthy of note. On reaction with O<sub>2</sub> or S<sub>8</sub>, **16**<sup>19a</sup> furnishes exclusively the dioxidation products **18a,b**,<sup>19c</sup> whereas reaction with gray selenium affords both **17a**<sup>19b</sup> and **18c**.<sup>19a</sup> On reaction with tellurium, only one phosphorus atom of **16** is oxidized to yield **17b**.<sup>19c</sup>

The photochemical and thermal rearrangements of a μ<sub>3</sub>-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

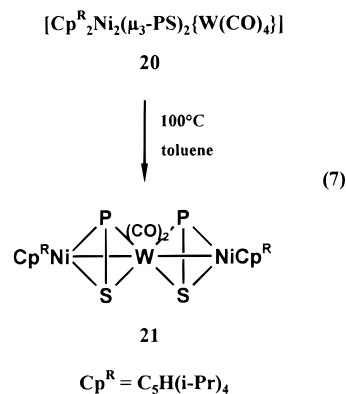
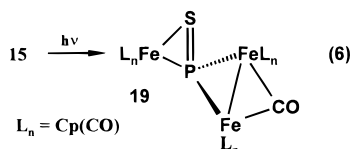
Scheme 2



Scheme 3



containing two main group atoms and two transition metal fragments, are joined by a common transition metal atom (W) vertex.<sup>18a</sup>

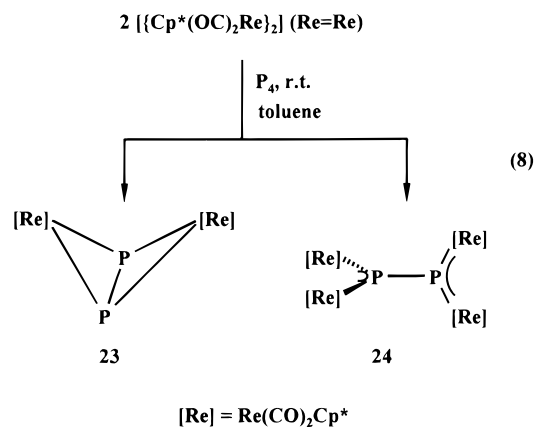


The P=S bond lengths of the μ<sub>3</sub>-PS ligands are in the range of 1.95–2.01 Å<sup>18a,b</sup> in **20** and, as expected, are

lengthened in **21** (2.09 Å, P–S single bond).<sup>18a</sup> 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].<sup>19b</sup>

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

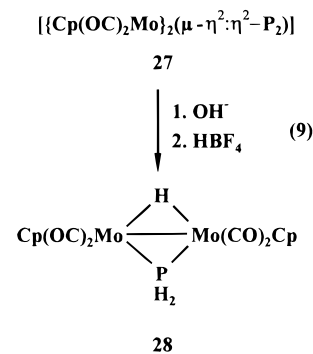
A remarkable mild activation of P<sub>4</sub> at room temperature has been realized according to eq 8.<sup>21</sup> In the diphosphini-



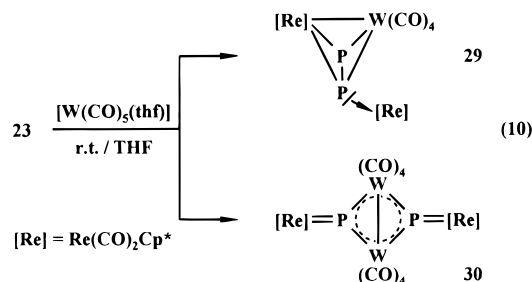
dine complex **24**, the unusual mesomeric  $\bar{P}-\bar{P}$  structure of the P<sub>2</sub> molecule is stabilized as a formal 8 σ electron donor ligand. On going from **23** to **24**, d(P–P) increases from 2.04 to 2.23 Å.<sup>21</sup> The Re<sub>2</sub>P planes in **24** are nearly orthogonal (91.1°), cf. [{Cp(OC)<sub>2</sub>Mn}<sub>4</sub>As<sub>2</sub>] (**25**).<sup>20b</sup>

To date, [{Cp\*(OC)<sub>2</sub>Mo}<sub>2</sub>(μ-η<sup>2</sup>:η<sup>2</sup>-Sb<sub>2</sub>)] (**26**) is the only example of a compound with an Sb<sub>2</sub>Mo<sub>2</sub> tetrahedrane structure. It is prepared by cothermolysis of [{Cp(OC)<sub>3</sub>Mo}<sub>2</sub>] with metallic antimony<sup>22a</sup> or with (tBuSb)<sub>4</sub> as source of Sb<sub>2</sub>.<sup>22b</sup> The Sb–Sb bond distance is in the range typical for double bonds.<sup>22a</sup>

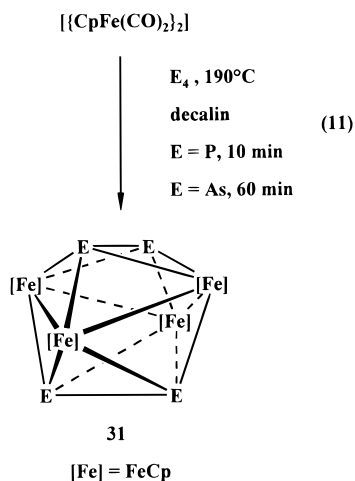
**Reactivity of P<sub>2</sub> Ligands.** Promising perspectives with regard to activation of P<sub>2</sub> ligands were recently discovered (eqs 9 and 10). The P–P bond of the starting material **27** is cleaved during the two-step reaction leading to **28**<sup>23a</sup> (eq 9). Metalation of **28** with tBuLi followed by reaction



with ECl<sub>3</sub> (E = As, Sb) affords [ $\{\text{Cp}(\text{OC})_2\text{Mo}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-PE})$ ], the first compounds containing PAs or PSb coordinatively stabilized in clusters having an Mo<sub>2</sub>PE tetrahedrane skeleton.<sup>23b</sup> An extremely mild cleavage of the P<sub>2</sub> 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)<sub>5</sub>(thf)] at room temperature. The phosphinidene complex **30**, with two planar 5e<sup>-</sup> donor P<sub>1</sub> ligands, is formed in addition to the chiral tetrahedrane **29** (eq 10).<sup>21</sup>

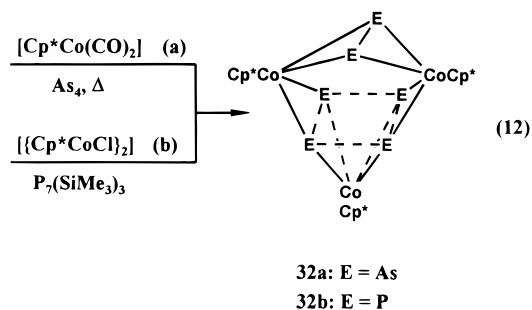


**(E<sub>2</sub>)<sub>n</sub> Ligands (E = P, As; n = 2, 3, 4).** Some remarkable cluster and cage-like molecules with (E<sub>2</sub>)<sub>n</sub> ligands have been prepared in the past few years. In addition to species of the [ $\{\text{L}_n\text{M}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-E}_2)_2$ ] type,<sup>4</sup> the clusters **31** (eq 11), with triangulated dodecahedral Fe<sub>4</sub>E<sub>4</sub> cores, have been obtained.<sup>24</sup> Interestingly, all the phosphorus atoms of

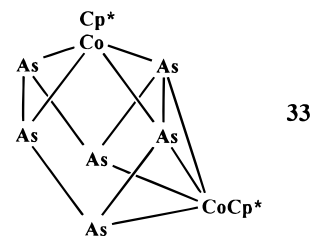


cluster **31** can be oxidized by S<sub>8</sub> or by gray selenium to afford the previously unknown XPPX ligands (X = S, Se).<sup>24</sup> On going from **31** (E = P) to [ $\{\text{CpFe}\}_4(\text{P}_2\text{S}_2)_2$ ], the mean phosphorus–phosphorus bond length increases from 2.31 to 2.37 Å.<sup>24</sup>

Complexes with a Co<sub>3</sub>E<sub>6</sub> skeleton are accessible as shown in eq 12. Although the E–E bond lengths in the Co<sub>2</sub>E<sub>2</sub> butterfly subunits of **32a,b** are in the typical ranges for double bonds (P=P = 2.05 Å,<sup>26a</sup> As=As = 2.29 Å<sup>25</sup>), the other two E<sub>2</sub> 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



