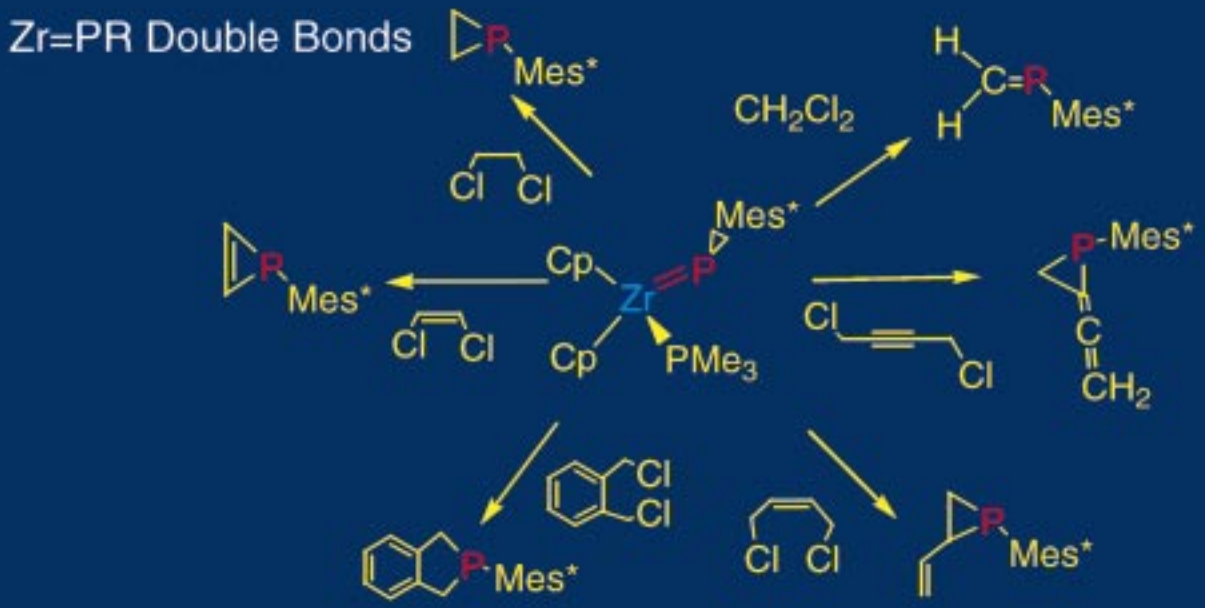
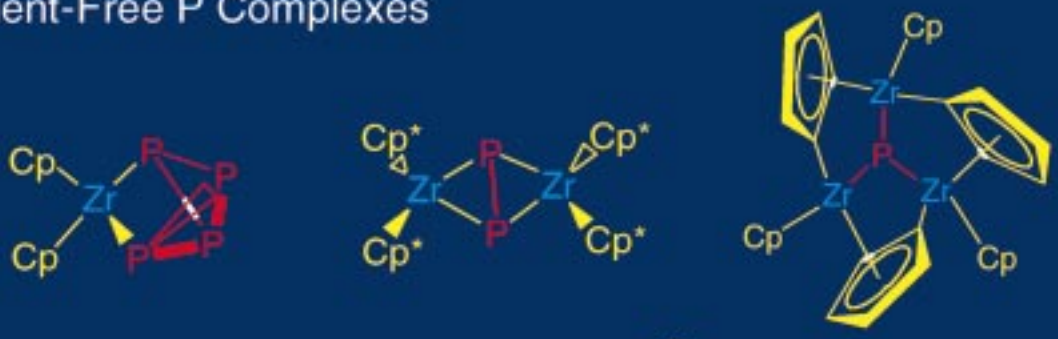
Zirconium–Phosphorus Chemistry

Zr–P Single Bonds

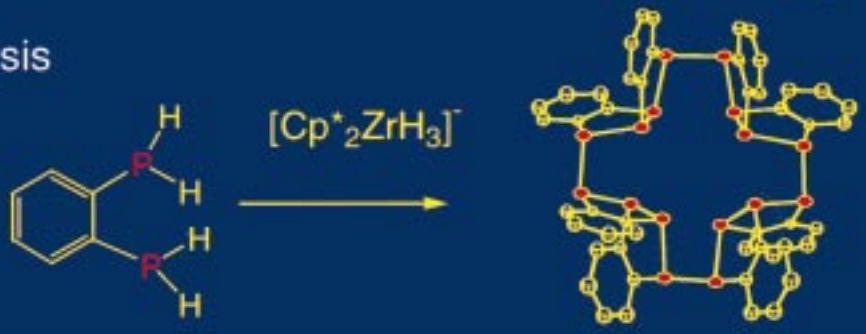
Zr=PR Double Bonds



Substituent-Free P Complexes



Catalysis



Zirconium – Phosphorus Chemistry: Strategies in Syntheses, Reactivity, Catalysis, and Utility

Douglas W. Stephan*

The extension of the principles of organometallic chemistry to applications in metal-mediated syntheses of main group compounds is an emerging subdiscipline that is drawing much current attention. This review focuses on a subset of this area, specifically the utility of Zr–P compounds in organophosphorus chemistry. Until the early 1980s only a handful of compounds containing Zr–P bonds were known, and virtually nothing was known about their reactivity. In the past fifteen years this area has developed dramatically. Early emphasis was on the synthesis and reactivity of complexes containing Zr–P single bonds. Subsequently, synthetic strategies for compounds containing Zr–P double bonds, phosphazirconacycles, and Zr complexes of substituent-free phosphorus were developed. Each of these classes of Zr–P compounds exhibits a unique reactivity that often permits the stoichiometric syntheses of unprecedented organophosphorus compounds. Moreover, in recent studies this reactivity has been exploited in catalytic syntheses of organophosphorus oligomers. Overall, the rich chemistry of Zr–P compounds and their utility in the preparation of phosphorus compounds illustrate the potential of this organometallic approach to the synthesis of main group compounds.

Keywords: homogeneous catalysis · phosphorus · P ligands · zirconium

1. Introduction

The battery of stoichiometric and catalytic synthetic strategies that are based on organometallic chemistry hinges on the principles of synthesis and reactivity of metal–carbon bonds. In the past ten years, there have been growing efforts to broaden the range of application of organometallic chemistry to include main group elements. These endeavors led to the characterization of a number of structurally unprecedented compounds, yet metal-mediated syntheses of main group compounds have only just begun to emerge. We and others have contributed to this hybrid field of main group/transition metal organometallic chemistry by focusing on the potential of Zr–P compounds. Upon commencement of these studies in the 1980s, the known Zr–P chemistry was very limited, and the reactivity of compounds containing Zr–P σ bonds was virtually unexplored. This review recounts developments in both the syntheses and reactivity of Zr–P complexes. Synthetic strategies for compounds containing Zr–P double bonds, phosphazirconacycles, and Zr complexes of substituent-free phosphorus are described. These classes of Zr–P derivatives demonstrate unique reactivity, often applicable to stoichiometric syntheses of unprecedented organophosphorus compounds. More recently, Zr–P chemistry has been extended to catalytic syntheses of organophosphorus oligomers. This progression from synthesis and reactivity to application in organophosphorus chemistry illustrates the potential of organometallic reagents in the synthesis of compounds of the main group elements.

[*] Prof. D. W. Stephan
School of Physical Sciences
College of Engineering and Science, Chemistry and Biochemistry
University of Windsor
Windsor, ON, N9B 3P4 (Canada)
Fax: (+1) 519-973-7098
E-mail: stephan@windsor.ca

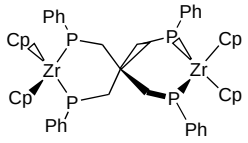
2. Synthesis and Reactivity of Zirconium Phosphanido and Phosphanato Complexes

The challenge addressed by early research was simply the development of synthetic methodologies for the preparation of species containing Zr–P σ bonds. Several approaches are described below. A detailed account of structural and spectroscopic data of some of these compounds formed part of an earlier review.[1]

2.1. Halide Metathesis

Zr–P chemistry began with the pioneering efforts of Issleib and Häckert.[2] The reaction of $[Cp_2MX_2]$ ($Cp = \eta^5$-C_5H_5) with

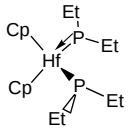
  1433-7851/00/3902-0315 $ 17.50+.50/0



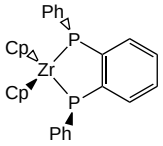
1

$LiPR_2$ was reported to give the Ti^{III} and Zr^{III} dimers $[\{Cp_2M(\mu\text{-}PR_2)\}_2]$ (R = Et, Bu) and the by-product P_2R_4. In the following year, Ellerman and Poersch described the first Zr^{IV}–P compound **1**, derived from the reaction of $[Cp_2ZrCl_2]$ and $[NaP(Ph)CH_2]_4C$ in liquid ammonia.[3]

These early papers prompted much of what was to follow in the 1980s. Baker et al. reported the synthesis of complexes of the form $[Cp_2M(PR_2)_2]$ (M = Zr, Hf; R = Et, Cy, Ph) in 1983.[4] These species could be reduced to the Zr^{III} analogues $[Na(thf)_x][Cp_2Zr(PR_2)_2]$. X-ray structural data for **2** revealed unequal Hf–P bond lengths (2.488(1), 2.682(1) Å), and this confirmed the ability of phosphorus to act as a π donor to give a formally 18-electron Hf center. Variable-temperature NMR data revealed a barrier to rotation about the Hf–P double bond of 6.0(2) kcal mol^{-1} in $[Cp_2Hf(PCy_2)_2]$. In the same year, Baker et al. also described a variety of homoleptic compounds, including $[Li(dme)_n][M(PCy_2)_5]$ (M = Zr, Hf; dme = 1,2-dimethoxyethane) and $[Li(dme)_n][M(PCy_2)_4]$ (M = Ti, Zr), which were derived from the metathesis of $LiPCy_2$ with appropriate THF adducts of metal halides.[5] Similar synthetic procedures gave a variety of silylphosphanido complexes of the form $[(C_5H_4R)_2M(X)_{2-n}\{P(SiMe_3)_2\}_n]$ (R = H, $SiMe_3$; M = Zr, Hf; X = Cl, Me), and a number of primary phosphanido complexes were prepared from lithium phosphanides and the corresponding metallocene dihalide or methylmetallocene halide.[6–11] The chelate complex **3** was prepared by the reaction of $[\{1,2\text{-}(PPh)_2C_6H_4\}\{Li(tmeda)\}_2]$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylendiamine) with $[Cp_2ZrCl_2]$.[12–14]

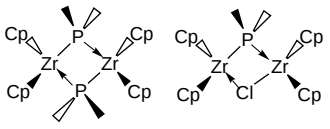


2



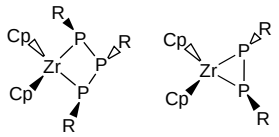
3

As mentioned above, Issleib et al. established in 1966 that electron-rich lithium phosphanides can reduce Zr^{IV} and Ti^{IV}.[2] However, it was not until 1988 that Gambarotta et al. reported the first X-ray structural data for the Zr^{III} dimers **4** and **5**.[15] We subsequently reported structural and magnetic studies on $[\{Cp_2M(\mu\text{-}PEt_2)\}_2]$ (M = Ti, Zr),[16] and Hey-Hawkins et al. structurally characterized $[\{Cp_2Zr(\mu\text{-}PHR)\}_2]$ (R = *t*Bu, adamantyl).[17] Theoretical studies on dinuclear Zr^{III} complexes led to the controversial proposal of "superlong" metal–metal bonds. Ab initio and Hartree–Fock–Slater calculations were used to support the notion that metal–metal bonds exist in these dimers, despite the fact that the metal atoms are separated by more than 3.5 Å.[18–20]



