Hydro- and Carbozirconation of Multiple-Bonded Low-Coordinated Phosphorus Species

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Hydrozirconation of phosphaimines RP=NR′ (**2a–c**) (**2a**, R = $N(SiMe_3)_2$, R′ = $SiMe_3$; **2b**, R = N(SiMe$_3$)(tBu), R′ = tBu; **2c**, R = tetramethylpiperidino, R′ = $SiMe_3$), phosphaalkene $(Me_3Si)_2NP{=}C(H)SiMe_3$ (**17**), or bis(imino)phosphorane $(Me_3Si)_2NP(=NSiMe_3)_2$ (**30**) by means of Cp_2ZrHCl takes place with the formation either of the three-membered rings zirconaazaphosphirane $Cp_2Zr(Cl)N(R')P(H)R$ (**3a–c**) and zirconaphosphirane $Cp_2Zr(Cl)C(H)(SiMe_3)P(H)N(SiMe_3)_2$ (**18**) or the four-membered ring zirconadiazaphosphetidine $Cp_2Zr(Cl)N(SiMe_3)P(H)[N(SiMe_3)_2]N(SiMe_3)$ (**31**). Similarly, carbozirconation of phosphaimine **2a** leads to the zirconaazaphosphirane $Cp_2Zr(Me)N(SiMe_3)P(Me)N(SiMe_3)_2$ (**7**). On the other hand, hydrozirconation of **2a** with Cp_2ZrH_2 or hydrozirconation of the thioiminophosphorane Me$_3$Si(tBu)NP(=S)(=NtBu) (**13**) gives rise respectively to the acyclic phosphine $(Me_3Si)_2NP(H)NHSiMe_3$ (**6**) or to the acyclic phosphine sulfide Me$_3$Si(tBu)NP(S)HN(H)tBu (**10b**). Addition of Cp_2ZrHCl to the chlorophosphaalkene $ClP{=}C(SiMe_3)_2$ (**19**) affords the diphosphene $(Me_3Si)_2CHP{=}PCH(SiMe_3)_2$ (**20**) and the diphosphirane $(Me_3Si)_2CHPC(SiMe_3)_2PH$ (**21**). An easy hydride–chlorine exchange involving Cp_2ZrHCl and free or complexed halogenated phosphines is observed and allows obtention of the corresponding P–H phosphines. Ligand exchange occurs when the zirconaphosphirane **18** is treated either with the phosphaimine **2a** or the bis(imino)phosphorane **30**, leading to the zirconaazaphosphirane **3a** or the zirconadiazaphosphetidine **31**, respectively. Synthesis of stable cationic cyclic zirconium species, the zirconaazaphosphirane cations $[(CH_3C{\equiv}N)Cp_2ZrN(SiMe_3)P(H)[N(SiMe_3)_2][X]$ (**15, 16**) (**15**, X = CF_3SO_3; **16**, X = BPh_4) or the zirconadiazaphosphetidine cation $[(CH_3C{\equiv}N)Cp_2ZrN(SiMe_3)P(H)[N(SiMe_3)_2]N(SiMe_3)][CF_3SO_3]$ (**38**), involving dissociation of a covalent zirconium–oxygen bond, are also reported.

Introduction

The chemistry of the group 4 metals in their higher oxidation states is characterized by their propensity to form strong bonds with hard donor atoms such as chlorine, fluorine, oxygen, or nitrogen. These strong metal–heteroatom interactions are often the driving force for many reactions involving compounds containing oxygen or nitrogen. Hydrozirconation, by means of Cp_2ZrHCl or Cp_2ZrH_2, of unsaturated organic species is also well-known and can be compared to hydroboration with alkylboranes.

As we have a longstanding interest both in the chemistry of unsaturated main group element species[1] and in the behavior of anionic or neutral metallic hydrides,[2] it appeared extremely interesting to explore the reactivity of zirconium derivatives such as Cp_2ZrHCl, Cp_2ZrH_2, or Cp_2ZrMe_2 toward halogenated or nonhalogenated low-coordinated phosphorus species such as iminophosphanes RP=NR′, phosphaalkenes RP=CR′$_2$, or bis(imino)-phosphoranes RP(=NR′)$_2$.

Such a study was of potential interest for several reasons. In particular we wished to know whether the presence of $\lambda^2\sigma^3$- or $\lambda^3\sigma^5$-phosphorus (λ = coordination number; σ = valency for phosphorus) facilitates the hydrozirconation and eventually the carbozirconation and allows the formation of small rings possessing phosphorus–zirconium dative bonds. A few three-membered rings[3] including in one case a phosphorus–carbon–zirconium ring[4] have been prepared so far, but none of the reported experiments involved Cp_2ZrHCl or Cp_2ZrMe_2 and low-coordinated heavier main-group elements. In our case, the polarity of phosphorus–nitrogen or phosphorus–carbon double bonds would play a key role.

We also wanted to know whether it is possible to take advantage of the high halophilicity of zirconium to initiate hydride–halogen exchange and therefore to prepare phosphorus derivatives difficult to obtain via classical reactions.

Last, it was also of interest to check whether the presence of phosphorus–zirconium or nitrogen–zirconium bonds makes easier to a certain extent the dissociation of the strong zirconium–chlorine or zirconium–oxygen bonds and helps in the stabilization of new cationic zirconium derivatives.

In previous communications,[5] we have reported a simple quantitative preparation of zirconaazaphosphiranes and zirconaphosphiranes and some preliminary results concerning the reactivity of these derivatives.

(1) See for example: Roques, C.; Mazières, M. R.; Majoral, J.-P.; Sanchez, M.; Foucaud, A. *Organometallics* **1989**, *54*, 5535. Majoral, J.-P.; Roques, C.; Mazières, M. R.; Jaud, J.; Sanchez, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1496. Dufour, N.; Caminade, A.-M.; Majoral, J.-P. *Tetrahedron Lett.* **1989**, *30*, 4813. Caminade, A.-M.; Roques, C.; Dufour, N.; Colombo, D.; Gonce, F.; Majoral, J.-P. *Tetrahedron Lett.* **1989**, *30*, 6869. Bertrand, G.; Majoral, J.-P.; Baceiredo, A. *Acc. Chem. Res.* **1986**, *19*, 17 and references therein.

(2) See for example: Attali, S.; Dahan, F.; Mathieu, R.; Caminade, A.-M.; Majoral, J.-P. *J. Am. Chem. Soc.* **1988**, *110*, 1990. Galindo del Pozo, A.; Caminade, A.-M.; Mathieu, R.; Majoral, J.-P. *J.Chem. Soc., Chem. Commun.* **1988**, 574. Caminade, A.-M.; Majoral, J.-P.; Sanchez, M.; Mathieu, R.; Attali, S.; Grand, A. *Organometallics* **1987**, *6*, 1459. Mathieu, R.; Caminade, A.-M.; Majoral, J.-P.; Daran, C. *J. Am. Chem. Soc.* **1986**, *108*, 8007 and references therein.

(3) See for example: Nigishi, E.; Takamashi, T. *Synthesis* **1988**, 1.1. Erker, G.; Schlund, R.; Krüger, C. *Organometallics* **1989**, *8*, 2349. Buchwald, S. L.; Wannamaker, M. W.; Watson, B. T. *J. Am. Chem. Soc.* **1989**, *111*, 776. Hey, E.; Müller, U. Z. *Naturforsch* **1989**, *44B*, 1538. Erker, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 397 and references therein.

(4) Karsch, H. H.; Denbelly, B.; Hofmann, J.; Pieper, U.; Müller, G. *J. Am. Chem. Soc.* **1988**, *110*, 3654.

(5) (a) Majoral, J.-P.; Dufour, N.; Meyer, F.; Caminade, A.-M.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1990**, 507. (b) Dufour, N.; Majoral, J.-P.; Caminade, A.-M.; Choukroun, R.; Dromzee, Y. *Organometallics* **1991**, *10*, 45.