Å, As–As = 2.32–2.58 Å), capped by two Cp\*Co fragments.<sup>25</sup>



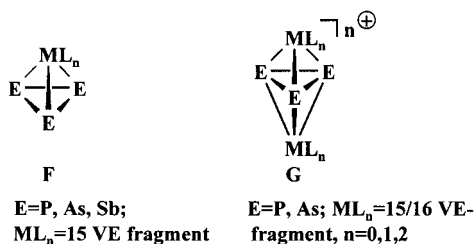
The reactions of E<sub>7</sub>(SiMe<sub>3</sub>)<sub>3</sub> with FeCl<sub>2</sub> and LiCp\* afford [ $\{\text{Cp}^*\text{Fe}\}_3\text{E}_6$ ]<sup>+</sup> (**32c**, E = P, Fe in place of Co;<sup>26a</sup> **32d**, E = As, Fe in place of Co<sup>26c</sup>) with four fewer electrons and an E<sub>6</sub> prismane unit in which one E–E bond has been cleaved (P–P = 2.27–2.39 Å;<sup>26a</sup> As–As = 2.51–2.71 Å<sup>26c</sup>). The corresponding Co<sub>3</sub>As<sub>6</sub> framework of [ $\{\text{Cp}^*\text{Co}\}_3\text{As}_6$ ]<sup>2+</sup> consists of two cyclo-As<sub>3</sub> units [ $\bar{d}(\text{As}–\text{As}) = 2.56$  Å], forming an elongated As<sub>6</sub> prismane (As⋯As = 2.85 Å).<sup>27</sup>

Compounds of the type **32** have been examined by means of density functional calculations.<sup>27</sup> The complexes **32a** and **33** serve as versatile starting materials for cluster expansion reactions.<sup>28</sup> The skeleton of [Pd<sub>9</sub>As<sub>8</sub>L<sub>8</sub>] (L = PPh<sub>3</sub>), prepared by the reaction of [PdCl<sub>2</sub>L<sub>2</sub>] with As(SiMe<sub>3</sub>)<sub>3</sub>, is made up of a Pd-centered Pd<sub>8</sub> cube, capped by four As<sub>2</sub> units.<sup>26d</sup>

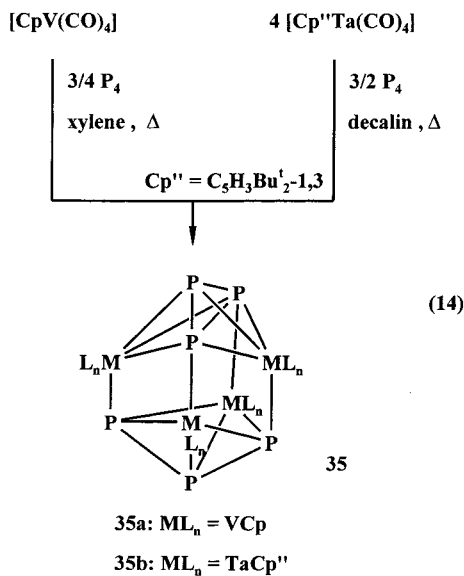
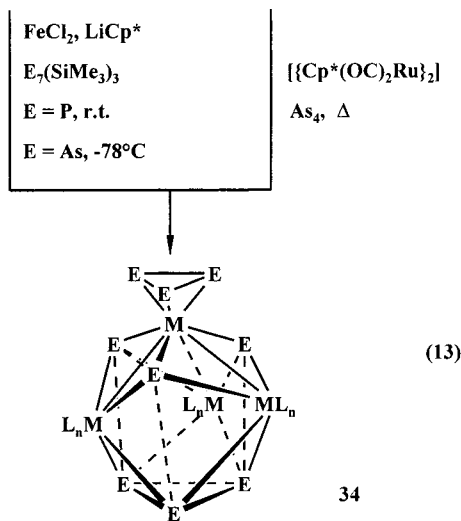
**E<sub>3</sub> Ligands (E = P, As, Sb).** In addition to the most important coordination modes<sup>4</sup> F and G (Scheme 4), other novel developments are the synthesis of [Cp\*(OC)<sub>2</sub>Mo(η<sup>3</sup>-Sb<sub>3</sub>)], containing a cyclo-Sb<sub>3</sub> ligand<sup>22b</sup> (cf. complex **26**), and reactivity studies on [(triphos)CoP<sub>3</sub>].<sup>29</sup> Its cyclo-P<sub>3</sub> ligand remains intact on protonation<sup>29a</sup> with CF<sub>3</sub>SO<sub>3</sub>H and on reaction with RHg<sup>+</sup>.<sup>29b</sup>

Further illustrative examples of the often unpredictable E<sub>n</sub> 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<sub>3</sub> tetrahedrane subunit has P–P bond lengths of 2.11–2.12 Å,<sup>26a</sup> (As–As = 2.31–2.33 Å);<sup>26b</sup> longer distances are seen for the cyclo-E<sub>3</sub> parts of the ME<sub>6</sub> nortricyclane skeletons, while the E⋯E separations are even larger [2.33/2.42 Å for  $\bar{d}(\text{P}–\text{P})/(\text{P}⋯\text{P})$  in **34a**; 2.57/2.73 Å for  $\bar{d}(\text{As}–\text{As})/(\text{As}⋯\text{As})$  in **34b**]. The M<sub>4</sub>P<sub>6</sub> skeleton of **35** consists of a distorted M<sub>4</sub>P<sub>4</sub> cubane with one pair of opposing faces, each capped

Scheme 4

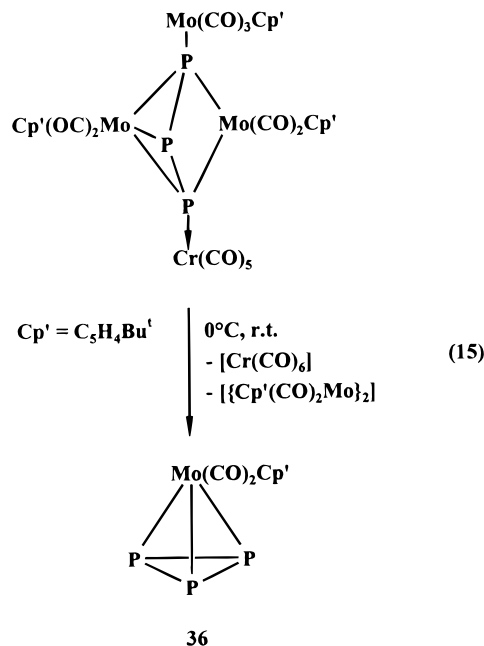


by one P atom from one of the two acyclic P<sub>3</sub> ligands (average P–P bond lengths, 2.18 Å in **35a**,<sup>30a</sup> 2.25 Å in **35b**<sup>30b</sup>).



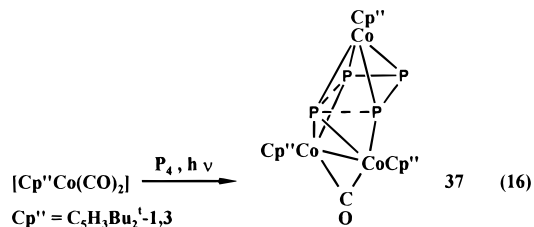
The complex type **36** is formed by an unexpected and irreversible ring closure reaction (eq 15).<sup>31</sup>

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

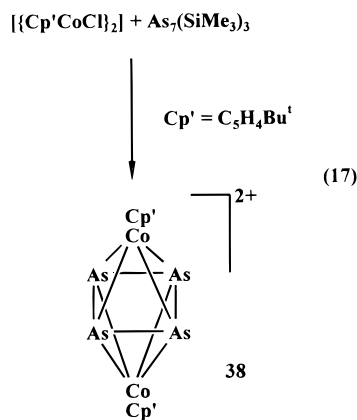


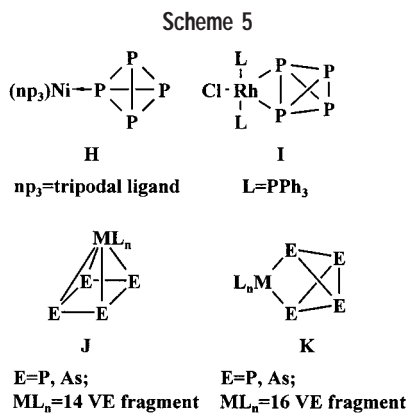
on<sup>2</sup> coordination of the P<sub>4</sub> tetrahedron have been reported. Photochemical<sup>32a</sup> or thermal reaction<sup>32b</sup> of P<sub>4</sub> with [W(CO)<sub>5</sub>L] furnishes [(OC)<sub>4</sub>W]{PW(CO)<sub>5</sub>}<sub>4</sub>] (structure **J**, Scheme 5), in which cyclo-P<sub>4</sub> exists as a 12e<sup>-</sup> donor ligand.