4 5

As early as 1972 Issleib et al. reported the synthesis of Ti and Zr complexes of the type $[Cp_2M(PPhPPhPPh)]$ from $[Cp_2MX_2]$ and $Li_2P_4Ph_4$.[21] In 1981, Köpf and Voigtländer described the complexes $[Cp_2M(PRPRPR)]$ (M = Ti, Zr, Hf; R = Ph, Et, Me),[22] but it was not until 1988 that Hey et al. reported the first crystal structure of $[Cp_2Hf(PPhPPhPPh)]$, derived from the metathetical reaction of the corresponding metallocene dihalide with LiPHPh.[23] The analogous compounds $[Cp_2M(PRPRPR)]$ (M = Zr, Hf; R = Ph, Cy) were prepared in a similar manner.[24–26] In contrast, Benac and Jones showed that reactions of LiPHR (R = Ph, *t*Bu) with various metallocene dihalides lead to several products, including **6**, **7**, $[Cp_2M(PR\text{–}PR)]$, and $[\{Cp_2M(\mu\text{-}PRH)\}_2]$; this implies that electronic and steric factors determine the reaction course.[27] Subsequently, a crystal structure of the diphosphanato derivative $[(\eta^5\text{-}C_5Me_4Et)_2Zr(PMesPMes)]$ (Mes = 2,4,6-$Me_3C_6H_2$), an analogue of **7**, was reported by Kurz and Hey-Hawkins.[28]



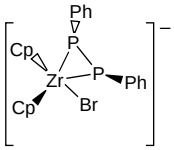
6 7

2.2. P–H Bond Activation

The tendency of phosphanido reagents to reduce Zr^{IV} to Zr^{III} prompted the quest for alternative synthetic pathways to

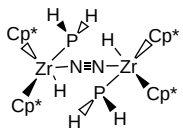
Doug Stephan was born in 1953 in Hamilton, ON, Canada where he completed his undergraduate studies in Chemistry at McMaster University in 1976. As an NSERC of Canada Scholar, he completed his graduate work on studies of catalytic asymmetric synthesis in 1980 at the University of Western Ontario under the aegis of Professor N. C. Payne. In the following two years, he held a NATO postdoctoral Fellowship at Harvard University in the laboratories of R. H. Holm. In 1982 he became an Assistant Professor at the University of Windsor, where he was subsequently promoted through the ranks to Professor in 1992. He has served on the NSERC of Canada grant selection committee and is currently on the editorial boards of the Canadian Journal of Chemistry and Organometallics. In 1995 he spent a DFG-supported sabbatical in the laboratories of Professor G. Erker in Münster. Generally, his research interest focuses on the synthesis and applications of Zr–P and Ti–S compounds in both stoichiometric and catalytic reactions as well as the development of new olefin polymerization catalysts.

Zr–P bonds. While strategies based on P–H bond activation offer potential routes to Zr–P double bonds (see Section 3.3), some pathways to Zr phosphanido and phosphanato complexes have been discovered. For example, the triphosphanato complex $[Cp_2Zr(PPhPPhPPh)]$ was obtained from the reaction of $PhPH_2$ with $[Cp_2ZrMe_2]$.[23] Other complexes of the type $[Cp_2Zr(PRPRPR)]$ (R = Ph, Cy) were obtained by oxidative addition of P–H bonds to Zr^{II}, generated in situ by reaction of $[Cp_2ZrCl_2]$ with Mg.[24] Addition of bromide ion to such a reaction mixture led to the interception of the anionic diphosphanato species **8**.[24]

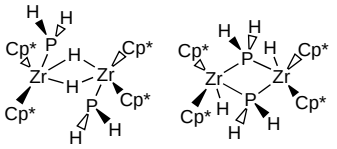


8

Marsh et al. reported further studies on oxidative addition of phosphane to Zr^{II} species.[29] Reaction of $[\{Cp^*_2Zr(N_2)\}_2(\mu\text{-}N_2)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) with PH_3 led to the stepwise formation of **9** and two isomers of **10**. The latter complex reacts with alkenes at higher temperatures to liberate the corresponding alkylphosphane and $[Cp^*_2Zr(H)_2]$.



9



10

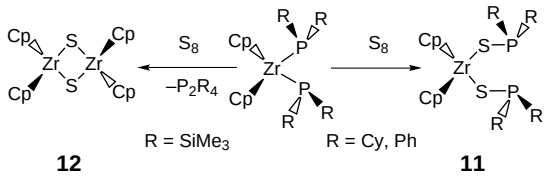
Alternatively, acidolysis of metal hydrides by primary or secondary phosphanes yields phosphanido complexes. Thus, Vaughan and Hillhouse prepared phosphanido complexes of the type $[Cp^*_2HfH(PHR)]$ and $[Cp^*_2HfH(PR_2)]$ from $[Cp^*_2HfH_2]$ with concurrent elimination of H_2.[6]

2.3. Reactivity

Initial reactivity studies by Wade et al. probed the chemistry of the complexes $[Cp_2M(PR_2)_2]$ with a variety of protic (alcohols, thiols, phosphanes, H_2O) or halogen-containing (Ph_2PCl, Me_3SiCl, MeI) reagents.[30] In general, such reactions lead to facile Zr–P bond scission with the liberation of the corresponding phosphane. Similarly, aminolysis of $[Cp_2ZrCl\{P(SiMe_3)_2\}]$ by aniline gave $[Cp_2ZrCl(NHPh)]$ and the corresponding secondary phosphane.[31] Attempts to replace the halide ion in $[Cp_2ZrCl(PR_2)]$ by reaction with $AlMe_3$, Me_3SiN_3, or LiOR resulted in displacement of the phosphanido group and the liberation of phosphane or $LiPR_2$.[7]

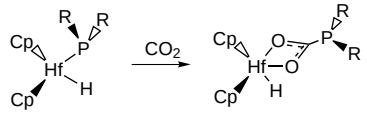
Despite the demonstrated lability of the Zr–P bond, one of our early reports revealed insertion chemistry of Zr–P bonds. The reaction of the complexes $[Cp_2Zr(PR_2)_2]$ (R = Ph, Cy) with S_8 gave **11**.[32] In contrast, the more sterically crowded phosphanido complex $[Cp_2Zr\{P(SiMe_3)_2\}_2]$ gave **12** and unidentified phosphorus products.[33]

Hf–P bond scission was observed in the reactions of $[Cp^*_2HfH(PR_2)]$ with H_2, CO, and C_2H_4, which led to the liberation of phosphane and formation of $[Cp^*_2Hf(H)_2]$, $[Cp^*_2Hf(CO)_2]$, and $[Cp^*_2Hf(CH_2CH_2CH_2CH_2)]$, respectively. In contrast, CO_2 inserts into the Hf–P bond of $[Cp^*_2HfH(PR_2)]$ to give **13**.[6]



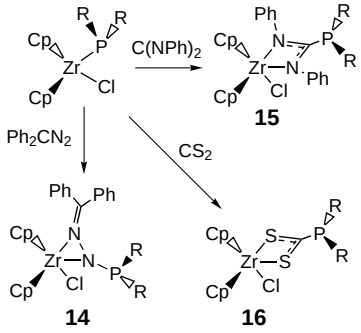
R = $SiMe_3$ R = Cy, Ph

12 **11**



13

Subsequent studies showed that a variety of reagents such as Ph_2CN_2, $C(PhN)_2$, and CS_2 insert into the Zr–P bond of $[Cp_2ZrCl(PR_2)]$ (R = $SiMe_3$) to give **14**,[34] **15**,[35] and **16**.[33]



15 **14** **16**

Complex **17**[36, 37] (Figure 1) was generated by insertion of P_4 into the Zr–P bonds of $[Cp_2Zr\{P(SiMe_3)_2\}_2]$. The reaction of $[(\eta^5\text{-}C_5Me_4Et)_2ZrCl(PHCy)]$ with PhNCS and CS_2 gave the insertion products **A** ($Cp' = \eta^5\text{-}C_5Me_4Et$) and **B** (an analogue of **16**).[38] Similarly, the compounds **C** (an analogue of **14**), **D** (R = Ph, *i*Pr; an analogue of **15**), and **E** ($Cp' = C_5H_4Me$) were obtained by insertion of Ph_2CN_2, $C(NR)_2$ (R = Ph, *i*Pr), and PhNC, respectively, into the Zr–P bonds of the corresponding phosphanido complexes.[34, 39, 40] The analogous insertion of phenylacetylene afforded **18**,[41] and further substitution with

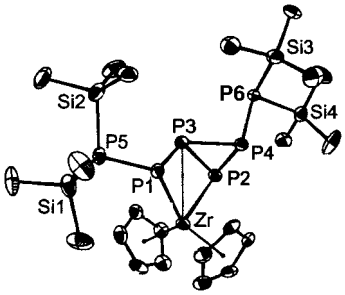
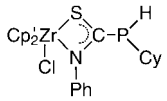
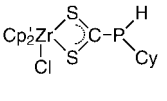


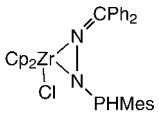
Figure 1. X-ray structure of $[Cp_2Zr\{PP(SiMe_3)_2PP[P(SiMe_3)_2]P\}]$ (**17**); reproduced with permission of The Royal Society of Chemistry.[36, 37]



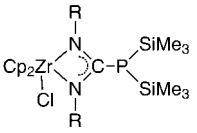
A



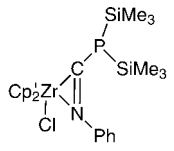
B



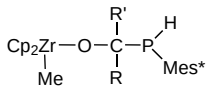
C



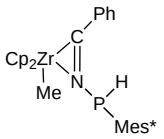
D



E

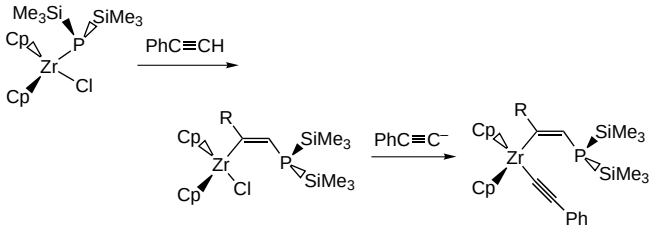


F



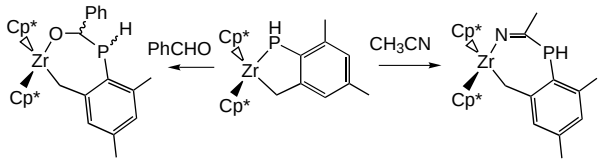
G

phenylacetylide anion gave **19**.[42] We showed that ketones, aldehydes, and nitriles also insert into the Zr–P bonds of $[Cp_2ZrMe(PHMes^*)]$ ($Mes^* = 2,4,6\text{-}tBu_3C_6H_2$) to give products of the type **F** (R = Ph; R′ = Ph, H) and **G**.[11] In a similar



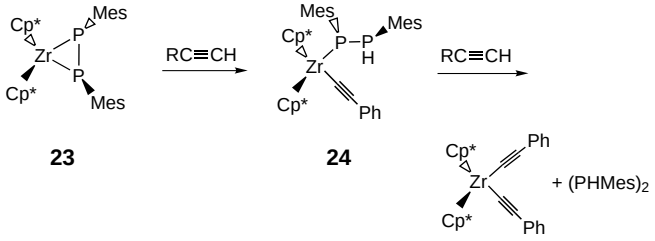
18 **19**

fashion, the chelate phosphanido complex **20** undergoes insertion of acetonitrile and benzaldehyde into the Zr–P bond to give **21** and **22**, respectively.[43, 44]



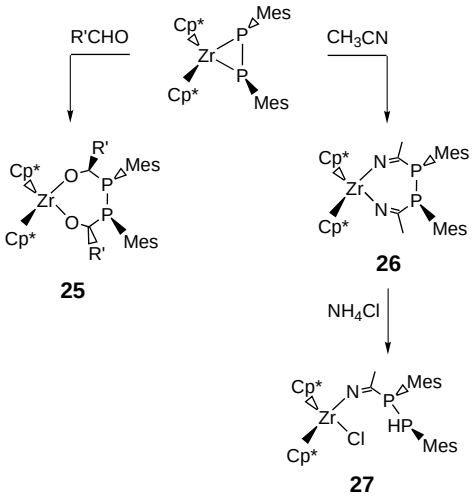
22 **20** **21**

Di- and triphosphanato complexes also exhibit facile Zr–P acidolysis and insertion reactions. For example, hydrolysis of $[Cp_2Zr\{(PPh)_2\}]$ gave the diphosphanes $(PHR)_2$.[27] Acidolysis of the diphosphanato complex **23** by primary phosphanes gave the corresponding bis-phosphanido complexes and liberated the substituted diphosphane $(PHMes)_2$.[44] Similarly, treatment of **23** with diiodomethane gave $[Cp_2^*ZrI_2]$ and an unidentified phosphorus product, while treatment with acetone afforded the dienolato complex $[Cp_2^*Zr\{OC(CH_2)\text{-}CH_3\}_2]$. Acidolysis of **23** by phenylacetylene yields sequentially **24** and $[Cp_2^*Zr(CCPh)_2]$.