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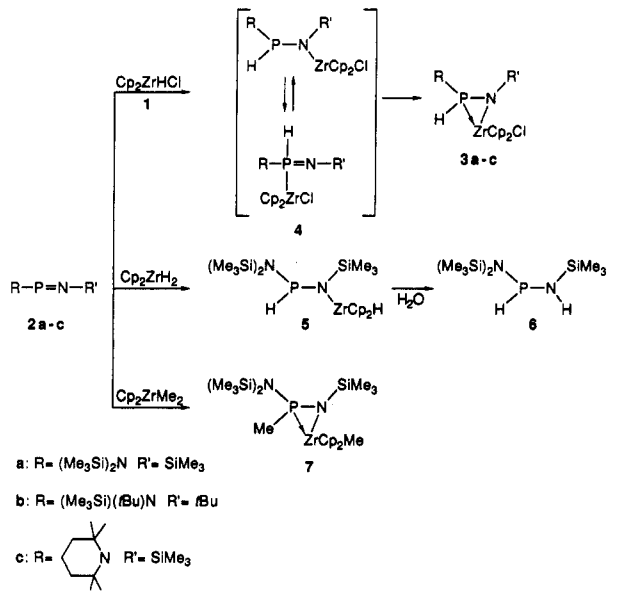
Scheme I



Herein we describe full details of this work as well as the following: (i) the preparation of new cationic zirconium phosphorus cyclic compounds, (ii) the first example of carbozirconation of dicoordinated phosphorus species, (iii) the direct transformation of zirconaphosphirane **18** to zirconaazaphosphirane **3a** or zirconadiazaphosphetidine **31** involving an unusual ligand exchange, and (iv) the easy hydride–chlorine exchange involving Cp_2ZrHCl and free or complexed halogenated phosphines.

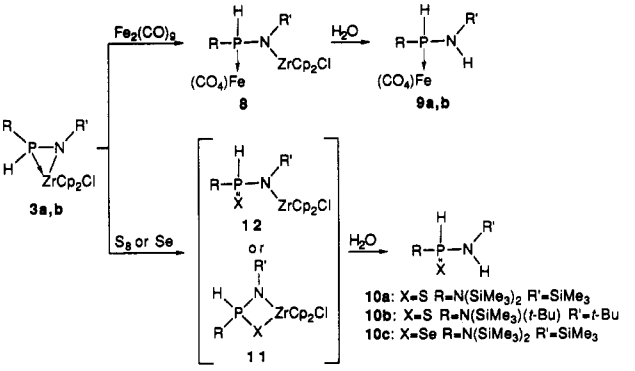
Results and Discussion

Addition of the hydride Cp_2ZrHCl (**1**) to a THF solution of phosphaimines **2a–c** at 0 °C afforded in nearly quantitative yield the zirconaazaphosphiranes **3a,b** (two isomers due to the presence of two different substituents on the exocyclic nitrogen atom) or **3c** (Scheme I), fully characterized by NMR, IR, and mass spectrometry (see Experimental Section) and in one case (**3a**) by single-crystal X-ray diffraction studies.[5b]

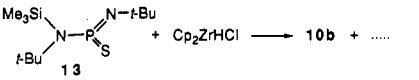
A 1-2 addition of Cp_2ZrHCl to the phosphorus nitrogen double bond of **2a–c** followed by cyclization is a reasonable postulation to explain the formation of these derivatives although an insertion of the phosphaimine into a Zr–H bond with transient formation of a metallaiminophosphorane $RP(H)(ZrCp_2Cl)=NR'$ (**4**) cannot be totally ruled out. Nevertheless no example of such a metallaphosphorane has been reported so far.

Such a cyclization was not observed when the phosphaimine **2a** was reacted with Cp_2ZrH_2 under the same experimental conditions. Two new species can be distinguished by ^{31}P NMR spectroscopy: **5**, δ = 12.8 ppm (d, $^1J_{PH}$ = 212 Hz), and **6**, δ = 33.9 ppm (d, $^1J_{PH}$ = 214 Hz). Pentane extraction allowed us to isolate **6**, while **5** disappeared during workup. This may be ascribed to the loss of the Cp_2ZrH fragment (hydrolysis of the zirconium nitrogen bond) and, therefore, transformation of **5** into **6** (Scheme I). Derivative **6** was already prepared by hydrogenation of **2a** using lithium aluminum hydride or borane–dimethylamine as reducing agent.[6] ^{31}P and ^1H NMR data for **5** are in agreement with a linear structure and not a cyclic structure—similar to **3a**, **3b**, or **3c**, which would have presented higher direct phosphorus–hydrogen coupling constant (see above). Indeed, $^1J_{PH}$ values of ≈ 200–240 Hz are typical of secondary phosphines of the $R_2NP(H)R$ type. Therefore, it seems that a zirconaazaphosphirane with a Zr–H bond—if formed—is not stable and rearranges into the corresponding linear form.

Scheme II



Scheme III



Interestingly, treatment of **2a** with Cp_2ZrMe_2 led to the zirconaazaphosphirane **7** (Scheme I). NMR data suggest a cyclic structure for **7**. Thus, the ^1H NMR spectrum exhibits two doublets for the Cp groups at 5.54 and 5.68 ppm with phosphorus–hydrogen coupling constants of 2.1 and 1.4 Hz. Similar J_{PH} values were observed for the zirconaazaphosphirane **3a** (2.7 and 1.9 Hz). The $^{31}P\{H\}$ resonance for **7** (+35.3 ppm) is ≈50–70 ppm upfield from the region expected for diamidoalkylphosphanes $[(Me_3Si)_2NP(Me)N(BMe_2)SiMe_3$, 103.5 ppm;[7] $MeP(NMe_2)_2$, 86.4 ppm; $EtP(NMe_2)_2$, 99.9 ppm; $C_6H_{11}P(NMe_2)_2$, 107.1 ppm].[8] The presence of a methyl group on phosphorus and on zirconium is confirmed by ^{13}C NMR spectroscopy.

Formation of **7** is of particular interest since this reaction is the first example of carbozirconation of an unsaturated main group element species. Dimethyldicyclopentadienylzirconocene was previously reported to react with ketenes, isocyanates, carbodiimides, etc., which insert into a Zr–Me bond with concomitant methylation on the sp^2 carbon.[3]

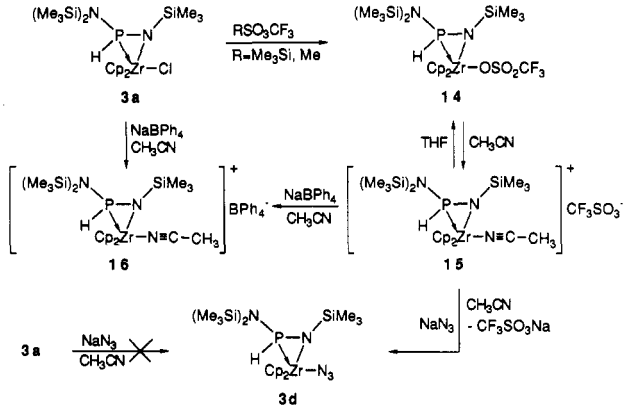
We have already reported[5b] ring-opening reactions involving zirconaazaphosphiranes **3a,b** and $Fe_2(CO)_9$, S_8, or Se (Scheme II). While a transient intermediate **8b** can be detected by ^{31}P NMR spectroscopy in the case of treatment of **3b** with $Fe_2(CO)_9$, we were not able to characterize an intermediate in the case of the addition of S_8 to **3a**: only the phosphane sulfide **10a** was isolated. One can postulate that reaction of **3a** with S_8 proceeded with ring-opening, sulfurization on phosphorus with formation either of the corresponding four-membered ring **11** or the linear *N*-zirconium species **12**. Hydrolysis of **11** or **12** afforded **10a** (the oxide $(Cp_2ZrCl)_2O$ was isolated). In the hope of generating a four-membered ring analogous to the hypothetical species **11**, Cp_2ZrHCl was added to the thioiminophosphorane **13** (Scheme III). ^{31}P NMR spectra of the resulting mixture revealed the presence of a major signal at 31.4 ppm besides that of a minor peak at 52.1 ppm. Successive extractions with pentane allowed the isolation of the major derivative, which was identified as

(6) Niecke, E.; Ringel, G. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 486.