The P<sub>4</sub> 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<sub>1</sub> and a P<sub>3</sub> unit (P...P = 2.50 Å).<sup>33</sup>



The 30 VE triple-decker cation **38** (closo type,  $n + 1 = 7$  SEPs; eq 17) has a cyclo-As<sub>4</sub> unit as the middle layer and was further characterized by density functional calculations;<sup>27</sup> the As–As bond lengths are in the range 2.455–2.47 Å.





**Mechanistic Aspects.** Mechanistic features of the reactions of E<sub>4</sub> tetrahedra with Cp<sup>M</sup>M(CO)<sub>n</sub> fragments are summarized in Scheme 6A,B. Photolysis of  $[\{Cp''Fe(CO)_2\}_2]$  with P<sub>4</sub> leads to the series of complexes **39–43**, possessing cyclic and acyclic P<sub>4</sub> ligands,<sup>34a</sup> by successive loss of CO ligands and cleavage of one to three P–P bonds in the P<sub>4</sub> subunit (Scheme 6A). Brief thermolysis of  $[\{Cp''Fe(CO)_2\}_2]$  (Cp'' = 1,2,4-<sup>t</sup>Bu<sub>3</sub>C<sub>5</sub>H<sub>2</sub>) with P<sub>4</sub> proceeds with exclusive cleavage of one P–P bond to furnish *exo,exo*- $[\{Cp''Fe(OC)_2FeP\}_2P_2]$  (cf. **39**) in 75% yield, the butterfly structure of which has been confirmed by crystallography.<sup>34b</sup> Reaction of this product with diphenylacetylene leads to the sandwich complex  $[Cp''Fe(\eta^5-P_3C_2Ph_2)]$ . This is the first example in which the triphosphacyclopentadienide unit *cyclo*-(P<sub>3</sub>C<sub>2</sub>Ph<sub>2</sub>)<sup>−</sup> has been formed directly from P<sub>4</sub> and an alkyne.<sup>34c</sup>

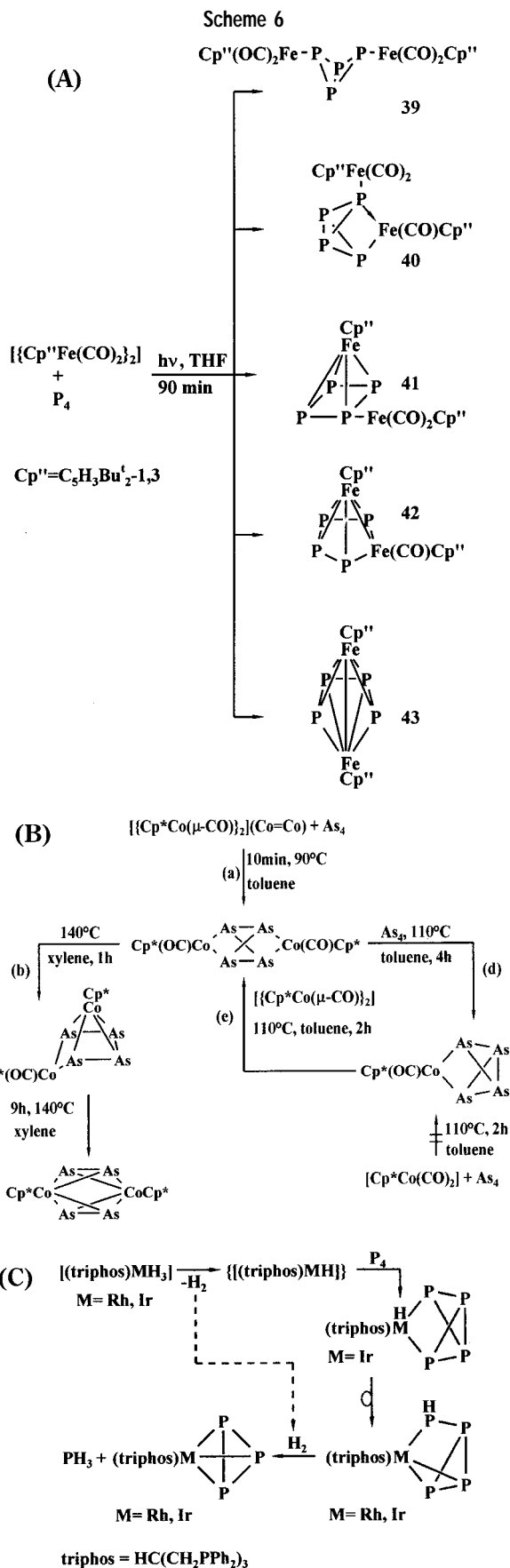
The CO elimination and As–As bond cleavage sequences a–e in Scheme 6B for the cothermolysis reaction of As<sub>4</sub> with  $[\{Cp^*Co(\mu-CO)\}_2]$  were deduced from <sup>1</sup>H NMR studies in comparison with known and structurally characterized cobalt complexes containing As<sub>4</sub> and (As<sub>2</sub>)<sub>2</sub> ligands.<sup>35</sup>

Convincing evidence for the mechanism (Scheme 6C) postulated for the hydrogenation of P<sub>4</sub> with [(triphos)MH<sub>3</sub>] (M = Rh, Ir) to give coordinated cyclo-P<sub>3</sub> and PH<sub>3</sub> has been presented.<sup>36</sup>

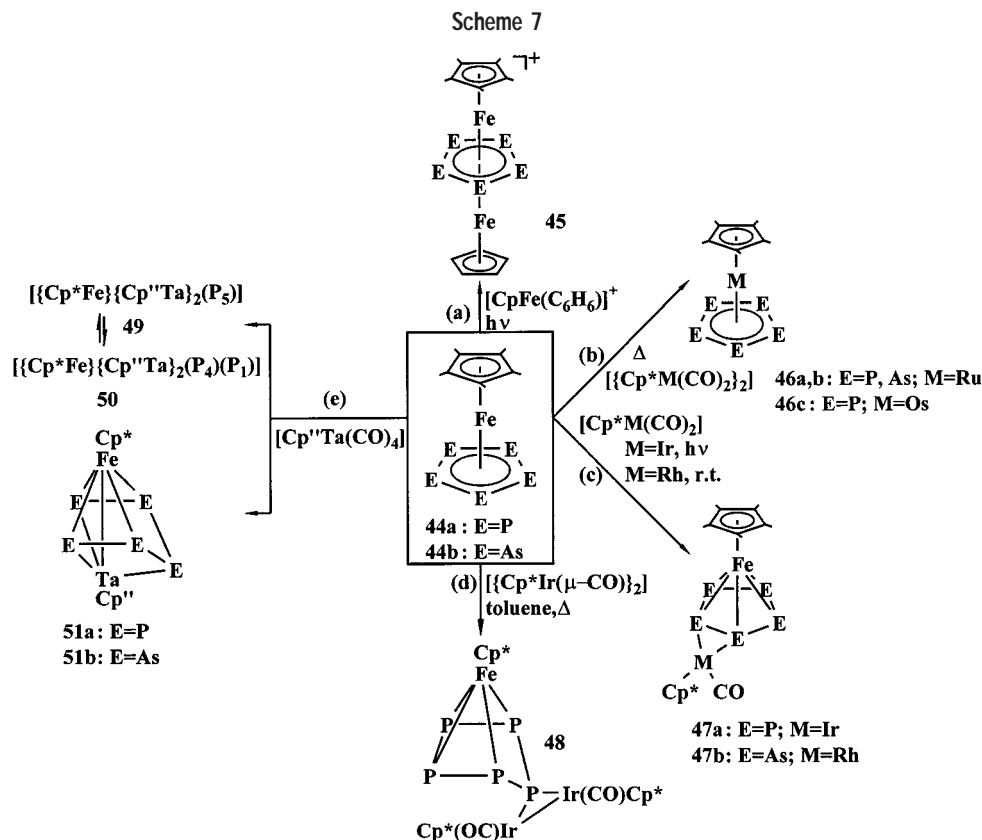
**E<sub>5</sub> Ligands (E = P, As).** On account of their surprising and manifold reactivities (Scheme 7), the most important members of this group are the sandwich complexes  $[Cp^*Fe(\eta^5-E_5)]$  (**44**), conveniently prepared by thermolysis of  $[\{Cp^*Fe(CO)_2\}_2]$  with E<sub>4</sub> (E = P, As).<sup>4</sup>

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

Although the P<sub>5</sub> ring in complex **48**, reaction d, has an envelope conformation,<sup>37d</sup> cisoid E<sub>5</sub> chain ligands are observed in complexes **51**, reaction e.<sup>30b,37d</sup> The system **49/50**, reaction e, involves an unusual equilibrium between two distorted cubanes with FeTa<sub>2</sub>P<sub>5</sub> skeletons: the