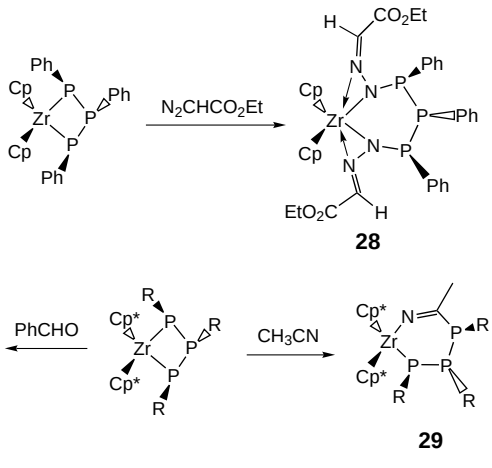
23 **24**

Insertion of nitriles and aldehydes into diphosphanato complexes gives **25** and **26**, and subsequent protolysis of the latter with NH_4Cl liberates the nitrile and provides **27**, which bears a pendent diphosphane group. Double insertion of



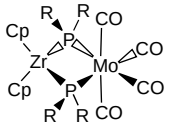
25 **26** **27**

diazoacetate into the Zr–P bonds of the triphosphanato complex $[Cp_2Zr(PPhPPhPPh)]$ affords **28**.[45] In the case of $[Cp_2^*Zr(PPhPPhPPh)]$, aldehydes and nitriles insert only once to give the unsymmetrical six-membered ring complexes **29** and **30**.[44]

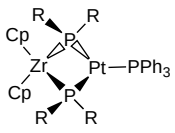


28 **30** **29**

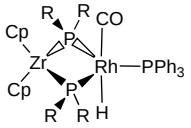
Another avenue for reactivity of zirconium phosphanido complexes was predicated on the basis that the donor ability of the lone pair of electrons on phosphorus would permit such complexes to act as metalloligands towards later transition metals to afford phosphorus-bridged early – late heterometallic complexes.[46] As early as 1977, Stelzer et al. reported the the formation of $[Cp_2Zr(\mu\text{-}PRR')_2Mo(CO)_4]$ by the displacement of labile ligands on Mo by the Zr phosphanido moiety.[47, 48] In the 1980s a number of groups exploited this concept to prepare a variety of Zr and Hf doubly phosphanido bridged complexes of the type $[Cp_2M(\mu\text{-}PR_2)_2M'L_n]$. Various bridging phosphanido groups (R = Ph, Et, Cy, $SiMe_3$) and a variety of late transition metal moieties ($M'L_n$) were included. Among them were $Mo(CO)_4$ (see **31**), $Cr(CO)_4$, $W(CO)_4$, $Fe(CO)_3$, $Ni(CO)_2$, $Fe(NO)_2$, $Ni(PPh_3)$, $Pd(PR_3)$, $Pt(PPh_3)$ (see **32**), Rh(indenyl), $RhH(PPh_3)(CO)$ (see **33**), $IrH(PPh_3)$-(CO), Ni(cod) (cod = 1,5-cyclooctadiene), and $ReH(CO)_3$.[49–59] The trimetallic complexes **34** (M = Zr, Hf; M′ = Ni, Pd, Pt), in which two early transition metal phosphanido moieties are coordinated to a central late transition metal center, were prepared by a similar method.[56]



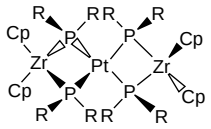
31



32



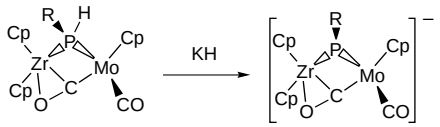
33



34

The two metal centers in the doubly phosphanido bridged heterobimetallic complexes did not show cooperative reactivity. Rather, the inclusion of the early-transition metalloligand provides only a limited ancillary effect. For example, complexes $[Cp_2Zr(\mu\text{-}PR_2)_2Pt(PPh_3)]$ exhibited typical ligand substitution reactions and failed to undergo oxidative addition reactions.[54, 55] This diminished reactivity was attributed to weak dative Pt–Zr interactions. Such donor – acceptor interactions were described on the basis of extended Hückel molecular orbital calculations.[56] Similarly, $[Cp_2Zr(\mu\text{-}PR_2)_2RhH(CO)(PPh_3)]$ (**33**) was shown to act as a catalyst precursor in the hydroformylation of 1-hexene.[58] While the reaction rate is considerably lower than that of typical monometallic Rh complexes, it is noteworthy that the selectivity for terminal aldehydes is dramatically increased.

Attempts to prepare complexes in which the early and late transition metal centers cooperatively activate a substrate led to the isolation of the singly phosphanido bridged heterobimetallic complexes $[Cp_2Zr(\mu\text{-}PR_2)(\mu\text{-}CO)MoCp(CO)]$, which are readily prepared by the reaction of $[Cp_2Zr(PR_2)_2]$ with $[CpMo(CO)_3H]$ or $[\{CpMo(CO)_3\}_2]$.[60] In the first case, Zr–P bond cleavage affords PHR_2 as by-product, while in the latter reaction, Mo–Mo bond reduction occurs concurrently with the oxidation of one of the phosphanido ligands to P_2R_4. Related singly phosphanido bridged heterobimetallic species were obtained directly from the redox reaction of the Zr^{III} complexes $[\{Cp_2Zr(\mu\text{-}PR_2)\}_2]$ with $[\{CpMo(CO)_3\}_2]$.[61] While structural data for the complexes $[Cp_2Zr(\mu\text{-}PR_2)(\mu\text{-}CO)$-$MoCp(CO)]$ show considerable C–O bond activation, as indicated by the C–O bond lengths (R = Ph: 1.230(5) Å; R = Et: 1.226(4) Å), attempts to effect further reaction of the η^1-η^2 carbonyl fragment were unsuccessful.[60] The related complex **35** undergoes deprotonation to generate the phosphinidene-bridged heterobimetallic anionic species **36**.[62] The reversibility of this deprotonation was demonstrated by deuterium labeling at phosphorus.



35 **36**

More recent studies have rekindled interest in heterobimetallic complexes, as the complexes $[Cp_2Zr\{\mu\text{-}P(SiMe_3)_2\}$-$Ni(CO)_2]$ and $[(\eta^5\text{-}C_5H_4R)_2Zr\{\mu\text{-}P(C_6H_2iPr_3)_2\}M(CO)_4]$ (R = Me, H; M = Mo, Cr) are active catalysts for the polymerization of ethylene.[63–66]

3. Synthetic Strategies Towards and Reactivity of Zr–P Double Bonds

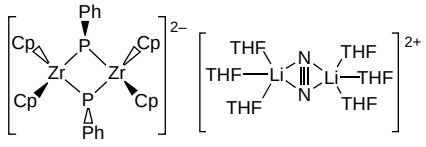
Species containing terminal Zr–P double bonds were viewed both as a synthetic challenge and a means to expand the range of Zr–P chemistry. This approach was concurrently developed for different metals (Mo, W, Ta) by the groups of Lappert, Cowley, Schrock, and Wolczanski.[67–70] Several of the initial synthetic routes to Zr–P double bonds were frustrated by the high reactivity of the putative Zr phosphinidene intermediates. Nonetheless, the isolation and study of a stable zirconocene phosphinidene complex was ultimately achieved.

3.1. Halide Elimination

In early attempts to generate early transition metal phosphinidene complexes, Vaughan and Hillhouse treated $[Cp^*_2HfX(PHR)]$ with a variety of bases, including KH, *n*BuLi, and $NaN(SiMe_3)_2$.[6] In one case, a single species exhibiting a singlet ^{31}P NMR signal at $\delta = 376$ was observed in solution. Although this promising result was suggestive of a phosphinidene species, this compound could not be isolated free of impurities, and consequently the formulation remained uncertain. In a similar vein, Arif and Cowley reported that the compound $[Cp_2ZrCl\{P(SiMe_3)Mes^*\}]$ failed to eliminate Me_3SiCl even under thermal or photochemical duress.[71]

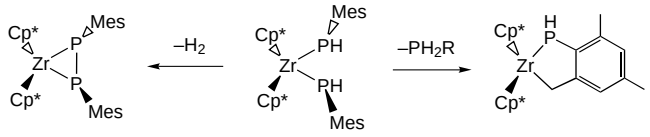
3.2. Halide Replacement Reactions

The most direct and, in retrospect, most naive strategy, involved reaction of the metallocene dihalides with Li_2PR. Such phosphanediides are strong reducing reagents and effect Zr–P bond formation with concurrent reduction to Zr^{III}. The resulting salts contain phosphinidene-bridged dianions $[\{Cp_2Zr(\mu\text{-}PR)\}_2]^{2-}$.[62] For R = Ph, crystallographic data confirmed the formulation of the dianion and also revealed an issue of peripheral interest. The Li cations in this salt are bridged in an unprecedented side-on manner by an N_2 molecule.[72] The extreme lability of the N_2 ligand in this species, even in the solid state, was consistent with the observed N–N distance of 1.06(1) Å. Subsequent studies by Bazhenova et al. confirmed the incorporation of N_2 in the solid state but disputed the formulation by suggesting that N_2 was partially reduced.[73] This was in contrast to our formulation for the complex **37**. Moreover, the proposal of a mixed-valent Zr^{IV}/Zr^{III} formulation is inconsistent with our observation of a half-field transition in the EPR spectrum, as well as the lability of the N_2 ligand.[72]



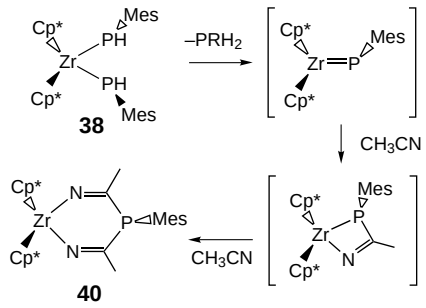
37

Reduction of Zr^{IV} can be avoided by alteration of the reaction conditions and use of sterically demanding substituents. For example, a simple halide replacement reaction provides the Zr^{IV} bis-phosphanido complex **38**. In benzene, this species is unstable with respect to elimination of phosphane and undergoes degradation into a mixture of **39** and **20**.[43, 44] The formation of these products supported the



39 **38** **20**

proposal of an intermediate Zr phosphinidene species $[Cp_2^*Zr{=}PR]$, generated by elimination of one equivalent of RPH_2. This transient Zr phosphinidene complex undergoes P–H or C–H addition to give the two observed products. Further evidence of the generation of a Zr phosphinidene intermediate was obtained from the reaction of LiPHMes with $[Cp_2^*ZrCl_2]$ in DME. Spectroscopic data supported the formation of a LiCl adduct of the zirconium phosphinidene complex $[Cp_2^*Zr(PMes)LiCl(dme)]$.[44] Moreover, the degradation of **38** in the presence of two equivalents of MeCN yields **40**; this confirms the intermediacy of a phosphinidene species.[43, 44]



The above approach was used with the more sterically demanding lithium phosphanide LiPHMes* in an effort to stabilize the terminal phosphinidene species. While reaction of $[Cp_2^*ZrCl_2]$ with one equivalent of the lithium reagent gave $[Cp_2^*Zr(PHMes^*)Cl]$, a second equivalent resulted in no further reaction. Presumably further substitution is precluded by steric congestion.[74] In marked contrast, $[Cp_2ZrCl_2]$ reacts with two equivalents of LiPHMes*. Loss of phosphane from the intermediate bis-phosphanido complex in the presence of PMe_3 afforded the first terminal Zr phosphinidene complex **41** (Figure 2), albeit in 40% yield.[44] The disparity of the ^{31}P NMR chemical shifts ($\delta = 792, -12$) of the two phosphorus atoms in **41** are consistent with the structural data, which confirm the presence of a Zr–P double bond (2.505(4) Å).[44] Moreover, this illustrates the subtle balance of steric features necessary to facilitate formation of a stable Zr phosphinidene complex and yet preclude further reaction.