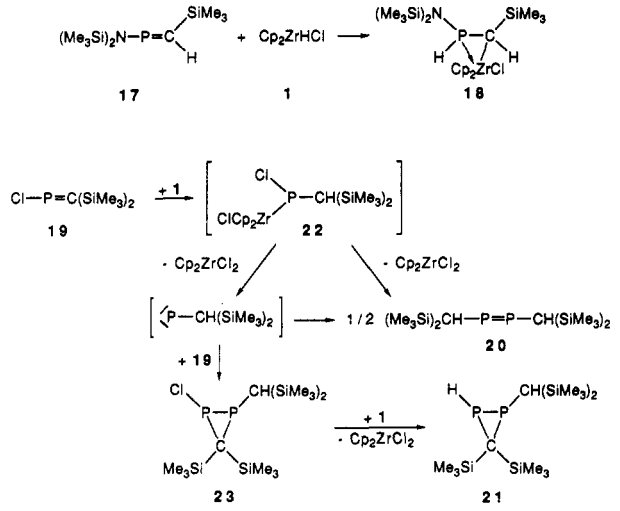
(7) Cowley, A. H.; Kilduff, J. E.; Wilburn, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 1575.

(8) Grutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van-Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*, 227 and references therein.

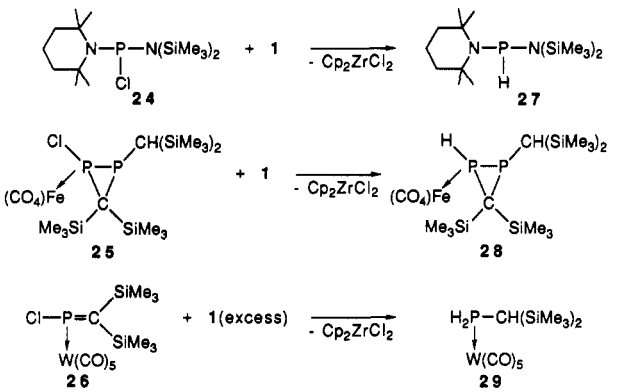
Scheme IV



Scheme V



Scheme VI



the phosphane sulfide **10b**. Formation of **10b** might be explained by hydrolysis of the very unstable four-membered ring **11**.

All these examples reported reactions involving ring opening of three- or four-membered rings. However ring retention was observed when **3a** was added to (trimethylsilyl)trifluoromethanesulfonate or methyltrifluoromethanesulfonate in dichloromethane (Scheme IV). The corresponding zirconaazaphosphirane **14** possessing a Zr–O covalent bond was formed as well as trimethylchlorosilane.[5b] Dissociation of the Zr–O bond occurred when dichloromethane was replaced by a more polar solvent such as acetonitrile: the ionic zirconium ring **15** was thus quantitatively obtained. IR spectroscopy confirmed the existence of an ionic triflate (ν_{SO_3} = 1270 cm^{-1} to be compared to ν_{Zr-OSO_2} = 1377 cm^{-1} characteristic of a covalently bound triflate in **14**[9]). The equivalent conductance of **15**, viz. 95 mho cm^2 equiv^{-1}, clearly indicated the ionic character of this derivative.

An easy exchange of anion took place when **15** was reacted with $NaBPh_4$ in acetonitrile giving rise to complex **16**, which could be directly obtained by reacting the zirconaazaphosphirane **3a** with $NaBPh_4$ in acetonitrile. Conductimetry measurements also confirmed the ionic character of **16** (equivalent conductance 70 mho cm^2 equiv^{-1}). Interestingly, a neutral form can be directly generated without the intervention of solvent effect. Indeed, treatment of **15** in acetonitrile with sodium azide resulted in the formation of the cyclic zirconium azide **3d** (ν_{N_3} = 2084 cm^{-1}; no conductivity was observed for **3d**). Noteworthy is the fact that **3d** was not formed when **3a** was treated with sodium azide in tetrahydrofuran or acetonitrile (Scheme IV). Proofs of ring retention in compounds **3d** and **14–16** are given by large phosphorus–proton coupling constants $^1J_{PH}$ from 330 to 377 Hz and by small phosphorus–Cp coupling constants from 1.8 to 2.8 Hz.

Hydrozirconation of phosphaalkenes is also reported. We demonstrated[5] that addition of Cp_2ZrHCl (**1**) to a tetrahydrofuran solution of the phosphaalkene **17** at −20 °C gave the metallacycle **18** in near-quantitative yield, while treatment of **1** with the P-halogenated phosphaalkene **19** afforded the diphosphene **20** as the major product of the reaction, the diphosphirane **21**, and some not yet identified products (Scheme V). Formation of **18** can formally be viewed as a 1-2 addition of **1** onto the phosphorus–carbon double bond followed by cyclization. Formation of **20** can be regarded as the result of a reverse 1-2 addition of the zirconium hydride to the P–C double bond with transient formation of **22** followed by Cp_2ZrCl_2 elimination. Derivative **21** might result from the insertion of a phosphinidene $(Me_3Si)_2CHP$ on the phosphorus–carbon double bond of **19**, the resulting P-halogenated three-membered ring **23** reacting with Cp_2ZrHCl to give **21**. Compound **21** can also be prepared directly by reaction of **23** independently prepared[2] with tributyltin hydride. Such a chlorine–hydride exchange initiated with **1** is not astonishing, since **1** easily reacted with halogenated phosphorus derivatives whatever the coordination mode of phosphorus. For example, addition of **1** to **24**, **25** (one isomer), or **26** afforded **27**, **28** (one isomer), or **29** in excellent yields (Scheme VI).

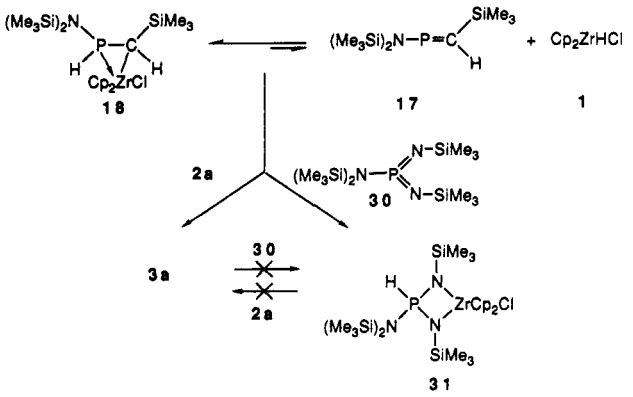
Of interest was the obtention of the secondary phosphine tungsten complex **29** by treatment of the corresponding halogenophosphaalkene complex **26** with Cp_2ZrHCl. Beside the expected chlorine–hydrogen exchange, hydrogenation of the phosphorus carbon double bond occurred.

It should be pointed out that no carbozirconation took place when the phosphaalkene **17** was reacted with Cp_2ZrMe_2.

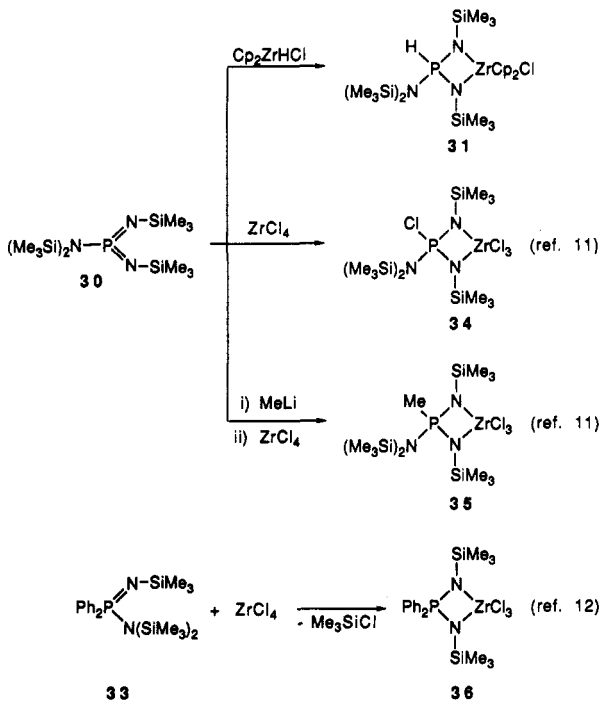
Surprisingly, a quite unusual exchange ligand occurred when a stoichiometric amount of phosphaimine **2a** was added to a THF solution of the zirconaphosphirane **18** at room temperature. ^{31}P NMR spectra of the resulting mixture consisted of a singlet at +33.3 ppm characteristic of the zirconaphosphirane **3a** and a singlet at 309.2 ppm due to the recovered phosphaalkene **17** (Scheme VII). An analogous exchange took place when **18** was reacted with the bis(imino)phosphorane **30**, leading to **17** and to the new four-membered ring **31** in which the zirconium is bonded to two nitrogen atoms, a chlorine atom, and two Cp groups. Evidence for the formation of **31** was confirmed by NMR

(9) Straus, D. A.; Zhang, C.; Quimbita, G. E.; Grumbine, S. D.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 2673 and references therein.