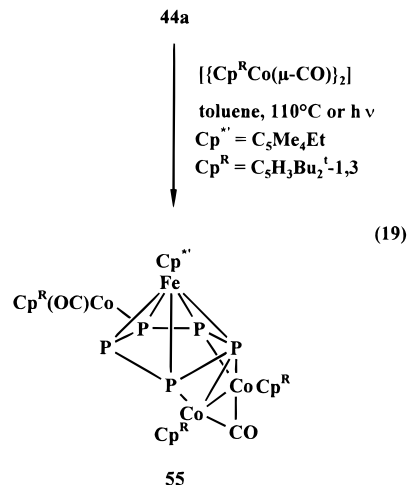
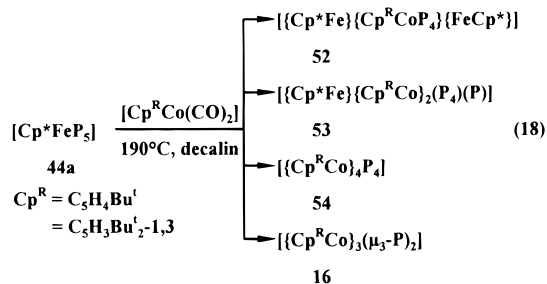


structure of **49** comprises an FeP<sub>5</sub> six-membered ring in the chair conformation, capped by two Cp''Ta fragments,



while the P<sub>5</sub> ligand in **50** is split into a P<sub>1</sub> unit and a trigonal pyramidal P<sub>4</sub> unit.<sup>30b</sup>

A broad palette of Cp<sup>R</sup>Co complexes containing “naked” P<sub>n</sub> ligands is obtained from the reactions of **44a** with [Cp<sup>R</sup>Co(CO)<sub>2</sub>] species (eq 18).<sup>19a</sup>



The “triple-decker” complex **52** (eq 18), with a planar CoP<sub>4</sub> five-membered ring as the middle layer, is worthy of special mention. Replacement of the mononuclear starting material [Cp<sup>R</sup>Co(CO)<sub>2</sub>] in this reaction by the dinuclear species [Cp<sup>R</sup>Co(μ-CO)<sub>2</sub>]<sub>2</sub> in eq 19 provides access to complex **55**.<sup>19a</sup>

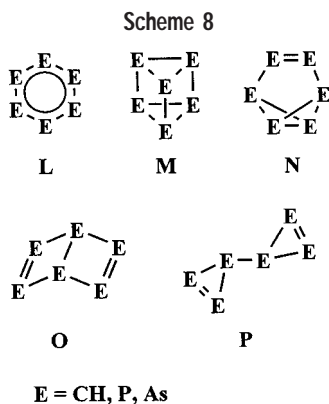
The X-ray crystallographic data for **55** reveal that two of the P–P bonds (each 2.35 Å, compared with an average of 2.13 Å for the other three bonds) are also involved in side-on (η<sup>2</sup>:η<sup>2</sup>) coordination to the Co<sub>2</sub>Cp<sup>R</sup><sub>2</sub>(μ-CO) fragment.<sup>19a</sup>

A novel synthetic approach to P<sub>5</sub> sandwich complexes has been verified for [Cp<sup>R</sup>Fe(η<sup>5</sup>-P<sub>5</sub>)] (**44c**) by the reaction of K[Fe(CO)<sub>2</sub>Cp<sup>R</sup>] (Cp<sup>R</sup> = 1,3-<sup>t</sup>Bu<sub>2</sub>C<sub>5</sub>H<sub>3</sub>) with [(OC)<sub>5</sub>Cr(PCl<sub>3</sub>)].<sup>31</sup> The cyclo-P<sub>5</sub> sandwich complexes of the type **44**

mentioned above show <sup>31</sup>P NMR chemical shifts in the range 153–167 ppm.

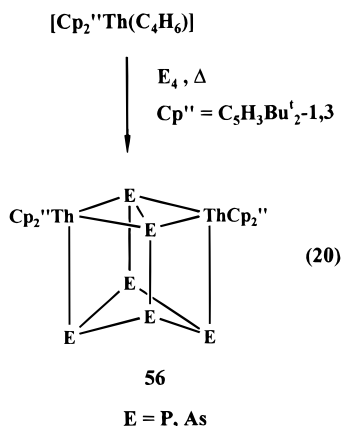
It is interesting to note that gray arsenic was used as starting material for the triple-decker sandwich [CpCr]<sub>2</sub>(μ-η<sup>5</sup>:η<sup>5</sup>-As<sub>5</sub>).<sup>38</sup> Magnetic susceptibility studies on the related P<sub>5</sub> species [Cp\*Cr]<sub>2</sub>(μ-η<sup>5</sup>:η<sup>5</sup>-P<sub>5</sub>)<sup>+</sup> revealed spin crossovers at 33 and 23 K.<sup>39</sup>

**E<sub>6</sub> Ligands (E = P, As).** Of the all-pnictogen analogues of the (CH)<sub>6</sub> valence isomers (Scheme 8), cyclo-E<sub>6</sub> (L) has been coordinatively stabilized as the middle layer of 28 VE triple-decker complexes.<sup>4</sup> The 26 VE triple-decker complex [Cp<sup>R</sup>Nb]<sub>2</sub>(μ-η<sup>6</sup>:η<sup>6</sup>-P<sub>6</sub>) experiences severe bis-allylic distortions which have been explained by means of extended Hückel calculations.<sup>40</sup> The formal E<sub>6</sub> prismane

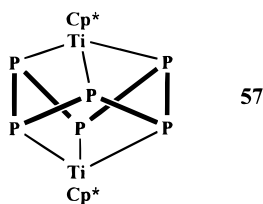


structure (**M**) is present as a subunit in nine-atom clusters of the  $\{[Cp^*M]_3E_6\}^{n+}$  type (see above).

The open-edge E<sub>6</sub> benzfulvalene structure (**N**, Scheme 8) has been stabilized in the complexes **56** (eq 20).<sup>41</sup>

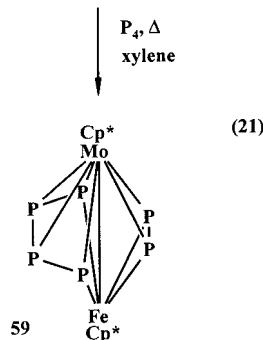
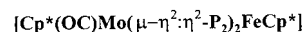
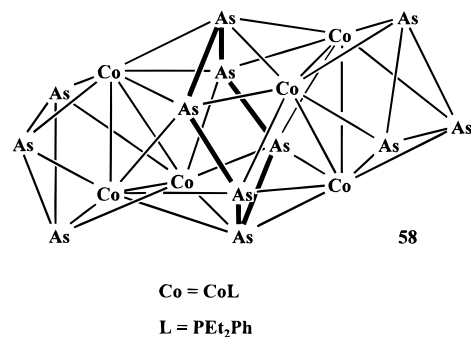


Although the E<sub>6</sub> bicyclopropenyl analogue **P** is still unknown, a part of this structure has been observed in the P<sub>8</sub> ligand of  $\{[Cp''Co]_3(P_3-P_5)\}$  (**62**, see below).<sup>42</sup> The complex **57**, prepared from  $[Cp^*Ti(CO)_2]$  and P<sub>4</sub>,<sup>4</sup> contains



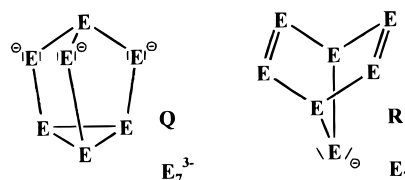
a cyclo-P<sub>6</sub> ligand in the chair conformation—which can formally be regarded as  $[cyclo-P_6]^{6-}$  ( $\cong cyclo-S_6$ )—as part of its Ti<sub>2</sub>P<sub>6</sub> cubane-like skeleton. In contrast, cyclo-As<sub>6</sub> is a subunit in the cluster  $[(LCo)_6As_{12}]$  (**58**), generated in the reaction of  $[CoCl_2L_2]$  with “K<sub>3</sub>As<sub>7</sub>”.<sup>26a</sup> The unusual Co<sub>6</sub>As<sub>12</sub> skeleton of **58** is built up of a Co<sub>6</sub>As<sub>6</sub> icosahedron, in which the cobalt atoms are capped by cyclo-As<sub>3</sub> ligands to form two face-sharing Co<sub>3</sub>As<sub>3</sub> octahedra. The remaining As<sub>6</sub> ring adopts the chair conformation.<sup>26a</sup>

In addition to the mentioned complexes with cleaved “E<sub>6</sub>” ligands (“E<sub>6</sub>” = 2 × E<sub>3</sub>, 3 × E<sub>2</sub>), compound **59**, containing a “P<sub>6</sub>” ligand (P<sub>4</sub>/P<sub>2</sub>), has been prepared as shown in eq 21.<sup>43</sup> The X-ray crystallographic data for **59** can best be interpreted in terms of two polyhedra (pentagonal MoFeP<sub>4</sub> pyramid and MoFeP<sub>2</sub> tetrahedrane) shar-