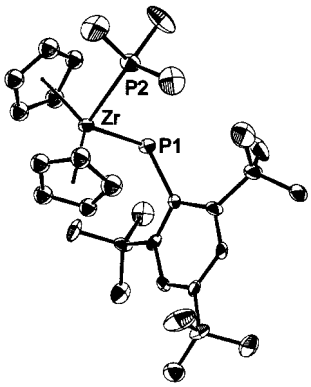


Figure 2. X-ray structure of $[Cp_2Zr(PMes^*)(PMe_3)]$ (**41**); reprinted with permission of *Organometallics*, copyright© American Chemical Society 1993.[44]

Of related interest is the reaction of $[Cp_2Zr(PHMes^*)Cl]$ with excess KH in THF, from which the novel anionic phosphinidene hydride salt **42** (Figure 3) was obtained in low yield. This can be formally viewed as the KH-stabilized adduct of the terminal phosphinidene complex.[74]

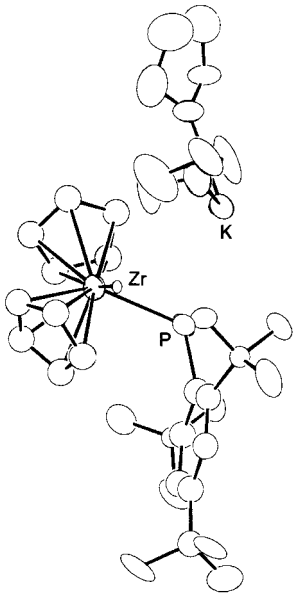
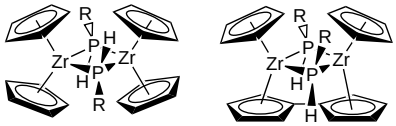


Figure 3. X-ray structure of $[K(thf)_2][Cp_2ZrH(PMes^*)]$ (**42**); reprinted with permission of *Organometallics*, copyright© American Chemical Society 1995.[74]

3.3. P–H Bond Activation

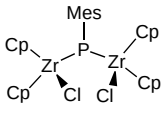
Although the above synthetic strategies proved successful in the interception of a terminal phosphinidene species, alternative routes were sought to more readily gain access to terminal phosphinidene complexes. Oxidative addition of the P–H bonds of primary phosphanes to low-valent Zr compounds was envisioned a proiri as proceeding via a phosphide – hydride intermediate which could lose H_2 to give a Zr phosphinidene moiety. However, experiments revealed that such a view is oversimplified. In fact, the course of the reaction depends both on the zirconium reagent and the phosphane.

Generation of Zr^{II} by the Negishi method with BuLi and reaction with RPH_2 (R = Ph, Cy, $SiPh_3$) affords Zr^{III} phosphanido-bridged dimers of the type **43** and/or **44**.[75] In the case of $(Ph_3Si)PH_2$, in addition to these products, a small amount of the phosphinidene-bridged dimer $[CpZr_2(\mu\text{-PHR})(\mu\text{-PR})(\mu\text{-}C_{10}H_8)]$ was also isolated. It is proposed that these reactions proceed through a mononuclear phosphinidene intermediate which is reduced in the course of C–H or Zr–H bond additions to the Zr–P double bond.[62]



43 **44**

Reduction of $[Cp_2ZrCl_2]$ by Mg in the presence of phosphanes also provides the phosphanido-bridged dimers $[\{Cp_2Zr(\mu\text{-PHR})\}_2]$ (R = Cy, $SiPh_3$). More sterically demanding substituents preclude formation of such Zr^{III} species. For example, use of $MesPH_2$ in the above reaction affords the phosphinidene-bridged complex **45**. However, in the analogous reaction of Mes^*PH_2, P–H, P–C, and C–H bond activation provided the P-capped trimer **46**[74, 76] (Figure 4).



45

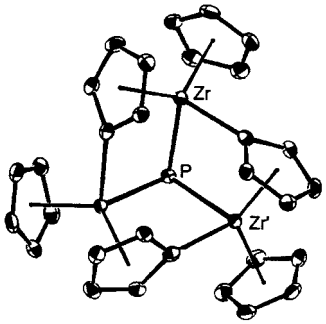
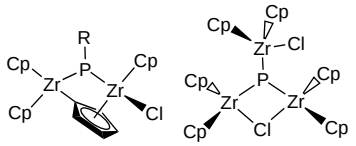


Figure 4. X-ray structure of $[\{CpZr(\mu\text{-}C_5H_4)\}_3(\mu_3\text{-P})]$ (**46**); reprinted with permission of *Organometallics*, copyright© American Chemical Society 1992.[76]

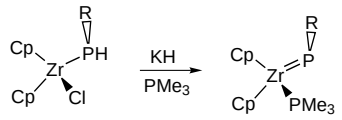
Reduction of $[Cp^*_2ZrCl_2]$ and $[Cp_2ZrCl_2]$ by Mg in the presence of $PhPH_2$ yielded the triphosphanato derivatives $[Cp^*_2Zr(PPhPPhPPh)]$ and $[Cp_2Zr(PPhPPhPPh)]$, respectively.

Schwartz's reagent $[\{Cp_2Zr(H)Cl\}_n]$ reacts with P–H bonds to give a variety of products, depending on the nature of the primary phosphane.[77] The Zr^{III} dimers $[\{Cp_2Zr(\mu\text{-PHR})\}_2]$ and **47** are obtained in relatively low yields from reactions with $PhPH_2$ and Ph_3SiPH_2, respectively. In the case of $MesPH_2$, reaction with $[\{Cp_2Zr(H)Cl\}_n]$ gives the phosphinidene-bridged species **45** directly. Addition of an excess of $[\{Cp_2Zr(H)Cl\}_n]$ to Mes^*PH_2 effects partial reduction and invokes P–C bond cleavage to afford the unusual complex $[\{Cp_2Zr\}_2(\mu_3\text{-P})(\mu_2\text{-Cl})(Cp_2ZrCl)]$ (**48**), in which the central phosphorus atom has planar geometry.[77]



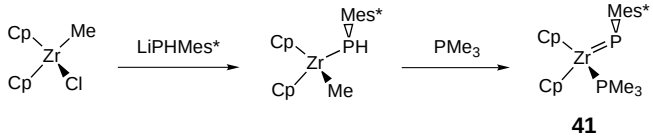
47 **48**

Addition of a base to primary phosphanido complexes is another avenue for exploring P–H reactivity. Treatment of $[Cp_2ZrCl(PHR)]$ (**49**; R = Mes, Mes*) with KH in the presence of PMe_3 invokes P–H bond cleavage and formation of the base-stabilized terminal phosphinidene complexes $[Cp_2Zr(PR)(PMe_3)]$ in approximately 40 % yield.[44] These



49 **41**

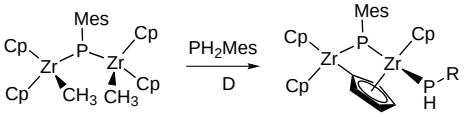
species are reactive, and isolation and complete characterization was only possible for the complex incorporating the Mes* substituent on phosphorus. A preferable route to this complex is the reaction of LiPHMes* with $[Cp_2Zr(Me)Cl]$. The intermediate phosphanido methyl complex gradually loses methane over 12 h at 25 °C in the presence of PMe_3 to provide the terminal phosphinidene complex **41** in quantitative yield.[78]



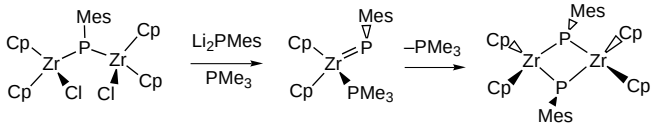
41

The analogous approach with sterically less demanding phosphanides takes an alternative pathway.[11] Reaction of $[Cp_2Zr(Me)Cl]$ with LiPHMes yields $[Cp_2ZrMe(PHMes)]$, which dimerizes with loss of phosphane to give $[(Cp_2ZrMe)_2(\mu\text{-PMes})]$ (**50**). This compound is obtained directly from the thermal reaction of the corresponding phosphane with $[Cp_2ZrMe_2]$. With an additional equivalent of phosphane, **50** undergoes cyclopentadienyl C–H bond activation to give the phosphinidene-bridged complex **51**. The

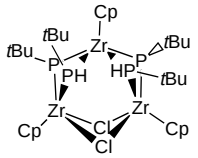
mesityl analogue of **41** is generated from the reaction of **45** with Li_2PMes in the presence of PMe_3, but the product is not isolable, as it loses PMe_3 to give the insoluble phosphinidene-bridged dimer **52**.



50 **51**



45 **52**



53

Recently, Hey-Hawkins et al. extended P–H bond activation to monocyclopentadienyl Zr complexes.[79] Treating LiPH*t*Bu with $[\{CpZrCl_3\}_n]$ results in a redox reaction in which Zr is partially reduced and the phosphanido group is oxidized to $(PHtBu)_2$. Among the products, the phosphinidene derivative **53** was obtained in low yield and crystallographically characterized.

3.4. Reactivity of Zirconium Phosphinidene Complexes

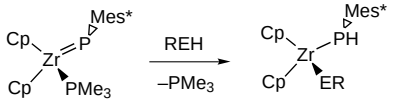
While the reactivity of bridging phosphinidene complexes has received limited attention, the facile, high-yield synthesis of the terminal zirconocene phosphinidene complex **41** permitted a more exhaustive examination of its reactivity. In accord with expectations based on the analogy of terminal Zr phosphinidene moieties to carbenes, such species proved to be highly reactive. Several classes of reactions have been uncovered. In the case of terminal Zr phosphinidene complexes, these reactions demonstrate their viability as synthons for a variety of organophosphorus compounds.

3.5. Protonation and Alkylation

Initial studies on the reactivity of Zr phosphinidene complexes focused on bridging phosphinidene complexes. Protonation and methylation of the dianions $[\{(Cp_2Zr)_2(\mu\text{-}PR)\}_2]^{2-}$ was readily achieved in a stepwise manner to afford the monoanionic and neutral phosphanido-bridged dimers $[(Cp_2Zr)_2(\mu\text{-}PR)(\mu\text{-}PHR)]^-$ and $[\{Cp_2Zr(\mu\text{-}PR'R)\}_2]$ (R′ = H, Me).[62] Protonation of the dianion was reversed by KH, similar to the interconversion of the phosphanido-bridged heterobimetallic complex **35** and the phosphinidene-bridged species **36**.