Scheme VII



Scheme VIII

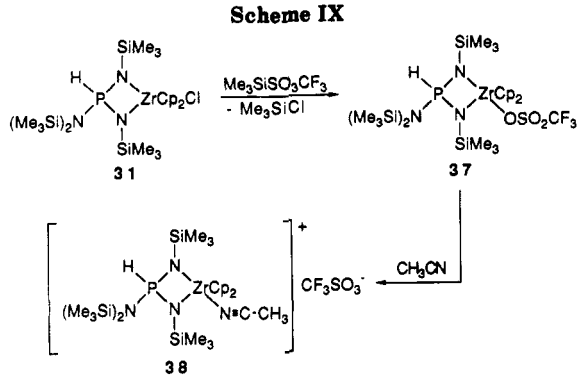


spectrometry (see Experimental Section). It is worth noting that no exchange ligand occurred when the zirconaphosphirane **18** was mixed with the phosphaalkyne P≡C-tBu (**32**), although **32** even reacted at −50 °C with Cp_2ZrHCl to give the expected 1-2 addition product.[10] It should be also noted that no exchange took place when **3a** was treated with the bis(imino)phosphorane **30** or when the four-membered ring **31** was added to the phosphaimine **2a**. Although the three-membered ring was the only detectable product when the phosphaalkene **17** was reacted with Cp_2ZrHCl, it is clear that **18** existed in equilibrium with the starting reagents, the equilibrium being largely displaced toward the cyclic form (Scheme VII). Therefore, the polarity of the double bond seems to be the driving force in this type of reaction, the polarity of the phosphorus–nitrogen bond being higher than that of the phosphorus–carbon double or triple bond.

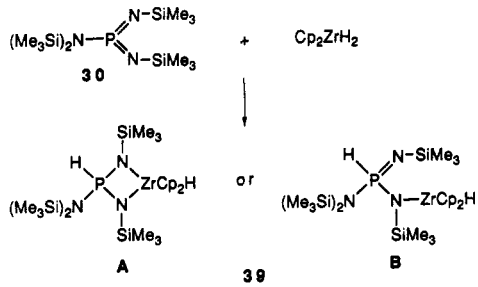
Compound **31** can be directly obtained by reacting the bis(imino)phosphorane **30** with Cp_2ZrHCl in solution at −20 °C (Scheme VIII). Up to now, organometalation of **30** was observed in the reactions with alkyl or aryl derivatives of main-group or transition elements. Indeed,

(10) Majoral, J.-P.; Dufour, N.; Caminade, A.-M.; Regitz, M. Unpublished results.

Scheme IX



Scheme X



treatment of $ZrCl_4$ with **30** or its lithium salt[11] or with (bis(trimethylsilyl)amino)diphenyl((trimethylsilyl)imino)phosphorane (**33**)[12] afforded the heterocycles **34–36** (Scheme VIII).

Reaction of **31** with Me_3SiOTf (OTf = OSO_2CF_3) in dichloromethane readily afforded the triflate derivative **37**. Chemical and spectroscopic properties for this yellow light solid suggested the presence of a covalent Zr–O bond. This derivative was soluble in nonpolar solvents, and the infrared spectrum in dichloromethane contained a band at 1322 cm^{-1} that could be attributed to the triflate group. A slight shielding effect was observed on the ^{31}P NMR spectrum, which showed a doublet at −2.3 ppm with $^1J_{PH}$ = 538 Hz. Evaporation of dichloromethane followed by dissolution of the resulting powder in acetonitrile led to the dissociation of the Zr–O bond and the formation of the corresponding ionic zirconium adduct **38** (Scheme IX). The infrared spectrum of **38** in acetonitrile was consistent with the presence of ionic triflate, since the band at 1322 cm^{-1} disappeared on behalf of the one at 1279 cm^{-1} (see above). ^{31}P, ^1H, and ^{13}C NMR data were consistent with the cyclic ionic structure. Conductimetry measurements in acetonitrile also indicated the ionic nature of **38**. In this case, the equivalent conductance of **38** measured for a 0.01 M solution at 24 °C was 106 mho cm^2 $equiv^{-1}$. This value compared well with the value found for **15** and **16** (see above).

Derivatives **15**, **16**, and **38** are the first examples of ionic zirconium phosphorus ring systems reported.

Hydrozirconation of bis(imino)phosphorane **30** was also performed with Cp_2ZrH_2 in THF and led to the P–H species **39** (Scheme X). Although the experimental values did not allow us to choose between a cyclic structure A or the corresponding linear form B, the polarity of the remaining phosphorus–nitrogen double bond in B strongly

(11) Romanenko, V. D.; Shulgin, V. F.; Skopenko, V. V.; Markowskii, L. N. *Zh. Obshch. Khim.* **1985**, *55*, 538. Markowskii, L. N.; Romanenko, V. D.; Shulgin, V. F.; Ruban, A. V.; Chernega, A. N.; Antipin, M. Yu; Struchkov, Yu. T. *Zh. Obshch. Khim.* **1985**, *55*, 1752. Niecke, E.; Kröher, R.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 864.

(12) Witt, M.; Stalke, D.; Henkel, T.; Roesky, H. W.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1991**, 663.

suggested cyclization and formation of the expected four-membered ring as usually observed (see Scheme VIII and ref 11). Attempts to obtain suitable crystals for X-ray analysis nevertheless failed and did not permit an unambiguous choice.

Conclusion

Hydrozirconation with Cp_2ZrHCl of $\lambda^2\sigma^3$-phosphorus species such as phosphaimines **2a–c**, phosphaalkene **17**, or $\lambda^3\sigma^5$-phosphorus compounds such as bis(imino)-phosphorane **30** proceeded with concomitant cyclization giving rise to functionalized three- and four-membered rings. Moreover, Cp_2ZrMe_2 reacted with **2a** affording a new example of carbozirconation in main group element chemistry. Ring opening and ring retention of some of these species were reported allowing the synthesis of the corresponding linear phosphine sulfides or complexes and the preparation of the first cationic cyclic zirconium phosphorus derivatives.

The halophilicity of zirconium has to be taken into account to explain the particular reaction observed between the P-halogenated phosphaalkene **17** and Cp_2ZrHCl. This halophilicity also allowed an easy hydride–chlorine exchange between free or complexed halogenated phosphines and the Schwartz reagent. The higher polarity of the phosphorus–nitrogen double bond compared to the phosphorus–carbon double bond led to unusual ligand exchanges and direct transformation of the zirconaphosphirane **18** to the zirconaazaphosphirane **3a** or the zirconadiazaphosphetidine **31**.

Experimental Section

General Methods. All experiments were performed in an atmosphere of dry argon. Dry and oxygen-free solvents were used at all times.

^1H and ^{13}C NMR spectra were recorded on a Bruker WM 250 or a Bruker AC 80 spectrometer. ^1H and ^{13}C NMR chemical shifts are reported in part per million relative to Me_4Si as internal reference. ^{31}P NMR spectra were obtained on a Bruker WM 250 or a Bruker AC 80 instrument. Downfield shifts are expressed with a positive sign, in parts per million, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Beckman IR 10 or Perkin-Elmer 225 spectrometer, using polystyrene for calibration. Mass spectra were obtained on a Varian MAT 311 A instrument. Compounds **1**,[13] **2a**,[14] **2b**,[15] **2c**,[16] **13**,[15] **17**,[17] **19**,[18] **24**,[16] **25**,[19] **23**,[19] **26**,[20] and **30**[21] were prepared according to the literature.

Synthesis of Zirconaazaphosphiranes 3a,b. A stoichiometric amount of Cp_2ZrHCl was added to a solution of phosphaimine **2a–c** (1 mmol) in THF (15 mL) at −20 °C. Dissolution and therefore reaction of Cp_2ZrHCl started at 0 °C. After stirring of the solution under argon for 15 min, the solvent was removed under reduced pressure and the resulting orange mixture was treated with 2 × 5 mL of pentane. Upon evaporation of pentane, **3a** (80%), **3b** (two isomers, 80%), and **3c** (75%) were obtained as air- and moisture-sensitive white powders.