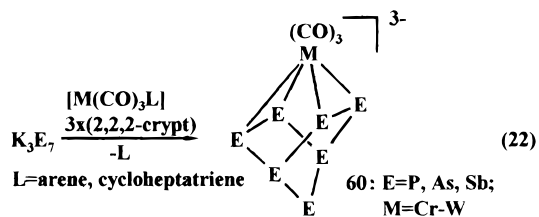
ing a common edge. The 54 cluster electrons are in accord with the electron-counting rules of Wade–Mingos.<sup>7</sup>

**E<sub>7</sub> and E<sub>8</sub> Ligands (E = P, As, Sb).** The currently known molecular E<sub>7</sub> 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  $[P_7\{Fe(CO)_2Cp\}_3]$ ,<sup>26a</sup> 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<sup>45</sup> and Tremel<sup>46</sup> opened up an intriguing chapter in the chemistry of Zintl ions<sup>44</sup> and provided a further bridge to solid-state chemistry.<sup>4</sup> Complexes **60**



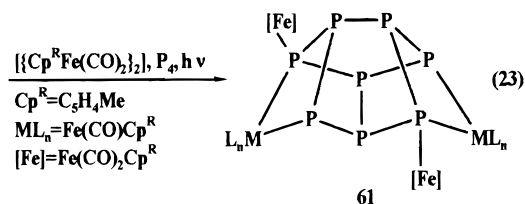
react with R<sub>4</sub>N<sup>+</sup> salts (R = Me, Et, <sup>n</sup>Bu) in ethylenediamine solution to furnish  $[\{\eta^4-RP_7\}\{W(CO)_3\}]^{2-}$ , in which R is bonded to the divalent P atom of **60**.<sup>45</sup> Many of these complexes exhibit fluxional behavior in solution.<sup>45</sup> The X-ray crystallographic data for the series  $[\{\eta^4-E_7\}\{M(CO)_3\}]^{3-}$  (**60**) reveal the following features:<sup>45,46</sup> (i) four



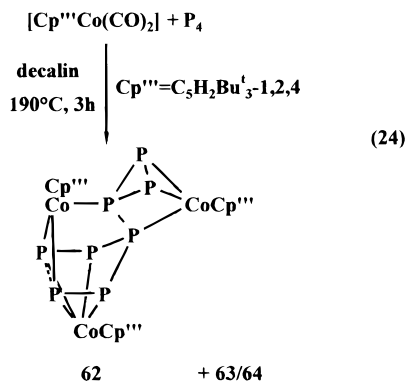
short E–E bonds ( $2 \times \eta^2$  and  $2 \times$  to the divalent E atom) as well as (ii) two nonbonding E···E separations for the trapezoidally arranged “E<sub>2</sub>” subunits coordinated to M(CO)<sub>3</sub> (E = P, As, M = Cr;<sup>45</sup> E = Sb, M = Mo<sup>46</sup>).

This class of compounds has also been studied by EH<sup>46</sup> and Fenske–Hall MO calculations.<sup>45</sup>

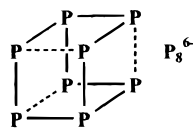
To date, neither cubic or square antiprismatic nor triangulated dodecahedral structures of E<sub>8</sub> have been stabilized coordinatively. However, the open-edge P<sub>8</sub>-cuneane structure—a structural motif of Hittorf’s phosphorus—is found in complex **61**, prepared as shown in eq 23 starting from P<sub>4</sub>. The P–P bond lengths of the “P<sub>2</sub>” bridges in **64** are 2.24 Å (cf. ref 47b).<sup>47a</sup>



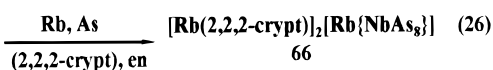
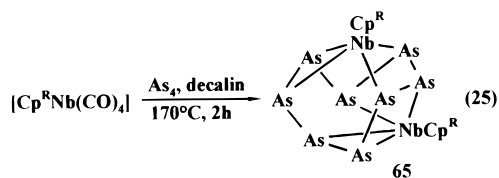
Cluster **62**, formed together with  $[\{\text{Cp}^{\text{'''}}\text{Co}\}_2(\text{P}_2)_2]$  (**63**) and  $[\{\text{Cp}^{\text{'''}}\text{Co}\}_3(\text{P}_{12})]$  (**64**) according to eq 24,<sup>42</sup> contains an unusual P<sub>8</sub> ligand composed of a P<sub>5</sub>–P<sub>3</sub> framework.



X-ray crystallography of MNiP<sub>8</sub> (M = Mo, W) revealed a “cube” structure of the P<sub>8</sub> unit (formally [P<sub>8</sub>]<sup>6-</sup>) in which 3 (shown by broken lines) of the 12 edges have been cleaved.<sup>48a</sup> Electronic band–structure calculations are indicative of a relevant covalent character in MoNiP<sub>8</sub>.<sup>48b</sup>

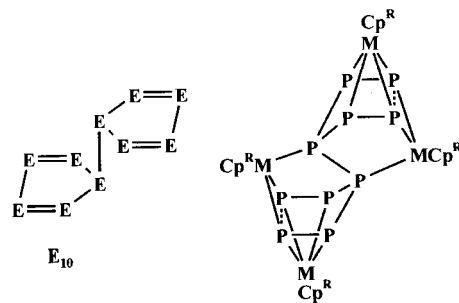


Two unique cyclo-As<sub>8</sub> ligands, forming parts of Nb clusters, have been prepared according to eqs 25 and 26.



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

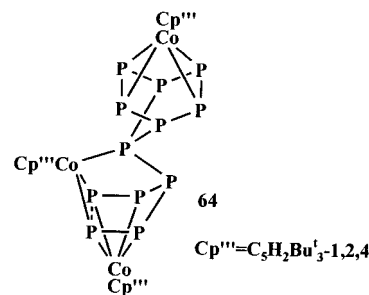
**E<sub>n</sub> Ligands (E = P, As; n > 8).** In contrast to the polyphosphides,<sup>8</sup> pnictogen-rich complexes with “naked” P<sub>n</sub> and As<sub>n</sub> ligands are relatively rare. The all-pnictogen analogue E<sub>10</sub> (E = P, As) of dihydrofulvalene (C<sub>10</sub>H<sub>10</sub>) exists in complex **67** as a P<sub>5</sub>–P<sub>5</sub>, 16e<sup>-</sup> donor ligand with a P···P separation of 2.62 Å.<sup>50</sup>



The P<sub>10</sub> ligand in the paramagnetic complex  $[\{\text{CpCr}(\text{CO})_2\}_5\text{P}_{10}]$  (**68**), presumably formed via a radical mechanism, can be regarded as a P<sub>7</sub> norbornane unit with a P<sub>2</sub> bridge and one terminal P atom.<sup>51</sup>

A number of interesting parallels can be drawn on comparing **62** (eq 24) and other P<sub>n</sub> ligands with polycyclic phosphanes,<sup>9</sup> polyphosphides,<sup>8</sup> and the results of theoretical calculations.<sup>52</sup>

The P<sub>7</sub>–P<sub>5</sub> structure for the P<sub>12</sub> ligand of **64** was deduced from extensive <sup>31</sup>P NMR investigations.<sup>42</sup> The

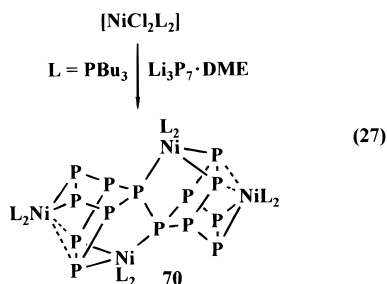


norbornadiene-like P<sub>7</sub> part of the P<sub>12</sub> ligand (12e<sup>-</sup> donor) corresponds to the P<sub>7</sub> skeleton of **60** (eq 22),<sup>45,46</sup> while the P<sub>5</sub> part should be equivalent to those in the P<sub>10</sub> complex **67**.<sup>50</sup> Formally, the P<sub>12</sub> ligand can be considered as the cycloaddition product of P<sub>10</sub> with P<sub>2</sub>.<sup>42</sup>