3.6. Additions to Zr=P Bonds

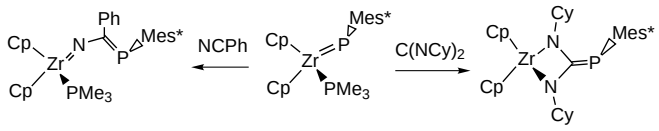
Phenol, thiophenol, aniline, and phosphanes add to **41** to afford complexes of the type **54** (ER = OPh, SPh, NHPh, PHR).[80]



41 **54**

3.7. Insertion Reactions

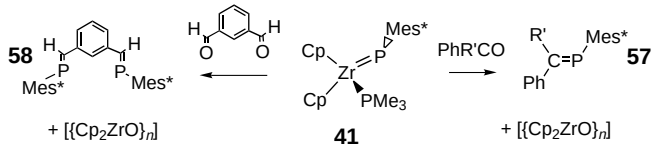
Benzonitrile and dicyclohexylcarbodiimide react with **41**.[78] In the former case, the net result was insertion of the nitrile into the Zr=P bond with intramolecular phosphinidene-group transfer to the C atom of the nitrile to give **55**. The reaction with dicyclohexylcarbodiimide proceeds by cycloaddition and subsequent rearrangement to give **56**. While these reactions are in effect insertions of the substrate between Zr and P, there are also examples of intramolecular phosphinidene group transfer.



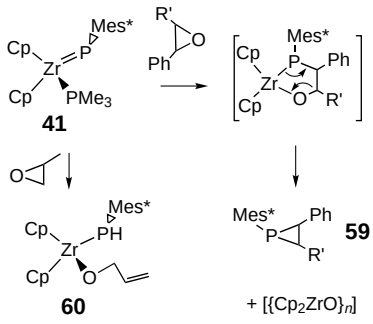
55 **41** **56**

3.8. Phosphinidene Group Transfer Reactions

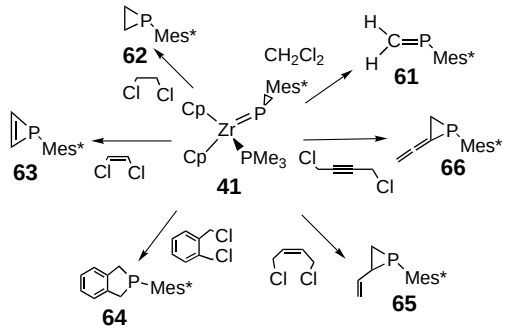
Reaction of **41** with ketones and aldehydes such as benzophenone or benzaldehyde proceeds in a facile manner in THF solution at room temperature.[78] The double-bond metathesis reaction affords the phosphaalkene **57** and the zirconocene oxide $[\{Cp_2ZrO\}_n]$. Separation of the products is simple owing to the insolubility of the zircocene oxide. In a similar manner, this reaction was applied in the synthesis of **58** from $C_6H_4(CHO)_2$. It is noteworthy that while the conventional organic synthesis of this bis-phosphaalkene provides a mixture of the *E* and *Z* isomers, the preparation from **41** affords only the *E* isomer in 86% yield of isolated product. Similar metathesis reactions with phenyl isothiocyanate afford the zirconocene sulfide dimer $[\{Cp_2Zr(\mu\text{-}S)\}_2]$ and the heterophosphaallene PhN=C=PMes*. Again, the insolubility of the Zr by-products makes product isolation simple. A limitation of this approach is demonstrated by the analogous reaction with cyclohexanone. In this case, enolization provides a proton source and results in the formation of the



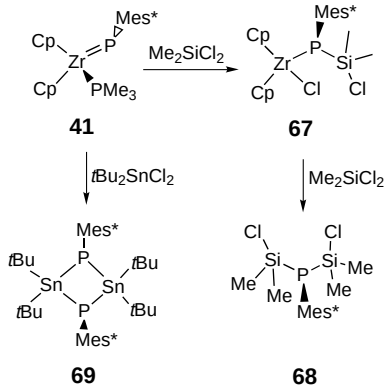
complex $[Cp_2Zr(PHMes^*)(OC_6H_9)]$. A similar situation is also observed in the reactions of **41** with epoxides. Phenyl- and 1,2-diphenyloxirane react cleanly with P/O exchange to give the corresponding phosphirane **59** (R = H, Ph) and zirconocene oxide. In contrast, propylene oxide gives $[Cp_2Zr(PHMes^*)(OC_3H_5)]$ **60** as a result of the existence of an enol form.[78]



Reaction of **41** with *gem* dihalides such as CH_2Cl_2 and $CHCl_3$ also provides access to the corresponding phosphaalkene **61** and H(Cl)C=PMes* with concurrent formation of $[Cp_2ZrCl_2]$.[78] In the case of $CHCl_3$, the *cis* and *trans* isomers of the phosphaalkene were obtained in a 1:2 ratio. This approach also allowed the preparation of the phosphirane **62**, the phosphirene **63**, and the phospholane **64** from the appropriate organic dihalides. In a similar manner, the substituted phosphiranes **65** and **66** were obtained from the analogous reactions of 1,4-dichloro-2-butene and 1,4-dichloro-2-butyne, respectively.[78] It is noteworthy that related substituted phosphiranes have also been recently prepared by acidolysis of bicyclic zirconacyclopentadiene phosphiranes derived from zirconocene-mediated cyclization of dialkynylphosphanes.[81]



Phosphinidene-group transfer to main group elements has also been achieved.[78] The silicon halide Me_2SiCl_2 adds to the phosphinidene complex **41** to give **67**, but this species did not eliminate $[Cp_2ZrCl_2]$ to form a phosphasilene. Instead, **67** reacts with excess Me_2SiCl_2 to yield the disilylphosphane **68**. In contrast, reactions of dialkyl metal dihalides R_2MCl_2 (R = Ge, Sn) or dialkytin sulfides with **41** were employed to prepare $(Me_2MPMes^*)_2$ (M = Ge, Sn) and **69** with the concurrent formation of $[Cp_2ZrCl_2]$ or $[\{Cp_2Zr(\mu\text{-}S)\}_2]$, respectively. Attempts to increase the steric bulk of substituents on Sn to facilitate the formation of a terminal Sn phosphinidene species resulted in no reaction, despite the use of more forcing conditions.

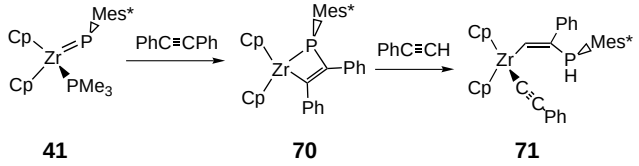


4. Phosphazirconacycles: Synthesis and Reactivity

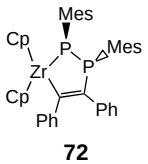
Another approach to reactive Zr–P compounds and thus to a variety of organophosphorus derivatives involves the use of phosphazirconacycles. While we have exploited reactions of Zr phosphinidene complexes to access such compounds, others have utilized reactions of phosphaalkynes and to a lesser extent phosphanylmethanides.

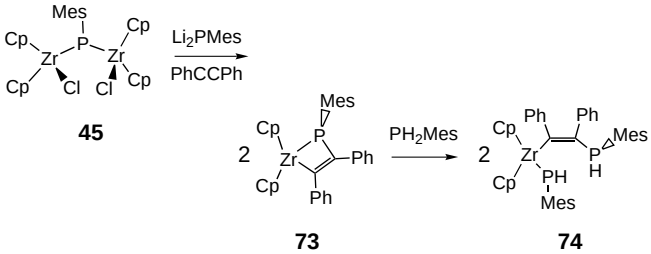
4.1. Cycloadditions to Zr Phosphinidene Complexes

Substituted acetylenes undergo [2+2] cycloadditions with **41** to provide the four-membered metallacycles **70**.[82, 83] These additions are reversible, and hence in the presence of a second acetylene, an equilibrium mixture of the two metallacycles is obtained. Primary acetylenes do not undergo such exchange; instead, they protonate the P atom to give the ring-opened complex **71**.



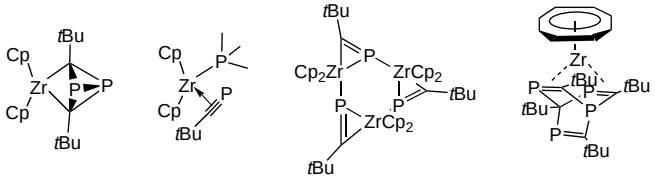
The analogous metallacycle **72** incorporating the sterically less demanding mesityl substituent was obtained from the reaction of $[Cp_2Zr(Me)Cl]$ with LiPHMes in the presence of diphenylacetylene.[82] Complex **73** was synthesized by the reaction of **45** with Li_2PMes in the presence of diphenylacetylene. Subsequent reaction of **73** with $MesPH_2$ effects ring-opening protonation at phosphorus to give **74**.





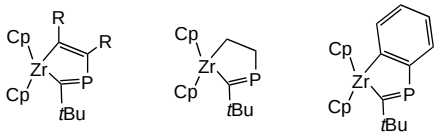
4.2. Phosphaalkyne-Based Metallacycles

The reaction of phosphaalkynes with transition metals has been extensively explored by Binger et al.[84, 85] The first Zr phosphaalkyne derivative **75** was prepared in 1987 by the reaction of $[Cp_2Zr]$ with *t*BuC≡P.[86] Structural characterization revealed the novel bicyclic structure. Binger also described the isolation of **76** and its subsequent reaction with BEt_3 to give the trimeric species **77**.[84] More recently, Binger et al. showed that reaction of $[Zr(cot)_2]$ (cot = cyclooctatetraene) with *t*BuC≡P affords the unusual complex **78**.[87] The



75 **76** **77** **78**

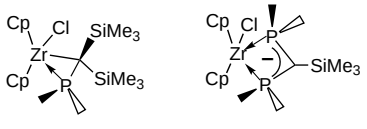
proposed mechanism for the formation of this species involves oxidative coupling, cycloaddition, and 1,2-addition reactions. This view is supported in part by the isolation and characterization of related Ti, Hf, and V complexes.[88–91] Complex **76** also reacts with acetylenes and olefins to give the metallacycles **79** and $[Cp_2\overline{Zr(CH_2CH_2P{=}C}tBu)]$ (**80**). The benzyne complex $[Cp_2Zr(C_6H_4)]$ reacts with phosphaalkyne to give the metallacycle **81**,[92] while Mathey et al. prepared the analogous phosphabenzyne complex.[93]



79 **80** **81**

4.3. Phosphanylmethanido Complexes

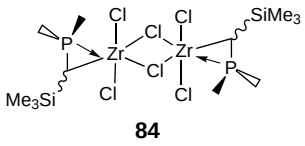
In 1988, Karsch et al. reported that reaction of $[Cp_2ZrCl_2]$ with $Li[C(SiMe_3)_2PMe_2]$ and $Li[CR(PR_2)_2]$ affords **82** and **83**, respectively, with three- and four-membered chelate rings.[94–98] Karsch et al. also reported complexes of the types **84**–**86** and $[ZrCl_2\{C(SiMe_3)_2(PMe_2)\}_2]$, all obtained by reactions of $ZrCl_4$ with phosphanylmethanides.[99]



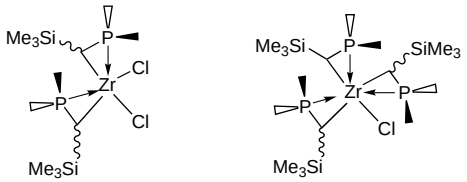
82 **83**

4.4. Reactivity

Phosphazirconacycles exhibit reactivity patterns similar to those of Zr phosphanido complexes. However, such compounds can also act as unique synthetic precursors for novel organophosphorus compounds.