3a: ^{31}P NMR (C_6D_6) δ 33.3 (d, $^1J_{PH}$ = 318 Hz); ^1H NMR (C_6D_6) δ 0.35 (s, 18 H, $N[Si(CH_3)_3]_2$), 0.53 (s, 9 H, $NSi(CH_3)_3$), 5.85 (d, J_{PH} = 2.7 Hz, 5 H, Cp), 5.99 (d, J_{PH} = 1.9 Hz, 5 H, Cp), 6.64 (d, $^1J_{PH}$ = 318 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 3.9 (s, $Si(CH_3)_3$), 110.2 (s, Cp), 111.1 (s, Cp); mass spectrum *m/e* 534. Anal. Calcd for $C_{19}H_{38}ClN_2PSi_3Zr$: C, 42.54; H, 7.14; N, 5.22. Found: C, 42.40; H, 7.11; N, 5.22.

3b: two isomers in 70:30 ratio. Isomer 1: ^{31}P NMR (C_6D_6) δ 3.5 (d, $^1J_{PH}$ = 335 Hz); ^1H NMR (C_6D_6) δ 0.35 (d, $^4J_{PH}$ = 1.1 Hz, 9 H, $NSi(CH_3)_3$), 1.30 (d, $^4J_{PH}$ = 1.1 Hz, 9 H, $C(CH_3)_3$), 1.36 (d, $^4J_{PH}$ = 2.0 Hz, 9 H, $C(CH_3)_3$), 5.80 (d, J_{PH} = 2.6 Hz, 5 H, Cp), 5.96 (d, J_{PH} = 1.6 Hz, 5 H, Cp), 6.56 (d, $^1J_{PH}$ = 332 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 7.1 (s, $Si(CH_3)_3$), 32.1 (d, $^3J_{CP}$ = 5.4 Hz, $C(CH_3)_3$), 33.8 (d, $^3J_{CP}$ = 12 Hz, $C(CH_3)_3$), 56.0–57.0 (m, $C(CH_3)_3$), 109.9 (s, Cp), 111.1 (s, Cp). Isomer 2: ^{31}P NMR (C_6D_6) δ −12.0 (d, $^1J_{PH}$ = 334 Hz); ^1H NMR (C_6D_6) δ 0.29 (d, $^4J_{PH}$ = 0.5 Hz, 9 H, $NSi(CH_3)_3$), 1.13 (s, 9 H, $C(CH_3)_3$), 1.44 (s, 9 H, $C(CH_3)_3$), 5.89 (d, J_{PH} = 2.0 Hz, 5 H, Cp), 6.09 (d, J_{PH} = 1.9 Hz, 5 H, Cp), 6.41 (d, $^1J_{PH}$ = 334.0 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 6.4 (s, $Si(CH_3)_3$), 31.8 (d, $^3J_{CP}$ = 4.8 Hz, $C(CH_3)_3$), 33.3 (d, $^3J_{CP}$ = 7.6 Hz, $C(CH_3)_3$), 56.0–57.0 (m, $C(CH_3)_3$), 111.2 (s, Cp), 113.8 (s, Cp); mass spectrum *m/e* 502. Anal. Calcd for $C_{21}H_{38}ClN_2PSiZr$: C, 50.02; H, 7.59; N, 5.56. Found: C, 49.69; H, 7.55; N, 5.31.

3c: ^{31}P NMR (C_6D_6) δ 22.0 (d, $^1J_{PH}$ = 307 Hz); ^1H NMR (C_6D_6) δ 0.47 (s, 9 H, $N[Si(CH_3)_3]_2$), 1.26 (s, 12 H, $C(CH_3)_2$), 1.32 (s, 6 H, CH_2), 5.74 (d, J_{PH} = 2.6 Hz, 5 H, Cp), 5.96 (d, J_{PH} = 1.8 Hz, 5 H, Cp), 6.67 (d, $^1J_{PH}$ = 307 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 4.4 (d, $^3J_{CP}$ = 2.5 Hz, $Si(CH_3)_3$), 17.7 (s, CCH_3), 30.0–35.0 (m, CH_2), 43.6 (d, $^2J_{CP}$ = 4.8, CCH_3), 109.8 (s, Cp), 112.1 (s, Cp); mass spectrum *m/e* 514. Anal. Calcd for $C_{22}H_{38}ClN_2PSiZr$: C, 51.18; H, 7.42; N, 5.43. Found: C, 50.78; H, 7.72; N, 5.40.

3d: ^{31}P NMR (CH_2Cl_2) δ 33.8 (d, $^1J_{PH}$ = 330 Hz); ^1H NMR (C_6D_6) δ 0.33 (s, 18 H, $N[Si(CH_3)_3]_2$), 0.41 (s, 9 H, $NSi(CH_3)_3$), 5.90 (d, J_{PH} = 2.7 Hz, 5 H, Cp), 6.10 (d, J_{PH} = 1.8 Hz, 5 H, Cp), 6.90 (d, $^1J_{PH}$ = 330 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 3.9 (s, $Si(CH_3)_3$) 110.1 (s, Cp), 111.4 (s, Cp); IR (CH_2Cl_2) 2084 (ν_{N_3}) cm^{-1}.

Synthesis of Diaminophosphane 6. A stoichiometric amount of Cp_2ZrH_2 was added to a solution of 1 mmol of phosphaimine **2a** (278 mg) in 15 mL of toluene at −20 °C. The reaction started at room temperature. After being stirred for 15 min, the pink solution was stripped in vacuo leaving a red oil. The colorless diaminophosphane **6**[6] (50%) was extracted with 2 × 5 mL of pentane.

Synthesis of Zirconaazaphosphirane 7. A THF solution (10 mL) of Cp_2ZrMe_2 (251 mg, 1 mmol) was added to a solution of the phosphaimine **2a** (278 mg, 1 mmol) in 20 mL of THF at −20 °C. The mixture was stirred for 30 min at room temperature and the solvent evaporated. The resulting orange oil was washed twice with 3 mL of a 1/1 CH_3CN/Et_2O solution giving rise to **7** (85%) as a white powder: ^{31}P NMR (C_6D_6) δ 35.3 (s); ^1H NMR (C_6D_6) δ 0.29 (s, 18 H, $N[Si(CH_3)_3]_2$), 0.32 (s, 9 H, $NSi(CH_3)_3$), 1.41 (d, $^2J_{PH}$ = 4.6 Hz, 3 H, PCH_3); 5.54 (d, J_{PH} = 2.1 Hz, 5 H, Cp), 5.68 (d, J_{PH} = 1.4 Hz, 5 H, Cp); ^{13}C NMR (C_6D_6) δ 5.1 (d, $^3J_{CP}$ = 5.0 Hz, $Si(CH_3)_3$), 6.7 (d, $^3J_{CP}$ = 2.5 Hz, $Si(CH_3)_3$), 20.4 (d, $^2J_{CP}$ = 6.6 Hz, $ZrCH_3$), 23.4 (d, $^1J_{CP}$ = 8.4 Hz, PCH_3), 106.9 (s, Cp), 109.1 (s, Cp); mass spectrum *m/e* 513 ($M^+ - CH_3$). Anal. Calcd for $C_{21}H_{43}N_2PSi_3Zr$: C, 47.58; H, 8.18; N, 5.29. Found: C, 47.37; H, 8.08; N, 5.14.

Synthesis of Phosphane Complexes 9a,b. Excess of $Fe_2(CO)_9$ (2 equiv) was added to a solution of the metallacycle **3a** or **3b** (0.8 mmol) in 10 mL of THF at −30 °C. The resulting solution was stirred overnight at room temperature. Evaporation of the solvent, followed by extraction with pentane (2 × 10 mL), resulted in dark-brown oils: **9a** (59%); **9b** (50%).

9a: ^{31}P NMR (C_6D_6) δ 87.6 (d, J_{PH} = 407 Hz); ^1H NMR (C_6D_6) δ 0.01 (s, 9 H, $Si(CH_3)_3$), 0.29 (s, 18 Hz, $N[Si(CH_3)_3]_2$), 7.72 (dd, $^1J_{PH}$ = 407.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 2.5 (s, $Si(CH_3)_3$), 3.8 (s, $Si(CH_3)_3$), 215.1 (d, $^2J_{CP}$ = 21.3 Hz, CO); mass spectrum *m/e* 448. Anal. Calcd for $C_{13}H_{29}FeN_2O_4PSi_3$: C, 34.81; H, 6.52; N, 6.25. Found: C, 34.76; H, 6.47; N, 6.19.