**Further Links.** Interesting agreements between theoretical calculations and experimental results were found for the complex (CuI)<sub>3</sub>P<sub>12</sub> (**68**).<sup>53</sup> Its P<sub>12</sub> skeleton consists of the theoretically predicted<sup>52</sup> <sup>1</sup>[P<sub>10</sub>]P<sub>2</sub> phosphorus strands. Alternatively, the strands may be considered to consist of linked P<sub>7</sub> norbornane units.<sup>53</sup> Another example of impressive agreements between theory and experiment is (CuI)<sub>2</sub>P<sub>14</sub> (**69**).<sup>54</sup> This novel, polymeric phosphorus allotrope with the translational unit [P<sub>14</sub><sup>±0</sup>] consists of [P<sub>12</sub>]

units linked by [P<sub>2</sub>] fragments<sup>54</sup> in harmony with the theoretically derived  $\{[P_{10}]P_2\}^{\circ}$  system.<sup>52</sup>

The complex  $[(L_2Ni)_4P_{14}]$  (**70**)<sup>26a</sup> was prepared in a straightforward reaction according to eq 27. X-ray crystallographic data show that the P<sub>14</sub> ligand of **70** consists of two linked P<sub>7</sub> cages with norbornadiene-like structure.<sup>26a</sup>



From the elegant works of Baudler,<sup>9</sup> von Schnering,<sup>8</sup> and Häser,<sup>52</sup> it is known that five-membered phosphorus rings as well as P<sub>7</sub>-norbornane-like (bicyclic P<sub>5</sub> 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,<sup>4</sup> an important recent result is that [cyclo-P<sub>5</sub>]<sup>-</sup> is almost as aromatic as its carbon analogue [C<sub>5</sub>H<sub>5</sub>]<sup>-</sup>.<sup>55</sup> The results of laser photoelectron detachment measurements in [P<sub>n</sub>]<sup>-</sup> (n = 1–9) and [P<sub>8</sub>]<sup>2-</sup> were compared with those of density functional calculations under simulated annealing.<sup>56</sup> The most stable forms are the butterfly isomer for [P<sub>4</sub>]<sup>-</sup>, D<sub>5h</sub> symmetry for [P<sub>5</sub>]<sup>-</sup>, and a cuneane-like structure for [P<sub>8</sub>]<sup>2-</sup>. The [P<sub>8</sub>]<sup>2-</sup> system is analogous to the planar, isoelectronic 10 π system [(CH)<sub>8</sub>]<sup>2-</sup>, while the situations in [P<sub>7</sub>]<sup>-</sup> and [P<sub>9</sub>]<sup>-</sup> are less clear.<sup>56</sup> Häser and Böcker have performed by far the most comprehensive ab initio calculations on covalent P<sub>n</sub> structures, including red phosphorus.<sup>52</sup> Their results have had and will continue to have an important and stimulating impact on investigations of complexes with “naked” P<sub>n</sub> ligands. Density functional studies on As<sub>n</sub> clusters (n = 2–11) produce structures analogous to those for the P<sub>n</sub> isomers but expanded by about 9%.<sup>57</sup>

## Concluding Remarks

The developments in the field of P<sub>n</sub> and As<sub>n</sub> 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<sub>n</sub> and As<sub>n</sub> 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<sup>R</sup> 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<sub>n</sub> and As<sub>n</sub> ligands is still unknown.

The author thanks the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Graduiertenkolleg “Phosphorus Chemistry as a Link between Different Chemical Disciplines” for financial support and all co-workers for their skillful and diligent research work.

## References

- Foust, A. S.; Foster, M. S.; Dahl, L. F. Organometallic Pnictogen Complexes. IV. Synthesis, Structure, and Bonding of New Organometallic Arsenic-Metal Atom Clusters Containing a Metal-Bridged Multiply Bonded As<sub>2</sub> Ligand: Co<sub>2</sub>(CO)<sub>6</sub>As<sub>2</sub> and Co<sub>2</sub>{(CO)<sub>5</sub>P-(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}As<sub>2</sub>. *J. Am. Chem. Soc.* **1969**, *91*, 5633.
- Ginsberg, A. P.; Lindsell, W. E.; McCullough, K. J.; Sprinkle, C. R.; Welch, A. J. Preparation and Properties of tetrahedro-tetraphosphorus Complexes of Rhodium and Iridium. Molecular and Electronic Structure of [RhCl(η<sup>2</sup>-P<sub>4</sub>)(PPh<sub>3</sub>)<sub>2</sub>]. *J. Am. Chem. Soc.* **1986**, *108*, 403.
- Di Vaira, M.; Sacconi, L. Transition metal complexes with cyclo-triphosphorus (η<sup>3</sup>-P<sub>3</sub>) and tetrahedro-Tetraphosphorus (η<sup>1</sup>-P<sub>4</sub>) ligands. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 330.
- Reviews: Scherer, O. J. Complexes with Substituent-free Acyclic and Cyclic Phosphorus, Arsenic, Antimony, and Bismuth Ligands. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1104. Whitmire, K. H. Main Group-Transition Metal Cluster Compounds of the Group 15 Elements. *Adv. Organomet. Chem.* **1998**, *42*, 1.
- Dillon, K. B.; Mathey, F.; Nixon, J. F. *Phosphorus: The Carbon Copy*; Wiley: New York, 1998.
- Hoffmann, R. Building Bridges Between Inorganic and Organic Chemistry. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.
- Wade, K. Structural and Bonding Patterns in Cluster Chemistry. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1990; p 249.
- von Schnering, H.-G.; Hönle, W. Bridging Chasms with Polyphosphides. *Chem. Rev.* **1988**, *88*, 243.
- Baudler, M.; Glinka, K. Monocyclic and Polycyclic Phosphanes. *Chem. Rev.* **1993**, *93*, 1623.
- Huttner, G.; Evertz, K. Phosphinidene Complexes and Their Higher Homologues. *Acc. Chem. Res.* **1986**, *19*, 406.
- Strube, A.; Huttner, G.; Zsolnai, L. Linear Twofold Coordination of Arsenic in [Cp'(CO)<sub>2</sub>Mn = As = Mn(CO)<sub>2</sub>Cp']<sup>+</sup>. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1529.
- Fermin, M. C.; Ho, J.; Stephan, D. W. Sterically Induced P–C Bond Cleavage: Routes to Substituent-Free Phosphorus Complexes of Zirconium. *Organometallics* **1995**, *14*, 4247.
- Johnson, M. J. A.; Lee, P. M.; Odom, A. L.; Davis, W. M.; Cummins, C. C. Atom-Bridged Intermediates in N- and P-Atom Transfer Reactions. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 87.
- (a) Cummins, C. C. Reductive cleavage and related reactions leading to molybdenum-element multiple bonds: new pathways offered by three-coordinate molybdenum (III). *Chem. Commun.* **1998**, 1777. (b) Scheer, M. Metal element triple bonds of the heavier group 15 elements. *Coord. Chem. Rev.* **1997**, *163*, 271.
- Ho, J.; Rousseau, R.; Stephan, D. W. Synthesis, Structure, and Bonding in Zirconocene Primary Phosphido (PHR<sup>-</sup>), Phosphinidene (PR<sup>2-</sup>), and Phosphide (P<sup>3-</sup>) Derivatives. *Organometallics* **1994**, *13*, 1918.