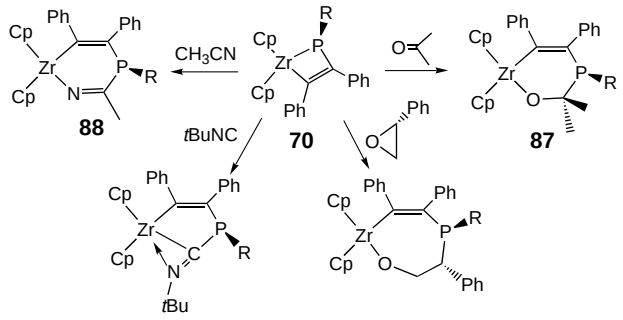
84



85 **86**

4.5. Insertion Reactions

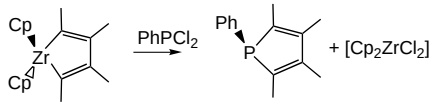
Phosphazirconacycles undergo insertion reactions to effect ring expansion. Ketones, aldehydes, nitriles, isonitriles and epoxides insert into the Zr–P bond of the metallacycles **70**.[82, 83] This expands the ring to five, six, and seven members in complexes such as **87**–**90**. The acetone-insertion product **87** reacts with benzaldehyde to replace acetone with benzaldehyde in the metallacycle. Kinetic data reveal that loss of acetone is the rate-limiting step; this suggests the intermediacy of a zirconocene alkylidene complex that is generated by a retro-[4+2] cycloaddition.



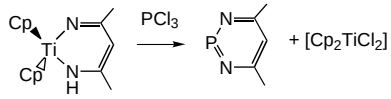
88 **70** **87** **89** **90**

4.6. Metallacycle-Transfer Reactions

Of greater utility from the perspective of organophosphorus chemistry are reactions in which Zr is replaced by other elements. Fagan and Nugent first reported this concept in 1988.[100, 101] By employing the Zr-containing compounds, metallacycle transfer to phosphorus was effected. The reactions of **91** or $[Cp_2Zr(CH_2CMe)_2]$ with $PhPCl_2$ gave the organophosphorus compound **92** and $PhP(CH_2CMe)_2$ in 85 and 67% yield, respectively, with concurrent formation of $[Cp_2ZrCl_2]$. A similar report by Tumas et al. in 1990 described the preparation of phospha- and arsacyclobutenes by reaction of $[Cp_2Ti\{CH_2C(Ph){=}CPh\}]$ with $PhECl_2$ (E = P, As).[102] In the same vein, Mathey et al. recently described the reaction of the Ti-based metallacycle **93** with PCl_3, which yields $[Cp_2TiCl_2]$ and **94**.[103] This methodology has been used in a



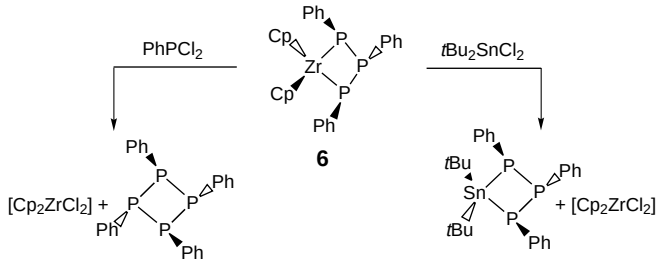
91 **92**



93 **94**

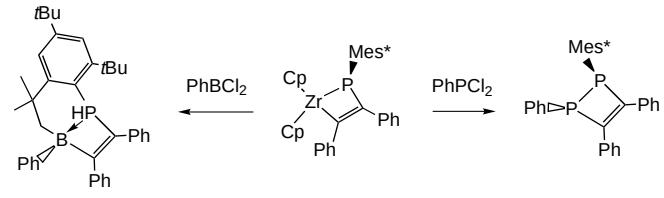
series of elegant preparations of various functionalized diazaphosphinines.

The principle of metal atom replacement can be applied to a variety of phosphazirconacycles as well. The reaction of **6** with $PhPCl_2$ provides a facile route to **95**, whereas reaction with tBu_2SnCl_2 gives **96** cleanly.[104]

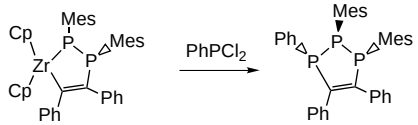


95 **6** **96**

In a similar manner, the metallacycle **70** reacts with $PhBCl_2$ to generate the intermediate phosphaboracyclobutene, which undergoes C–H bond activation to give **97**. The analogous reaction with $PhPCl_2$ gives the diphosphacyclobutene **98**. Similarly, reaction of $PhPCl_2$ with **72** yields the triphosphacyclopentene **99**.[104] These latter two reactions afford rare

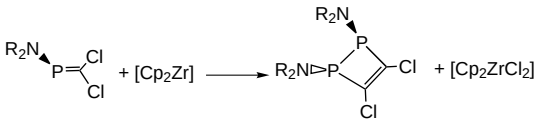


97 **70** **98**



72 **99**

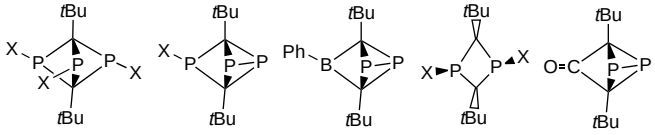
examples of di- and triphosphacycles in which the substituents on phosphorus can be specifically varied. Related 3,4-dihalo-1,2-dihydro-1,2-diphosphetes **100** were prepared by Majoral et al., who used zirconocene to couple dichlorophosphaalkenes.[105] The proposed mechanism involves coordination of the phosphaalkene, oxidative addition of C–Cl, and subsequent elimination of $[Cp_2ZrCl_2]$.



100

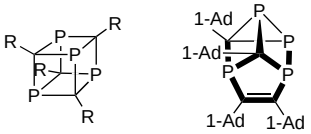
4.7. Reactions of Phosphaalkyne Complexes

Complex **76** is a highly reactive species that acts as a synthon for a number of unusual and unique organophosphorus compounds. In an initial report, reaction with PCl_5 or PBr_3 was shown to give the tricyclic species **101**.[106] In the case of X = Cl the formulation was confirmed by X-ray crystallography. Related reactions affording the cyclic compounds **102** – **104** were also reported.[84] The reaction of $[Cp_2Ti(CO)_2]$ with the phosphaalkyne gave the tricyclic species **105**.[107]



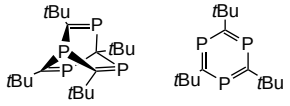
101 **102** **103** **104** **105**

Binger et al. also showed that the reaction of **76** with Cl_3CCCl_3 gives the tetraphosphacubanes $(RCP)_4$ (R = *t*Bu, CMe_2Et, 1-adamantyl (1-Ad)) **106** in 70% yield.[108] With R = adamantyl, the tetracyclic compound **107** was also obtained. Crossover experiments were consistent with the suggestion that the corresponding diphosphetes and their Diels – Alder dimers act as intermediates.[109]

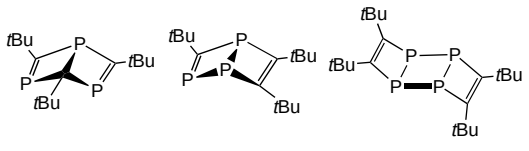


106 **107**

Treatment of **78** with Cl_3CCCl_3 liberates the 1,3,5,7-tetraphosphabarrelene **108**.[87] Related Ti and Hf chemistry affords access to several other novel phosphacycles, including the 1,3,5-triphosphabenzene **109**, the Dewar-1,3,5-triphosphabenzene **110**, the Dewar-1,2,4-triphosphabenzene **111**, and the cyclic dimer of a 1,2-diphosphete **112**.[88]



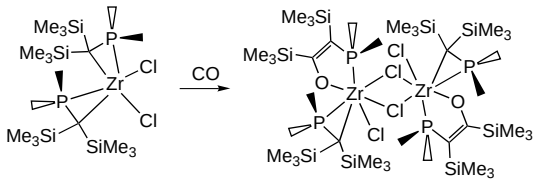
108 **109**



110 **111** **112**

4.8. Reactions of Phosphanylmethanido Complexes

Karsch et al. described the reaction of carbon monoxide with **113**, which is thought to proceed by CO insertion into the Zr–C bond followed by silyl group transfer to give the dimeric complex **114**.[99]

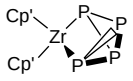


113 **114**

5. Synthesis and Reactivity of Zirconium Complexes Containing Subsituent-Free Phosphorus

5.1. Synthesis

Another class of Zr–P derivatives worthy of investigation are those containing substituent-free phosphorus. Similar to **17**,[110] a variety of complexes containing elemental phosphorus as ligands have been studied extensively by Scherer et al.[111, 112] Oxidative addition of P_4 to $[Cp'_2Zr(CO)_2]$ gave the complexes **115** ($Cp' = Cp^*$, 1,3-tBu$_2$C$_5$H$_3$).[113]



115

The above-mentioned serendipitous preparation of **46** and **48** spurred our own interest in naked-phosphorus compounds of zirconium.[74, 76] Treatment of $[Cp^*_2Zr(PHMes^*)Cl]$ with an excess of KH results in P–C and P–H bond activation.[74, 114] This reaction yields both both paramagnetic and diamagnetic products. The minor product of this reaction is the paramagnetic complex **116** (Figure 5).[114] This mixed-valent dimer

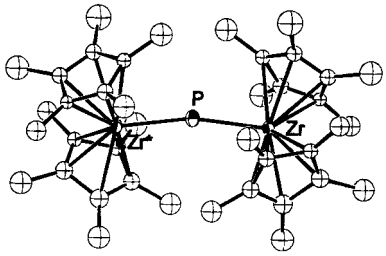


Figure 5. X-ray structure of $[\{Cp^*_2Zr\}_2(\mu\text{-P})]$ (**116**); reprinted with permission of *Organometallics*, copyright© American Chemical Society 1995.[74]

contains two Zr centers which are linearly bridged by a single phosphorus atom. The major diamagnetic product was formulated as **117** on the basis of spectroscopic, mass spectrometric, and analytical data. This formulation was supported by an alternative synthesis: Reaction of $[\{Cp^*_2Zr(N_2)\}_2(\mu\text{-}N_2)]$ with an excess of Mes*PH_2 proceeds smoothly with P–H and C–H activation to give **118** in high yield. This complex can be deprotonated with KH to give **119**, which reacts with $[Cp^*_2ZrCl_2]$ to give **117**. It is noteworthy that reaction of **117** with excess phosphane and KH results in further incorporation of substituent-free phosphorus atoms and formation of **120** (Figure 6). This species forms an infinite ladder structure of P and bridging K atoms in the solid state.[74, 114]

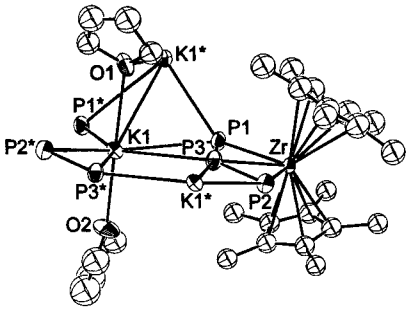
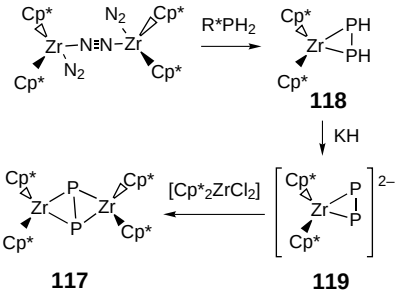
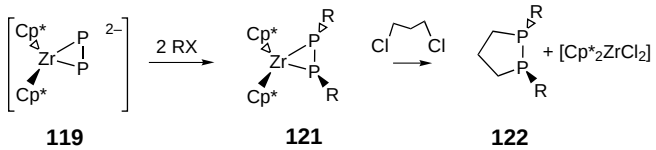


Figure 6. X-ray structure of $[K(thf)_{1.5}][Cp^*_2Zr(P_3)]$ (**120**); reprinted with permission of *Organometallics*, copyright© American Chemical Society 1995.[74]



5.2. Reactivity

The reactivity of Zr complexes with substituent-free phosphorus ligands has received only limited attention. They can be viewed as synthons for organophosphorus compounds for which no limitations are imposed by initially present substituents. Thus, one can contemplate a series of reactions in which desired substituents are introduced sequentially. In preliminary studies, we have explored the reactions of **119**.[115] This compound reacts stoichiometrically with two equivalents of alkyl halides such as benzyl chloride or cyclohexyl chloride to yield complexes of the type **121**. Subsequent reaction with dichloropropane yields cyclic diphosphanes **122** and $[Cp^*_2ZrCl_2]$.