9b: ^{31}P NMR (C_6D_6) δ 65.4 (dd, $^1J_{PH}$ = 435 Hz, $^2J_{PH}$ = 20 Hz); ^1H NMR (C_6D_6) δ 0.26 (s, 9 H, $Si(CH_3)_3$), 0.97 (s, 9 Hz, $C(CH_3)_3$), 1.16 (s, 9 H, $C(CH_3)_3$) 7.90 (dd, $^1J_{PH}$ = 435 Hz, $^3J_{HH}$ = 7 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 5.6 (s, $Si(CH_3)_3$), 30.0 (d, $^3J_{PC}$ = 4.2 Hz, $C(CH_3)_3$), 33.1 (d, $^3J_{PC}$ = 4.7 Hz, $C(CH_3)_3$), 54.3 (d, $^2J_{PC}$ = 13.4 Hz, $C(CH_3)_3$), 58.4 (s, $C(CH_3)_3$), 215.2 (d, $^2J_{CP}$ = 20.8 Hz, CO); mass spectrum *m/e* 416. Anal. Calcd for $C_{15}H_{29}FeN_2O_4PSi$: C, 43.27; H, 7.02; N, 6.73. Found: C, 43.19; H, 7.11; N, 6.64.

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Synthesis of Phosphane Sulfides 10a[6] and 10b, from Metallacycles 3a and 3b. Powdered sulfur (0.9 mmol) in 10 mL of toluene was added to a solution of 0.6 mmol of metallacycle **3a** (167 mg) or **3b** (148 mg) at room temperature, and the mixture was stirred for 2 days. After filtration, the resulting solution was concentrated. The slightly yellow **10b**, or green **10a**, product, which turned out to depose slowly in THF and benzene, was obtained in quantitative yield.

10a: ^{31}P NMR (C_6D_6) δ 36.3 (d, $^1J_{PH}$ = 534 Hz); mass spectrum m/e 312. Anal. Calcd for $C_9H_{29}N_2PSSi_3$: C, 34.57; H, 9.35; N, 8.96. Found: C, 34.17; H, 9.29; N, 8.52.

10b: ^{31}P NMR (C_6D_6) δ 31.40 (d, $^1J_{PH}$ = 536 Hz); ^{1}H NMR (C_6D_6) δ 0.44 (s, 9 H, $Si(CH_3)_3$), 1.15 (s, 9 Hz, $HNC(CH_3)_3$), 1.48 (s, 9 H, $SiNC(CH_3)_3$), 8.20 (d, J_{PH} = 536 Hz, 1 H, PH); mass spectrum m/e 280. Anal. Calcd for $C_{11}H_{29}N_2PSSi$: C, 47.10; H, 10.42; N, 9.99. Found: C, 47.35; H, 10.39; N, 9.80.

Synthesis of 10b from Thioiminophosphorane 13. Cp_2ZrHCl (2 mmol) was added at once to a solution of thioiminophosphorane **13** (2 mmol, 556 mg) in 20 mL of THF. The resulting green solution was stirred at −20 °C for 30 min. Evaporation of the solvent followed by extraction with pentane (2 × 5 mL) afforded a yellow green residue identified as **10b** (50%).

Synthesis of 10c from Metallacycle 3a. An excess of selenium (1.5 equiv) was added at room temperature to a solution of 0.6 mmol of metallacycle **3a** (167 mg) in 10 mL of toluene. The heterogeneous solution was stirred for 2 days. After filtration, the resulting solution was concentrated to give a pale yellow powder washed with pentane (2 × 10 mL) identified as **10c** (45%). ^{31}P NMR (C_6D_6): δ 19.60 (ddd, $^1J_{PH}$ = 521 Hz, $^2J_{PH}$ = 7 Hz, J_{PSe} = 761 Hz); ^{1}H NMR (C_6D_6) δ 0.09 (d, $^4J_{PH}$ = 0.6 Hz, 9 H, $Si(CH_3)_3$), 0.31 (d, $^4J_{PH}$ = 0.6 Hz, 18 H, $N[Si(CH_3)_3]_2$), 8.09 (d, $^1J_{PH}$ = 521.0 Hz, 1 H, PH); mass spectrum m/e 360. Anal. Calcd for $C_9H_{29}N_2PSeSi_3$: C, 30.06; H, 8.13; N, 7.79. Found: C, 30.46; H, 8.28; N, 7.65.

Synthesis of Zirconaazaphosphirane 14.[5b] $Me_3SiOSO_2CF_3$ (1 mmol, 222 mg) was added dropwise with stirring to the zirconaazaphosphirane (1 mmol, 536 mg) in 20 mL of CH_2Cl_2 at −20 °C. A pale yellow solution was formed within seconds. The reaction mixture was warmed to room temperature for 15 min. The solvent was removed in vacuo giving rise to a yellow powder, which was washed with 2 × 10 mL of ether. **14** was obtained as a waxlike white substance (65%): ^{31}P NMR (C_6D_6) δ 40.9 (d, $^1J_{PH}$ = 353 Hz); ^{1}H NMR (C_6D_6) δ 0.30 (s, 18 H, $N[Si(CH_3)_3]_2$), 0.32 (s, 9 H, $NSi(CH_3)_3$), 5.96 (d, J_{PH} = 2.7 Hz, 5 H, Cp), 6.11 (d, J_{PH} = 1.8 Hz, 5 H, Cp), 6.89 (d, $^1J_{HP}$ = 353.0 Hz, 1 H, P–H); ^{13}C NMR (C_6D_6) δ 2.7 (d, $^3J_{CP}$ = 2.6 Hz) and 4.1 (br s, $NSi(CH_3)_3$), 110.5 (d, J_{PC} = 1.2 Hz, Cp), 111.4 (s, Cp), 120.2 (q, $^1J_{CF}$ = 319.0 Hz, CF_3SO_3); IR (KBr) 1377 (ν_{SO_3}) cm^{-1}. Anal. Calcd for $C_{20}H_{38}F_3N_2O_3PSSi_3$: C, 36.95; H, 5.89; N, 4.31. Found: C, 36.86; H, 5.77; N, 4.18.

Synthesis of Cation 15 from 14.[5b] Evaporation of a dichloromethane solution of **14** gave a yellow residue, which was dissolved in acetonitrile giving rise to the ionic structure **15**: ^{31}P NMR (CD_3CN) δ 28.9 (d, $^1J_{PH}$ = 377 Hz); ^{1}H NMR (CD_3CN) δ 0.28 (s, 9 H, $NSi(CH_3)_3$), 0.53 (s, 18 H, $N[Si(CH_3)_3]_2$), 2.09 (s, free CH_3CN due to the CD_3CN–CH_3CN fast exchange, coordinated CH_3CN is not seen in CD_3CN solution), 6.16 (d, J_{PH} = 2.6 Hz, 5 H, Cp), 6.27 (d, J_{PH} = 1.7 Hz, 5 H, Cp), 7.18 (d, $^1J_{HP}$ = 377.0 Hz, 1 H, P–H); ^{13}C NMR (CD_3CN) δ 3.1 (d, J_{CP} = 2.6 Hz) and 4.3 (s, $NSi(CH_3)_3$), 110.6 and 111.5 (s, Cp), 120.2 (q, $^1J_{CF}$ = 319.0 Hz, CF_3SO_3); IR (CD_3CN) 1270 (ν_{SO_3} ionic) cm^{-1}. Anal. Calcd for $C_{22}H_{41}F_3N_3O_3PSSi_3Zr$: C, 38.24; H, 5.98; N, 6.08. Found: C, 38.11; H, 5.91; N, 5.94. Removal of acetonitrile followed by addition of THF allowed one to recover **14**.