- (16) Matthews, H. E.; Feldman, P. A.; Bernath, P. F. Upper Limits to Interstellar PO. *Astrophys. J.* **1987**, *312*, 358.
- (17) (a) Scherer, O. J.; Braun, J.; Walther, P.; Heckmann, G.; Wolmershäuser, G. Phosphorus Monoxide (PO) as Complex Ligand. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 852. (b) Wang, W.; Carty, A. J. Phosphorus monoxide coordination chemistry. *New. J. Chem.* **1997**, *21*, 773.
- (18) (a) Scherer, O. J.; Vondung, C.; Wolmershäuser, G. PS Ligands as Building Blocks of Chiral Dimetallatetrahedranes with a Common Vertex. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1303. (b) Lorenz, I.-P.; Pohl, W.; Polborn, K. Triferriothioxophosphoranes: First Structural Characterization of a  $\mu_3$ -P=S complex. *Chem. Ber.* **1996**, *129*, 11.
- (19) (a) Scherer, O. J.; Weigel, S.; Wolmershäuser, G. [Cp\*FeP<sub>5</sub>] as a Useful Source for the Synthesis of Cobalt Complexes with "naked" P<sub>n</sub> Ligands. *Chem. Eur. J.* **1998**, *4*, 1910. (b) Weigel, S.; Wolmershäuser, G.; Scherer, O. J. [Cp\*Co]<sub>3</sub>( $\mu_3$ -P)( $\mu_3$ -PSe), ein Dreikerncluster mit einem PSe-Liganden. *Z. Anorg. Allg. Chem.* **1998**, *624*, 559. (c) Unpublished results.
- (20) (a) Herrmann, W. A.; Koumbouris, B.; Zahn, T.; Ziegler, M. L. Arsanediyl (Arsinidene) and Diarsene Complexes by Metal-Induced Degradation of Monoarsane. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 812. (b) Huttner, G.; Sigwarth, B.; Scheidsteiger, O.; Zsolnai, L.; Orama, O. Diarsenic, As<sub>2</sub>, as a Four-, Six-, or Eight-Electron Donor Ligand. *Organometallics* **1985**, *4*, 326.
- (21) Scherer, O. J.; Ehses, M.; Wolmershäuser, G. Activation of P<sub>4</sub> and P<sub>2</sub> by Transition Metal Complexes at Room Temperature. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 507.
- (22) (a) Harper, J. R.; Rheingold, A. L. Synthesis and molecular structure of [ $\eta^5$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>]<sub>2</sub>( $\mu$ , $\eta^2$ -Sb<sub>2</sub>). *J. Organomet. Chem.* **1990**, *390*, C36. (b) Breunig, H. J.; Rösler, R.; Lork, E. Complexes with Sb<sub>2</sub> and cyclo-Sb<sub>3</sub> Ligands: The Tetrahedranes [C<sub>5</sub>H<sub>5</sub>(CO)<sub>2</sub>-Mo]<sub>2</sub>Sb<sub>2</sub>, [C<sub>5</sub>H<sub>5</sub>(CO)<sub>2</sub>MoSb<sub>3</sub>], and [C<sub>5</sub>Me<sub>5</sub>(CO)<sub>2</sub>-MoSb<sub>3</sub>]. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2819.
- (23) (a) Davies, J. E.; Mays, M. J.; Raithby, P. R.; Shields, G. P.; Tompkin, P. K. Synthesis and characterisation of [M<sub>2</sub>( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>4</sub>( $\mu$ -PH<sub>2</sub>)( $\mu$ -H)] (M = Mo, W); a new route to  $\mu$ -PH<sub>2</sub> complexes involving novel activation of a bridging diphosphorus ligand. *Chem. Commun.* **1997**, 361. (b) Davies, J. E.; Kerr, L. C.; Mays, M. J.; Raithby, P. R.; Tompkin, P. K.; Woods, A. D. Reaction of Group 15 Trichlorides ECl<sub>3</sub> with the Anion [Mo<sub>2</sub>Cp<sub>2</sub>(CO)<sub>4</sub>( $\mu$ -PH<sub>2</sub>)]<sup>-</sup>: Synthesis and Characterization of the First Complexes Featuring a Hetero  $\mu$ ,  $\eta^2$ -PE Ligand (E = As, Sb). *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1428.
- (24) Scherer, O. J.; Kemény, G.; Wolmershäuser, G. [Cp<sub>4</sub>-Fe<sub>4</sub>(E<sub>2</sub>)<sub>2</sub>] Clusters with Triangulated Dodecahedral Fe<sub>4</sub>E<sub>4</sub> Skeletons (E = P, As). *Chem. Ber.* **1995**, *128*, 1145.
- (25) Scherer, O. J.; Pfeiffer, K.; Heckmann, G.; Wolmershäuser, G. [(C<sub>5</sub>Me<sub>4</sub>R)Co(As<sub>2</sub>)]-Molekülbausteine. *J. Organomet. Chem.* **1992**, *425*, 141.
- (26) (a) Ahlrichs, R.; Fenske, D.; Fromm, K.; Krautscheid, H.; Krautscheid, U.; Treutler, O. Zintl Anions as Starting Compounds for the Synthesis of Polynuclear Transition Metal Complexes. *Chem. Eur. J.* **1996**, *2*, 238. (b) Scherer, O. J.; Blath, C.; Heckmann, G.; Wolmershäuser, G. [(C<sub>5</sub>Me<sub>4</sub>R)Ru]<sub>3</sub>Ru( $\eta^3$ -As<sub>3</sub>)-( $\mu_3$ , $\eta^3$ -As<sub>3</sub>)( $\mu_3$ -As)<sub>3</sub>], arsenreiche Vierkerncluster. *J. Organomet. Chem.* **1991**, *409*, C15. (c) Von Hänisch, C.; Fenske, D. [(Cp\*Fe)<sub>3</sub>( $\eta^3$ -As<sub>3</sub>)Fe]As<sub>6</sub>] und [(Cp\*Fe)<sub>3</sub>-As<sub>6</sub>][FeCl<sub>3</sub>(THF)], zwei neue Eisen-Arsen-Cluster mit As<sub>6</sub>- und As<sub>3</sub>-Fragmenten. *Z. Anorg. Allg. Chem.* **1998**, *624*, 367. (d) Fenske, D.; Persau, C. Synthesen und Kristallstrukturen von [Pd<sub>9</sub>As<sub>8</sub>(PPh<sub>3</sub>)<sub>8</sub>] und [Pd<sub>9</sub>-Sb<sub>6</sub>(PPh<sub>3</sub>)<sub>8</sub>]. *Z. Anorg. Allg. Chem.* **1991**, *593*, 61.
- (27) Von Hänisch, C.; Fenske, D.; Weigend, F.; Ahlrichs, R. A Square As<sub>4</sub> and a Prismatic As<sub>6</sub> Structure as Complex Ligands. *Chem. Eur. J.* **1997**, *3*, 1494.
- (28) Detzel, M.; Pfeiffer, K.; Scherer, O. J.; Wolmershäuser, G. Cage Extension to Clusters with Co<sub>2</sub>/Co<sub>3</sub>MoAs<sub>6</sub> Polyhedron Frameworks. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 914.
- (29) (a) Di Vaira, M.; Stoppioni, P.; Midollini, S.; Laschi, F.; Zanello, P. H<sup>+</sup> Addition to the Heteroatomic CoP<sub>3</sub> Cluster. Synthesis of the Radical CoP<sub>3</sub><sup>+</sup> Cluster and Electrochemical Study. *Polyhedron* **1991**, *10*, 2123. (b) Di Vaira, M.; Rovai, D.; Stoppioni, P. Addition of RHg<sup>+</sup> Fragments to P-P Bonds of Heteroatomic Clusters. *Polyhedron* **1990**, *9*, 2477.
- (30) (a) Herberhold, M.; Frohmader, G.; Milius, W. Neue Vanadium-Komplexe mit substituentenfreien Phosphorliganden. *J. Organomet. Chem.* **1996**, *522*, 185. (b) Scherer, O. J.; Mohr, T.; Wolmershäuser, G. Cleavage of an acyclic P<sub>5</sub> ligand into P<sub>4</sub>/P<sub>1</sub> and P<sub>3</sub>/P<sub>2</sub> building blocks. *J. Organomet. Chem.* **1997**, *529*, 379. Mohr, T. Thesis, Universität Kaiserslautern, 1996.
- (31) Scheer, M.; Schuster, K.; Krug, A.; Hartung, H. [Cr(CO)<sub>5</sub>PCl<sub>3</sub>]-A Starting Material for Phosphorus-Rich P<sub>x</sub> Ligand Complexes. *Chem. Ber./Recueil* **1997**, *130*, 1299.
- (32) (a) Barr, M. E.; Smith, S. K.; Spencer, B.; Dahl, L. F. Photochemical Synthesis and Stereophysical Characterization of W(CO)<sub>4</sub>[cyclo-(PW(CO)<sub>5</sub>)<sub>4</sub>]: Experimental-Theoretical Bonding Analysis of its Unprecedented Pentametal-Coordinated cyclo-P<sub>4</sub> Ligand. *Organometallics* **1991**, *10*, 3983. (b) Scheer, M.; Herrmann, E.; Sieler, J.; Oehme, M. The cyclo tetraphospha ligand as a 12 electron donor. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 969.
- (33) Scheer, M.; Becker, U.; Chisholm, M. H.; Huffman, J. C.; Lemoigno, F.; Eisenstein, O. [Cp''Co(P<sub>4</sub>)-{(Cp''Co)( $\mu$ -CO)}] (Cp'' = C<sub>5</sub>H<sub>3</sub>But<sub>2</sub>): A Complex with a P<sub>4</sub> Unit on the Way to a P<sub>1</sub> and P<sub>3</sub> Ligand. *Inorg. Chem.* **1995**, *34*, 3117.
- (34) (a) Scherer, O. J.; Schwarz, G.; Wolmershäuser, G. Eisen-Zweikernkomplexe mit unterschiedlichen P<sub>4</sub>-Liganden. *Z. Anorg. Allg. Chem.* **1996**, *622*, 951. (b) Scherer, O. J.; Hilt, T.; Wolmershäuser, G. P<sub>4</sub> Activation with [Cp'''(OC)<sub>2</sub>Fe]<sub>2</sub> (Cp''' = C<sub>5</sub>H<sub>2</sub>But<sub>3</sub>-1,2,4): Exclusive Formation of the Exo/Exo-Butterfly Complex [Cp'''(OC)<sub>2</sub>Fe]<sub>2</sub>( $\mu$ - $\eta^1$ :  $\eta^1$ -P<sub>4</sub>). *Organometallics* **1998**, *17*, 4110. (c) Unpublished results.
- (35) Scherer, O. J.; Pfeiffer, K.; Wolmershäuser, G. Cobaltkomplexe mit As<sub>4</sub>-Liganden. *Chem. Ber.* **1992**, *125*, 2367.
- (36) Peruzzini, M.; Ramirez, J. A.; Vizza, F. Hydrogenation of white phosphorus to phosphane with rhodium and iridium trihydrides. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2255.
- (37) (a) Scherer, O. J.; Brück, T.; Wolmershäuser, G. Pentaphosphaferrocene als Komplexliganden. *Chem. Ber.* **1989**, *122*, 2049. (b) Rink, B.; Scherer, O. J.; Wolmershäuser, G. Übertragung eines cyclo-E<sub>5</sub>-Liganden (E = P, As) von einem Eisen- auf ein Ruthenium- und ein Osmium-Zentrum. *Chem. Ber.* **1995**, *128*, 71. (c) Detzel, M.; Friedrich, G.; Scherer, O. J.; Wolmershäuser, G.  $\eta^5$ : $\eta^2$  Coordination of a cyclo-E<sub>5</sub> Ligand, E = P, As. *Angew. Chem., Int. Ed.*