119 **121** **122**

6. Catalytic Dehydrocoupling Reactions

In 1995, we reported the synthesis of the novel potassium salt of the zirconocene trihydride anion.[116] Subsequently, the efficient and almost quantitative synthesis of the Li

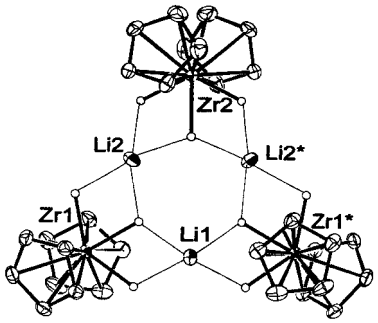
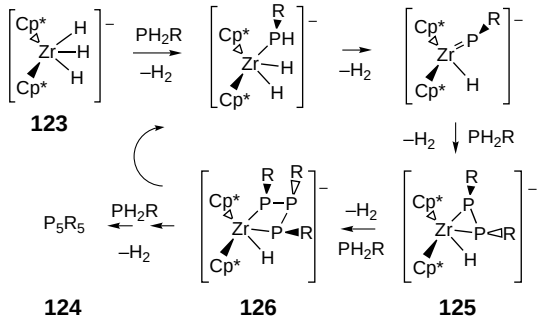
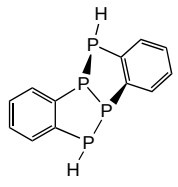


Figure 7. X-ray structure of the lithium salt of $[Cp^*_2ZrH_3]^-$ (**123**); reprinted with permission of *J. Am. Chem. Soc.*, copyright© American Chemical Society 1997.[117]

analogue **123** was reported (Figure 7).[117] The presence of 1% of this compound was found to effect the catalytic dehydrocoupling of primary phosphanes at 80–100 °C for 24 h to give **124**. Stoichiometric reactions of **123** with phosphanes led to the isolation of the complexes **125** and **126**; this implies the intermediacy of these species in the catalytic cycle. In addition, transient spectroscopic data and the previous characterization of **42** were consistent with the formation of a phosphinidene hydride complex anion intermediate.[74] These data led to a proposal for the initial steps of the catalysis. The steps between the triphosphanato anion and the products remain to be elucidated. Further insertion or alternatively thermal degradation of **126** to $(PR)_3$ and thermal reorganization have been proposed as subsequent steps in the formation of **124**.



The catalytic oligomerization of 1,2-diphosphanylbenzene by 1% of **123** was also examined.[118] Quenching of the reaction after only 30 min revealed the formation of **127**. Allowing the catalysis to continue for 12 h led to complete dehydrocoupling and formation of the macrocycle **128** (Figure 8), which contains 16 phosphorus atoms in a contiguous ring of P–P bonds. Stoichiometric reactions of 1,2-diphosphanylbenzene and **123** lead first to the chelate anion **129** and subsequently **130**. The minor product **131** was obtained upon thermolysis of **130**. Crystallographic studies showed that this dianionic complex **131** contains a $[C_6H_4(P)_2]_4$ macrocycle that encircles two Cp*Zr fragments. The role, if any, of this species in the reaction and the mechanistic details of the catalytic cycle are currently under study.



127

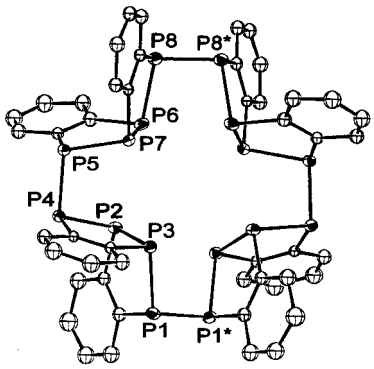
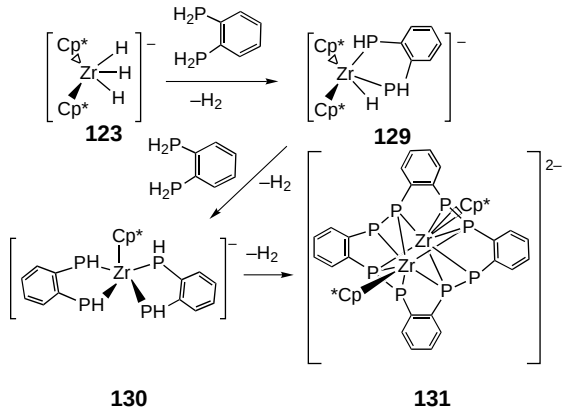


Figure 8. X-ray structure of $[C_6H_4(P)_2]_8$ (**128**); reprinted with permission of *J. Am. Chem. Soc.*, copyright© American Chemical Society 1997.[118]



In related work, Harrod et al. recently reported the catalytic dehydrocoupling of phosphanes by $[Cp_2TiMe_2]$ in the presence of silanes gives mixtures of linear and cyclic oligophosphanes.[119] More recently, they exploited these systems to effect catalytic cross-coupling of phosphanes and silanes to give RR′HSi(PRR″) and RR′Si(PRR″)$_2$ in facile one-pot syntheses.[120]

7. Summary and Outlook

In the past two decades Zr–P chemistry has gone from being virtually unexplored to the point where a large variety of Zr–P compounds have been prepared and their basic reactivity patterns characterized. A number of these species, including Zr phosphinidene complexes, phosphazirconacycles, Zr phosphaalkyne complexes, and Zr complexes with substituent-free phosphorus ligands have proved to be useful in stoichiometric syntheses of organophosphorus compounds. Moreover, catalytic syntheses of polyphosphanes and silylphosphanes are being developed on the basis of catalytic dehydrocoupling.

In the continuing development of Zr–P chemistry, there are a number of avenues worthy of pursuit. Clearly, there is considerable latitude for the development of new Zr–P reagents for syntheses of novel organophosphorus compounds. Aspects of stereochemistry, in particular chirality at phosphorus, have yet to be addressed, yet the use of optically active Zr reagents is of major interest in stereospecific

polymerization chemistry. Elaboration of the catalytic syntheses with Zr catalysts potentially offers new routes to a wider variety of novel phosphorus compounds. Moreover, unprecedented oligomers and polymers containing phosphorus may provide unique new materials. While metal-mediated syntheses of main group compounds in general terms has only begun to be uncovered, the chemistry of Zr–P compounds stands out as a subset that richly illustrates this potential.

Received: September 22, 1998
Revised: January 28, 1999 [A 304]