Synthesis of Cationic Zirconaazaphosphirane 16.[5b] **(i) From Zirconaazaphosphirane 3a.** An excess of $NaBPh_4$ (682 mg, 2.00 mmol) was added to a solution of zirconaazaphosphirane **3a** (879 mg, 1.64 mmol) in 25 mL of acetonitrile at 0 °C. A light yellow color developed during the dissolution of $NaBPh_4$. The mixture was allowed to react at room temperature. Volatiles were removed, and the yellow residue was extracted with 2 × 10 mL of dichloromethane, affording a yellow powder **16** (72%): ^{31}P NMR (CH_3CN) δ 29.1 (d, $^1J_{PH}$ = 377 Hz); ^{1}H NMR (CD_3CN), δ 0.41 (s, 9 H, $NSi(CH_3)_3$), 0.66 (s, 18 H, $N[Si(CH_3)_3]_2$), 2.09 (s, free CH_3CN; coordinated CH_3CN in CD_2Cl_2 solution, 1.60 (s, 3 H)), 6.19 (d, J_{PH} = 2.6 Hz, 5 H, Cp), 6.30 (d, J_{PH} = 1.8 Hz, 5 H, Cp), 7.23 (m, 12 H, p, m $(C_6H_5)_4B$), 7.29 (d, $^1J_{PH}$ = 377.0 Hz, 1 H, PH), 7.59 (m, 8 H, *o*-H $(C_6H_5)_4B$); ^{13}C NMR (CD_3CN) δ 3.5 and 4.7 (s, $NSi(CH_3)_3$), 110.7 and 111.6 (s, Cp); $(C_6H_5)_4B$ at 123.0 (s), 126.9 (q, $^1J_{CB}$ = 2.7 Hz), 137 (s), and 165.1 (q, J_{BC} = 50.0 Hz); IR (CH_2Cl_2) ν_{CN} 2302 and 2253 cm^{-1} (free CH_3CN), 2281 (coordinated CH_3CN) cm^{-1}. Anal. Calcd for $C_{45}H_{61}BN_3PSi_3Zr$: C, 62.76; H, 7.14; N, 4.88. Found: C, 62.64; H, 7.10; N, 4.76.

(ii) From Cationic Zirconaazaphosphirane 15. The reaction was carried out as above with 2 mmol of $NaBPh_4$ (682 mg) and 1.64 mmol of zirconaazaphosphirane (1.04 mg).

Synthesis of Zirconaphosphirane 18. A stoichiometric amount of Cp_2ZrHCl was added to a solution of 1 mmol of phosphaalkene **17** (277 mg) in 20 mL of THF at −20 °C with stirring for 15 min. The reaction started when the temperature reached ~0 °C as indicated by an orange coloration of the reaction mixture. The mixture was stirred for 30 min at room temperature and stripped in vacuo, leaving an orange oil. **18** (78%) was obtained as an air- and moisture-sensitive white powder after extraction with 2 × 15 mL of pentane followed by filtration: ^{31}P NMR (C_6D_6) δ 42.60 (d, J_{PH} = 346 Hz); ^{1}H NMR (C_6D_6) δ 0.26 (s, 18 H, $N[Si(CH_3)_3]_2$), 0.40 (s, 9 H, $CSi(CH_3)_3$), 5.74 (d, J_{PH} = 1.8 Hz, 5 H, Cp), 5.81 (d, J_{PH} = 2.4 Hz, 5 H, Cp), 5.88 (dd, $^1J_{PH}$ = 343.0 Hz, $^3J_{HH}$ = 15.0 Hz, 1 H, PH), 7.34 (dd, $^2J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 15.0 Hz, 1 H, CH); ^{13}C NMR (C_6D_6) δ 4.2, 4.4, 4.7 (s, $Si(CH_3)_3$), 108.4 (s, Cp), 110.4 (s, Cp); mass spectrum m/e 533. Anal. Calcd for $C_{20}H_{39}ClNPSi_3Zr$: C, 44.86; H, 7.34; N, 2.62. Found: C, 44.54; H, 7.30; N, 2.37.

Synthesis of Diphosphene 20 and Diphosphirane 21. A stoichiometric amount of Cp_2ZrHCl (258 mg, 1 mmol) was added to a solution of phosphaalkene **19** (326 mg, 1 mmol) in 20 mL of THF at −80 °C. An orange color developed at −50 °C during the dissolution of Cp_2ZrHCl. The mixture was allowed to react at 0 °C for 30 min and at room temperature for 15 min. ^{31}P NMR spectra clearly indicated the formation of **20** ($\delta(^{31}P)$ = 309.4 ppm),[22] as the major product of the reaction, and **21**.

Synthesis of Diphosphirane 21 from Diphosphirane 23. A stoichiometric amount of Bu_3SnH (60 mg) was added to a solution of diphosphirane **23** (85 mg, 0.2 mmol) in 10 mL of THF at −10 °C. The reaction mixture was warmed to room temperature. The color changed from orange to yellow. The mixture was stirred for 5 h at room temperature. At the end of the reaction, the solution was evaporated to dryness and diphosphirane **21** was purified by chromatography on Florisil with pentane as eluent (75%): ^{31}P NMR (C_6D_6) δ −244.9 (dd, $^1J_{PH}$ = 149 Hz, $^1J_{PP}$ = 161 Hz), −134.4 (d, $^1J_{PP}$ = 161 Hz); ^{1}H NMR (C_6D_6) δ 0.14 (d, $^4J_{PH}$ = 2.6 Hz, 9 H, $C(SiMe_3)_2$), 0.23 (d, $^3J_{PH}$ = 1.1 Hz, 9 H, $CH(SiMe_3)_2$), 0.28 (dd, $^4J_{PH}$ = 0.7 and 0.6 Hz, 9 H, $C(SiMe_3)_2$), 0.37 (d, $^4J_{PH}$ = 1.95 Hz, 9 H, $CH(SiMe_3)_2$); ^{13}C NMR (C_6D_6) δ 1.2, 1.6, 3.4, 3.5 ($Si(CH_3)_3$), 7.7 (d, $^1J_{CH}$ = 84.6 Hz, CH), 22.5 (dd, $^1J_{CP}$ = 72.0 Hz, $^1J_{CP}$ = 79.0 Hz, $CSi(CH_3)_3$).

Synthesis of Diaminophosphane 27. To a solution of chlorophosphine **24** (1.51 g, 4.1 mmol) in 20 mL of THF was added with stirring 1 equiv of Cp_2ZrHCl. The brown solution was stirred overnight. After removal of the solvent, the product was extracted with pentane, affording an orange oil, **27** (80%): ^{31}P NMR (C_6D_6) δ 44.4 (d, $^1J_{PH}$ = 219 Hz); ^{1}H NMR (C_6D_6) δ 0.33 (d, $^4J_{PH}$ = 0.7 Hz, 9 H, $Si(CH_3)_3$), 1.30 (s, 12 H, C–CH_3), 1.38 (s, 6 H, CH_2), 6.63 (d, $^1J_{PH}$ = 219.0 Hz, PH); mass spectrum m/e 332. Anal. Calcd for $C_{15}H_{37}N_2PSi_2$: C, 54.16; H, 11.21; N, 8.42. Found: C, 54.50; H, 11.16; N, 8.69.

Synthesis of Diphosphirane Complex 28. A stoichiometric amount of Bu_3SnH (1.16 g, 4 mmol) was added to a solution of diphosphirane complex, **25**, in hexane at −10 °C. The reaction mixture was warmed to room temperature and stirred for 2 h. Then the solution was controlled by ^{31}P NMR. **28**: ^{31}P NMR (C_6D_6) δ −124.1 (d, $^1J_{PP}$ = 239 Hz), −92.3 (dd, $^1J_{PH}$ = 334 Hz, $^1J_{PP}$ = 239 Hz).

Synthesis of Secondary Phosphine Tungsten Complex 29. Cp_2ZrHCl (257 mg, 1 mmol), complex **26** (548 mg, 1 mmol), and THF were mixed at −40 °C. The resulting brown solution was stirred from −40 °C to room temperature for 2 h. The solvent then was removed in vacuo. Extraction with pentane (2 × 5 mL) afforded a waxlike brown substance, **29** (80%): ^{31}P NMR (C_6D_6)

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δ -116.5 (tdd, $^1J_{PH}$ = 333 Hz, $^2J_{PH}$ = 6 Hz, J_{PW} = 219 Hz); ^{1}H NMR (C_6D_6) δ -0.08 and 0.28 (s, 18 H, $Si(CH_3)_3$), 1.1 (d, J_{HH} = 7.0 Hz, 1 H, CH), 4.08 (dd, J_{PH} = 333.0 Hz, J_{HH} = 6.0 Hz, 2 H, H_2P). Anal. Calcd for $C_{12}H_{21}O_5PSi_2W$: C, 27.91; H, 4.10. Found: C, 27.72; H, 4.00.