- Engl.* **1995**, *34*, 1321. (d) Detzel, M.; Mohr, T.; Scherer, O. J.; Wolmershäuser, G. [Cp\*Fe( $\eta^5$ -P<sub>5</sub>)], a Sandwich Complex with Diverse Ligand Properties. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1110.
- (38) Goh, L. Y.; Wong, R. C. S.; Yip, W.-H.; Mak, T. C. W. Synthesis and Thermolysis of Di- and Triarsenic Complexes of Chromium. Crystal Structure of [CpCr(CO)<sub>2</sub>]<sub>2</sub>As<sub>2</sub>. *Organometallics* **1991**, *10*, 875.
- (39) Hughes, A. K.; Murphy, V. J.; O'Hare, D. Synthesis, X-Ray Structure and Spin Crossover in the Triple-decker Complex [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Cr( $\mu^2$ : $\eta^5$ -P<sub>5</sub>)Cr( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)]<sup>+</sup>[A<sup>-</sup>] (A = PF<sub>6</sub>, SbF<sub>6</sub>). *J. Chem. Soc., Chem. Commun.* **1994**, 163.
- (40) Reddy, A. C.; Jemmis, E. D.; Scherer, O. J.; Winter, R.; Heckmann, G.; Wolmershäuser, G. Electronic Structure of Triple-Decker Sandwich Complexes with P<sub>6</sub> Middle Rings. Synthesis and X-ray Structure Determination of Bis( $\eta^5$ -1,3-di-tert-butylcyclopentadienyl) ( $\mu$ - $\eta^6$ :  $\eta^6$ -hexaphosphorin)diniobium. *Organometallics* **1992**, *11*, 3894.
- (41) (a) Scherer, O. J.; Werner, B.; Heckmann, G.; Wolmershäuser, G. Bicyclic P<sub>6</sub> as Complex Ligand. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 553. (b) Scherer, O. J.; Schulze, J.; Wolmershäuser, G. Bicyclisches As<sub>6</sub> als Komplexligand. *J. Organomet. Chem.* **1994**, *484*, C5.
- (42) Scherer, O. J.; Berg, G.; Wolmershäuser, G. P<sub>8</sub> and P<sub>12</sub> as Complex Ligands. *Chem. Ber.* **1996**, *129*, 53.
- (43) Hofmann, C.; Scherer, O. J.; Wolmershäuser, G. [Cp\*FeP<sub>6</sub>MoCp\*]: A dinuclear complex with a P<sub>4</sub> and a P<sub>2</sub> ligand. *J. Organomet. Chem.* **1998**, *559*, 219.
- (44) *Chemistry, Structure, and Bonding of Zintl Phases and Ions*; Kauzlarich, S. M., Ed.; Verlag Chemie: Weinheim, New York, 1996.
- (45) Charles, S.; Danis, J. A.; Fettinger, J. C.; Eichhorn, B. W. Rapid Inversion of Phosphorus in the [ $\eta^4$ -(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>SnP<sub>7</sub>W(CO)<sub>3</sub>]<sup>2-</sup> and [(en)(CO)<sub>3</sub>W( $\eta^1$ ,  $\eta^4$ -P<sub>7</sub>)M(CO)<sub>3</sub>]<sup>3-</sup> Ions where M = Cr, W. *Inorg. Chem.* **1997**, *36*, 3772 and references therein.
- (46) Bolle, U.; Tremel, W. Insertion of a Transition Metal Fragment into a Heptaantimonide (3<sup>-</sup>) Anion: Synthesis and Structure of [Sb<sub>7</sub>Mo(CO)<sub>3</sub>]<sup>3-</sup>. *J. Chem. Soc., Chem. Commun.* **1994**, 217.
- (47) (a) Barr, M. E.; Adams, B. R.; Weller, R. R.; Dahl, L. F. Synthesis and Structural Bonding Analysis of ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)<sub>4</sub>Fe<sub>4</sub>(CO)<sub>6</sub>P<sub>8</sub> and ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me)<sub>4</sub>Fe<sub>6</sub>(CO)<sub>13</sub>P<sub>8</sub>: Two Unprecedented Transition-Metal Complexes Containing the Cage-like Subunit of Hittorf's Monoclinic Phosphorus Allotrope. *J. Am. Chem. Soc.* **1991**, *113*, 3052. (b) Scheer, M.; Becker, U.; Matern, E. Ir-Komplexe mit P<sub>4</sub>-Bicyclotetraphosphan und P<sub>8</sub>-Cunean als Liganden-CO-Insertion in eine Ir-P-Bindung. *Chem. Ber.* **1996**, *129*, 721.
- (48) (a) Dewalsky, M. V.; Jeitschko, W. Preparation, Physical Properties and Crystal Structure of MoNiP<sub>8</sub> and WNiP<sub>8</sub>. *Acta Chem. Scand.* **1991**, *45*, 828. (b) Llundell, M.; Alvarez, S.; Alemany, P.; Hoffmann, R. Electronic Structure, Bonding, and Electrical Properties of MoNiP<sub>8</sub>. *Inorg. Chem.* **1996**, *35*, 4683.
- (49) Scherer, O. J.; Winter, R.; Heckmann, G.; Wolmershäuser, G. Cyclo-As<sub>8</sub> as Complex Ligand. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 850.
- (50) Scherer, O. J.; Höbel, B.; Wolmershäuser, G. Double Open-Edged P<sub>10</sub> Dihydrofulvalene as a 16-Electron Donor Ligand. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1027.
- (51) Goh, L. Y.; Wong, R. C. S.; Sinn, E. Novel Polycyclic Phosphane-to-Metal Coordination. Reaction of [CpCr(CO)<sub>3</sub>]<sub>2</sub> with Elemental Phosphorus and Structure and Paramagnetism of the Odd-Electron Complex [CpCr(CO)<sub>2</sub>]<sub>5</sub>P<sub>10</sub>. *Organometallics* **1993**, *12*, 888.
- (52) Böcker, S.; Häser, M. Covalent Structures of Phosphorus: A Comprehensive Theoretical Study. *Z. Anorg. Allg. Chem.* **1995**, *621*, 258 and references therein.
- (53) Pfitzner, A.; Freudenthaler, E. (CuI)<sub>3</sub>P<sub>12</sub>: A Solid Containing a New Polymer of Phosphorus Predicted by Theory. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1647.
- (54) Pfitzner, A.; Freudenthaler, E. (CuI)<sub>2</sub>P<sub>14</sub>: ein neues Phosphorpolymer in einer Kupferhalogenid-Matrix. *Z. Naturforsch.* **1997**, *52b*, 199.
- (55) Dransfeld, A.; Nyulászi, L.; Schleyer, P. v. R. The Aromaticity of Polyphosphaphospholes Decreases with the Pyramidalicity of the Tricoordinate Phosphorus. *Inorg. Chem.* **1998**, *37*, 4413.
- (56) Jones, R. O.; Ganteför, G.; Hunsicker, S.; Pieperhoff, P. Structure and spectroscopy of phosphorus cluster anions: Theory (simulated annealing) and experiment (photoelectron detachment). *J. Chem. Phys.* **1995**, *103*, 9549.
- (57) Ballone, P.; Jones, R. O. Density functional study of phosphorus and arsenic clusters using local and nonlocal energy functionals. *J. Chem. Phys.* **1994**, *100*, 4941.

AR970317C