[1] E. Hey-Hawkins, *Chem. Rev.* **1994**, *94*, 1661.
[2] K. Issleib, H. Häckert, *Z. Naturforsch. B* **1966**, *21*, 519.
[3] J. Ellerman, P. Poersch, *Angew. Chem.* **1967**, *79*, 380; *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 355.
[4] R. T. Baker, J. F. Whitney, S. S. Wreford, *Organometallics* **1983**, *2*, 1049.
[5] R. T. Baker, P. J. Krusic, T. H. Tulip, J. C. Calabrese, S. S. Wreford, *J. Am. Chem. Soc.* **1983**, *105*, 6763.
[6] G. A. Vaughan, G. L. Hillhouse, *Organometallics* **1989**, *8*, 1760.
[7] L. Weber, G. Meine, R. Boese, N. Augart, *Organometallics* **1987**, *6*, 2484.
[8] F. Lindenberg, E. Hey-Hawkins, *J. Organomet. Chem.* **1992**, *435*, 291.
[9] E. Hey-Hawkins, S. Kurz, G. Baum, *Z. Naturforsch. B* **1995**, *50*, 239.
[10] S. Kurz, E. Hey-Hawkins, *J. Organomet. Chem.* **1994**, *479*, 125.
[11] T. L. Breen, D. W. Stephan, *Organometallics* **1996**, *15*, 4509.
[12] R. Bohra, P. B. Hitchcock, M. F. Lappert, W.-P. Leung, *J. Chem. Soc. Chem. Commun.* **1989**, 728.
[13] H. Kopf, V. Richtering, *J. Organomet. Chem.* **1988**, *346*, 355.
[14] E. Hey, *J. Organomet. Chem.* **1989**, *378*, 375.
[15] M. Y. Chiang, S. Gambarotta, F. Von Bohuis, *Organometallics* **1988**, *7*, 1864.
[16] D. G. Dick, D. W. Stephan, *Can. J. Chem.* **1991**, *69*, 1146.
[17] E. Hey-Hawkins, S. Kurz, J. Sieler, G. Baum, *J. Organomet. Chem.* **1995**, *486*, 229.
[18] B. Benard, M. M. Rohmer, *J. Am. Chem. Soc.* **1992**, *114*, 4785.
[19] M.-M. Rohmer, M. Benard, *Orgaometallics* **1991**, *10*, 157.
[20] R. L. Dekock, M. A. Peterson, L. E. L. Reynolds, L.-H. Chen, E. J. Baerends, P. Vernooijs, *Organometallics* **1993**, *12*, 2794.
[21] K. Issleib, F. Krech, *Angew. Chem.* **1972**, *84*, 582; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 527.
[22] H. Kopf, R. Voigtlander, *Chem. Ber.* **1981**, *114*, 2731.
[23] E. Hey, S. G. Bott, J. L. Atwood, *Chem. Ber.* **1988**, *121*, 561.
[24] J. Ho, T. L. Breen, A. Ozarowski, D. W. Stephan, *Inorg. Chem.* **1994**, *33*, 865.
[25] K. Fromm, G. Baum, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* **1992**, *615*, 35.
[26] E. Hey, *Z. Naturforsch. B.* **1988**, *43*, 1271.
[27] B. L. Benac, R. A. Jones, *Polyhedron* **1989**, *8*, 1774.
[28] S. Kurz, E. Hey-Hawkins, *J. Organomet. Chem.* **1993**, *462*, 203.
[29] S. Nielsen-Marsh, R. J. Crowte, P. G. Edwards, *J. Chem. Soc. Chem. Commun.* **1992**, 699.
[30] S. R. Wade, M. G. H. Wallbridge, G. R. Willey, *J. Chem. Soc. Dalton Trans.* **1983**, 2555.
[31] F. Lindenberg, E. Hey-Hawkins, G. Baum, *Z. Naturforsch. B* **1995**, *50*, 1359.
[32] L. Gelmini, D. W. Stephan, *Organometallics* **1987**, *6*, 1515.
[33] E. Hey, M. F. Lappert, J. L. Atwood, S. G. Bott, *J. Chem. Soc. Chem. Commun.* **1987**, 421.
[34] E. Hey, M. F. Lappert, J. L. Atwood, S. G. Bott, *Polyhedron* **1988**, *7*, 2083.
[35] E. Hey-Hawkins, F. Lindenberg, *Z. Naturforsch. B* **1993**, *48*, 951.
[36] E. Hey, M. F. Lappert, J. L. Attwood, S. G. Bott, *J. Chem. Soc. Chem. Commun.* **1987**, 597.
[37] E. Hey-Hawkins, M. F. Lappert, J. L. Atwood, S. G. Bott, *J. Chem. Soc. Dalton Trans* **1991**, 939.
[38] U. Segerer, E. Hey-Hawkins, *Polyhedron* **1997**, *16*, 2537.
[39] E. Hey, U. Muller, *Z. Naturforsch. B* **1989**, *44*, 1538.
[40] F. Lindenberg, J. Sieler, E. Hey-Hawkins, *Polyhedron* **1996**, *15*, 1459.
[41] E. Hey-Hawkins, F. Lindenberg, *Chem. Ber.* **1992**, *125*, 1815.
[42] F. Lindenberg, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1531.
[43] Z. Hou, D. W. Stephan, *J. Am. Chem. Soc.* **1992**, *114*, 10088.
[44] Z. Hou, T. L. Breen, D. W. Stephan, *Organometallics* **1993**, *12*, 3158.
[45] E. Hey, F. Weller, *Chem. Ber.* **1988**, *121*, 1207.
[46] D. W. Stephan, *Coord. Chem. Rev.* **1989**, *95*, 41.
[47] G. Johannesen, O. Stelzer, *Chem. Ber.* **1977**, *110*, 3438.
[48] O. Stelzer, E. Unger, *Chem. Ber.* **1977**, *110*, 3430.
[49] L. Gelmini, L. C. Matassa, D. W. Stephan, *Inorg. Chem.* **1985**, *24*, 2585.
[50] M. G. B. Drew, S. R. Wade, M. G. H. Wallbridge, G. R. Willey, *J. Chem. Soc. Dalton Trans.* **1986**, 713.
[51] T. S. Targos, R. P. Rosen, R. R. Whittle, G. L. Geoffroy, *Inorg. Chem.* **1985**, *24*, 1375.
[52] R. T. Baker, T. H. Tulip, S. S. Wreford, *Inorg. Chem.* **1985**, *24*, 1379.
[53] S. A. Yousif-Ross, A. Wojicki, *Inorg. Chim. Acta* **1990**, *171*, 115.
[54] L. Gelmini, D. W. Stephan, *Inorg. Chim. Acta* **1986**, *111*, L17.
[55] L. Gelmini, D. W. Stephan, *Inorg. Chem.* **1986**, *25*, 1222.
[56] R. T. Baker, W. C. Fultz, T. B. Marder, I. D. Williams, *Organometallics* **1990**, *9*, 2357.
[57] R. T. Baker, , T. H. Tlip, *Organometallics* **1986**, *5*, 839.
[58] L. Gelmini, D. W. Stephan, *Organometallics* **1988**, *7*, 849.
[59] P. Y. Zheng, D. W. Stephan, *Can. J. Chem.* **1989**, *67*, 1584.
[60] P. Y. Zheng, T. T. Nadasdi, D. W. Stephan, *Organometallics* **1989**, *8*, 1393.
[61] D. G. Dick, D. W. Stephan, *Organometallics* **1990**, *9*, 1910.
[62] J. Ho, Z. Hou, R. J. Drake, D. W. Stephan, *Organometallics* **1993**, *12*, 3145.
[63] F. Lindenberg, T. Shribman, J. Sieler, E. Hey-Hawkins, M. S. Eisen, *J. Organomet. Chem.* **1996**, *515*, 19.
[64] F. Lindenberg, T. Gelbrich, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* **1995**, *621*, 771.
[65] U. Senff, S. Kurz, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1255.
[66] T. Shribman, S. Kurz, U. Senff, F. Lindenberg, E. Hey-Hawkins, M. S. Eisen, *J. Mol. Catal.* **1998**, *129*, 191.
[67] P. B. Hitchcock, M. F. Lappert, W. P. Leung, *J. Chem. Soc. Chem. Commun.* **1987**, 1282.
[68] A. H. Cowley, R. L. Geerts, C. M. Nunn, *J. Am. Chem. Soc.* **1987**, *109*, 6523.
[69] C. C. Cummins, R. R. Schrock, W. M. Davis, *Angew. Chem.* **1993**, *105*, 758; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 756.
[70] J. B. Bonanno, P. T. Wolczanski, E. B. Lobkovski, *J. Am. Chem. Soc.* **1994**, *116*, 11159.
[71] A. M. Arif, A. H. Cowley, C. M. Nunn, M. Pakalski, *J. Chem. Soc. Chem. Commun.* **1987**, 994.
[72] J. Ho, R. J. Drake, D. W. Stephan, *J. Am. Chem. Soc.* **1993**, *115*, 3792.
[73] T. A. Bazhenova, A. V. Kulikov, A. F. Shestakov, A. E. Shilov, M. Y. Antipin, K. A. Lyssenko, Y. T. Struchkov, V. D. Makhaev, *J. Am. Chem. Soc.* **1995**, *117*, 12176.
[74] M. C. Fermin, J. Ho, D. W. Stephan, *Organometallics* **1995**, *14*, 4247.
[75] J. Ho, D. W. Stephan, *Organometallics*, **1991**, *10*, 3001.
[76] J. Ho, D. W. Stephan, *Organometallics* **1992**, *11*, 1014.
[77] J. Ho, R. Rousseau, D. W. Stephan, *Organometallics* **1994**, *12*, 1918.
[78] T. L. Breen, D. W. Stephan, *J. Am. Chem. Soc.* **1995**, *117*, 11914.
[79] C. Frenzel, E. Hey-Hawkins, U. Muller, I. Strenger, *Z. Anorg. Allg. Chem.* **1997**, *623*, 277.
[80] T. L. Breen, D. W. Stephan, *Organometallics* **1997**, *16*, 365.
[81] A. Mahieu, Y. Miquel, A. Igau, B. Donnadieu, J.-P. Majoral, *Organometallics* **1997**, *16*, 3086.
[82] T. L. Breen, D. W. Stephan, *Organometallics* **1996**, *15*, 5729.
[83] T. L. Breen, D. W. Stephan, *J. Am. Chem. Soc.* **1996**, *118*, 4204.
[84] P. Binger in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, New York, **1990**, p. 90.

[85] P. Binger, B. Biedenbach, A. T. Herrmann, F. Langhauser, P. Betz, R. Goddard, C. Krüger, *Chem. Ber.* **1990**, *123*, 1617.
[86] P. Binger, B. Biedenbach, C. Krüger, M. Regitz, *Angew. Chem.* **1987**, *99*, 798; *Angew. Chem. Int. Ed.* **1987**, *26*, 764.
[87] P. Binger, G. Glaser, B. Gabor, R. Mynott, *Angew. Chem.* **1995**, *107*, 114. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 81.
[88] P. Binger, G. Glaser, S. Albus, C. Krüger, *Chem. Ber.* **1995**, *128*, 1261.
[89] R. Milczarek, W. Rüsseler, P. Binger, K. Jonas, K. Angermund, C. Krüger, M. Regitz, *Angew. Chem.* **1987**, *99*, 957; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 908.
[90] P. Binger, S. Leininger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann, C. Krüger, *Angew. Chem.* **1995**, *107*, 2411; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2227.
[91] P. Binger, S. Leininger, K. Günther, U. Bergstrasser, *Chem. Ber.* **1997**, *130*, 1491.
[92] P. Binger, R. Biedenbach, M. Mynott, M. Regitz, *Chem. Ber.* **1988**, *121*, 1455.
[93] P. Rosa, P. Le Floch, L. Ricard, F. Mathey, *J. Am. Chem. Soc.* **1997**, *119*, 9417.
[94] H. H. Karsch, B. Deubelly, J. Hofmann, U. Pieper, G. Muller, *J. Am. Chem. Soc.* **1988**, *110*, 3654.
[95] N. E. Schore, S. J. Young, M. M. Olmstead, P. Hofmann, *Organometallics* **1983**, *2*, 1769.
[96] N. E. Schore, H. Hope, *J. Am. Chem. Soc.* **1980**, *102*, 4251.
[97] H. H. Karsch, B. Duebelly, G. Grauvogl, J. Lachmann, G. Muller, *Organometallics* **1992**, *11*, 4245.
[98] H. H. Karsch, G. Grauvogl, B. Duebelly, G. Muller, *Organometallics* **1992**, *11*, 4238.
[99] H. H. Karsch, G. Grauvogl, M. Kawecki, P. Bissinger, O. Kumberger, A. Schier, U. Muller, *Organometallics* **1994**, *13*, 610.
[100] P. J. Fagan, W. A. Nugent, *J. Am. Chem. Soc.* **1988**, *110*, 2310.
[101] P. J. Fagan, W. A. Nugent, J. C. Calabrese, *J. Am. Chem. Soc.* **1994**, *116*, 1880.
[102] W. Tumas, J. A. Suriano, R. L. Harlow, *Angew. Chem.* **1990**, *102*, 89; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 75.
[103] N. Avarvari, P. Le Floch, L. Ricard, F. Mathey, *Organometallics* **1997**, *16*, 4089.
[104] T. L. Breen, D. W. Stephan, *Organometallics* **1997**, *16*, 365.
[105] N. Cenac, A. Chrostowska, J.-M. Sotiropoulos, B. Donnadieu, A. Igau, G. Pfister-Guillouzo, J.-P. Majoral, *Organometallics* **1997**, *16*, 4551.
[106] P. Binger, T. Wettling, R. Schneider, F. Zurmuhlen, U. Bergstrasser, J. Hoffmann, G. Maas, M. Regitz, *Angew. Chem.* **1988**, *100*, 873; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 207.
[107] A. Barron, A. H. Cowley, S. W. Hall, C. N. Nunn, *Angew. Chem.* **1988**, *100*, 873; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 837.
[108] T. Wettling, B. Geissler, R. Schneider, S. Barth, P. Binger, M. Regitz, *Angew. Chem.* **1992**, *104*, 761; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 758.
[109] B. Geissler, T. Wettling, S. Barth, P. Binger, M. Regitz, *Synthesis* **1994**, 1337.
[110] E. Hey, M. F. Lappert, J. L. Attwood, S. G. Bott, *J. Chem. Soc. Chem. Commun.* **1987**, 421.
[111] O. J. Scherer, *Comments Inorg. Chem.* **1987**, *6*, 1.
[112] O. J. Scherer, *Angew. Chem.* **1990**, *102*, 1137; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1104.
[113] O. J. Scherer, M. Swarowsky, H. Swarowsky, G. Wolmershauser, *Angew. Chem.* **1988**, *100*, 738. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 694.
[114] M. C. Fermin, J. Ho, D. W. Stephan, *J. Am. Chem. Soc.* **1994**, *116*, 6033.
[115] D. W. Stephan, unpublished results.
[116] M. C. Fermin, D. W. Stephan, *J. Am. Chem. Soc.* **1995**, *117*, 12645.
[117] N. Etkin, A. J. Hoskin, D. W. Stephan, *J. Am. Chem. Soc.* **1997**, *119*, 11420.
[118] N. Etkin, M. C. Fermin, D. W. Stephan, *J. Am. Chem. Soc.* **1997**, *119*, 2954.
[119] S. Xin, H. G. Woo, J. F. Harrod, E. Samuel, A. M. Lebuis, *J. Am. Chem. Soc.* **1997**, *119*, 5307.
[120] R. Shu, L. Hao, J. F. Harrod, H.-G. Woo, E. Samuel, *J. Am. Chem. Soc.* **1998**, *120*, 12988.