Synthesis of Zirconadiazaphosphetidine 31. Cp_2ZrHCl (257 mg, 1 mmol) was added to a solution of 1 mmol of (bis(trimethylsilyl)amino)bis((trimethylsilyl)imino)phosphorane **30** (453 mg) in 15 mL of THF at -20 °C. The yellow solution was stirred at this temperature for 30 min. After extraction of the solvent, the yellow residue was washed with benzene. The complex then precipitated as a white powder (82%): ^{31}P NMR (C_6D_6) δ 2.8 (d, $^1J_{PH}$ = 517 Hz); ^{1}H NMR (C_6D_6) δ 0.16 (s, 18 H, $N[Si(CH_3)_3]_2$), 0.43 and 0.61 (s, 9 H, $N-Si(CH_3)_3$), 6.31 (s, 5 H, Cp), 6.27 (s, 5 H, Cp), 7.54 (d, $^1J_{PH}$ = 517.0 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 6.1 (d, $^3J_{CP}$ = 8.2 Hz, $Si(CH_3)_3$), 6.2 (d, $^3J_{CP}$ = 4.6 Hz, $Si(CH_3)_3$), 8.0 (d, $^3J_{CP}$ = 4.1 Hz, $Si(CH_3)_3$), 114.3 (s, Cp), 116.3 (s, Cp); mass spectrum m/e 621. Anal. Calcd for $C_{22}H_{47}ClN_3PSi_4Zr$: C, 42.37; H, 7.60; N, 6.74. Found: C, 42.15; H, 7.25; N, 6.55.

Synthesis of Zirconadiazaphosphetidine Triflate 37. $Me_3SiOSO_2CF_3$ (222 mg, 1 mmol) was added dropwise with stirring to **31** (621 mg, 1 mmol) in 20 mL of CH_2Cl_2 at -20 °C. A clear yellow solution was formed within seconds. The reaction mixture was warmed to room temperature over 30 min. The solvent then was removed in vacuo to give a yellow light solid, **37** (75%): ^{31}P NMR (C_6D_6) δ -2.3 (d, $^1J_{PH}$ = 538 Hz); ^{1}H NMR (C_6D_6) δ 0.27-0.55 (m, 36 H, $Si(CH_3)_3$), 6.56 (s, 5 H, Cp), 6.59 (s, 5 H, Cp), 7.42 (d, $^1J_{PH}$ = 538.0 Hz, 1 H, PH); ^{13}C NMR (C_6D_6) δ 3.9 (d, $^3J_{CP}$ = 4.3 Hz, $Si(CH_3)_3$), 4.9 (s, $Si(CH_3)_3$), 115.3 (s, Cp), 116.8 (s, Cp), 120.0 (q, $^1J_{CF}$ = 320.0 Hz, CF_3SO_3). Anal. Calcd for $C_{23}H_{47}F_3N_3O_3PSSi_4Zr$: C, 37.47; H, 6.43; N, 5.70. Found: C, 37.06; H, 6.34; N, 5.61; IR (KBr) 1322 (ν_{SO_3}) cm^{-1}.

Synthesis of Cationic Zirconadiazaphosphetidine Triflate 38. Zirconadiazaphosphetidine triflate **37** was dissolved in acetonitrile. **38**: ^{31}P NMR (CD_3CN) δ 1.6 (d, $^1J_{PH}$ = 536 Hz); IR (CD_3CN) 1279 (ν_{SO_3} ionic) cm^{-1}.

Synthesis of Zirconadiazaphosphetidine 39. Cp_2ZrH_2 (1 mmol) was added at once to a solution of 1 mmol of (bis(trimethylsilyl)amino)bis((trimethylsilyl)imino)phosphorane (**30**) in 15 mL of toluene at -20 °C. The yellow solution was stirred for 30 min at this temperature. After extraction of the solvent, the yellow residue was washed with pentane. The complex **39** (80%) precipitated as a white powder: ^{31}P NMR (C_6D_6) δ -2.9 (dd, $^1J_{PH}$ = 509 Hz, $^2J_{PH}$ = 40 Hz); ^{1}H NMR (C_6D_6) δ 0.24, 0.30, 0.33, 0.40 (s, 36 H, $Si(CH_3)_3$), 4.68 (d, $^3J_{PH}$ = 40.0 Hz, 1 H, ZrH), 7.31 (d, $^1J_{PH}$ = 509.0 Hz, 1 H, PH), 5.74 (s, 5 H, Cp); 5.82 (s, 5 H, Cp); ^{13}C NMR (C_6D_6) δ 4.0-5.0 (m, $Si(CH_3)_3$), 104.3 (s, Cp), 105.6 (s, Cp). Anal. Calcd for $C_{22}H_{48}N_3PSi_4Zr$: C, 44.85; H, 8.21; N, 7.13. Found: C, 45.03; H, 7.97; N, 7.45.

Registry No. 1, 37342-97-5; **2a**, 50732-21-3; **2b**, 53787-01-2; **2c**, 72821-01-3; **3a**, 128337-85-9; **3b**, 131104-31-9; **3c**, 138694-46-9; **3d**, 138753-35-2; **6**, 63104-54-1; **7**, 138694-47-0; **9a**, 131104-37-5; **9b**, 131104-33-1; **10a**, 63104-56-3; **10b**, 138694-44-7; **10c**, 63104-57-4; **13**, 53973-90-3; **14**, 131104-34-2; **15**, 131104-36-4; **16**, 131130-18-2; **17**, 76173-65-4; **18**, 128337-84-8; **19**, 79454-85-6; **20**, 96043-64-0; **21**, 128429-18-5; **23**, 113389-13-2; **24**, 90500-31-5; **25**, 113192-44-2; **26**, 138694-50-5; **27**, 138694-45-8; **28**, 138694-48-1; **29**, 138694-49-2; **30**, 52111-28-1; **31**, 138694-51-6; **37**, 138694-52-7; **38**, 138694-54-9; **39A**, 138694-56-1; **39B**, 138694-55-0; Cp_2ZrH_2, 37342-98-6; Cp_2ZrMe_2, 12636-72-5; $Fe_2(CO)_9$, 15321-51-4; $Me_3SiOSO_2CF_3$, 27607-77-8.

Silaheterocycles. 14.[1] Regiospecific Cycloaddition Reactions of Dichloroneopentylsilene with Cyclohexa-1,3-diene. A Novel 7-Silabicyclo[4.2.0]oct-2-ene → 2-Silabicyclo[2.2.2]oct-5-ene Rearrangement

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In the presence of cyclohexa-1,3-diene (**2**), dichloroneopentylsilene (**1**), generated in situ from trichlorovinylsilane and *t*-BuLi, favors the regioselective formation of the anti/syn isomeric [2+2] cycloadducts (**3**, 74%) over the [4+2] addition, leading to the endo/exo isomer Diels-Alder compounds **4** (26%). On standing, the thermodynamically less stable silacyclobutane derivatives **3** completely isomerize to give the [4+2] products within several weeks. Possible reaction pathways, including a zwitterionic intermediate **A**, are discussed. In contrast, the dimethyl- and diphenyl-substituted [2+2] adducts (**7**, **8**), available from **3** by substitution reactions, show different isomerization behavior. They cannot be transformed into the Diels-Alder compounds, but the syn [2+2] isomers slowly form the thermodynamically more stable anti derivatives at room temperature. On thermolysis they yield open-chain products by a retro ene reaction. The high synthetic potential of strongly electrophilic **1** is demonstrated by the comparison of the cycloaddition behavior with diorgano-substituted neopentylsilenes $R_2Si{=}CHCH_2Bu$-*t*: Reaction of $Me_2Si{=}CHCH_2Bu$-*t* with **2** favors the [4+2] product formation, while $Ph_2Si{=}CHCH_2Bu$-*t* yields the Diels-Alder adducts exclusively.

Introduction

Our investigations on the cycloaddition behavior of dichloroneopentylsilene, $Cl_2Si{=}CHCH_2Bu$-*t* (**1**), formed by treating vinyltrichlorosilane with *t*-BuLi in nonpolar solvents,[2] revealed some surprising results, which have not been obtained in earlier work for diorgano-substituted derivatives by the group of Jones.[3] With cyclopentadienes,[4] aromatic dienes such as naphthalene[5] and

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