Zirconium-Promoted Ring Opening. Scope and Limitations

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Hydrozirconation by means of $[Cp_2ZrHCl]_n$ (**2**) of phospholene $PhP\overline{CH_2CH{=}CHCH_2}$ (**1**) leads to the β-zirconated phospholane **3** which reacts with phosphenium salts $R_2P^+OSO_2CF_3^-$ (**4**, R = N^iPr_2; **5**, R = NCy_2) to give unsaturated acyclic 1,1-diphosphines **6** or **7**. Compound **3** also reacts with other electrophiles like $[CH_2{=}NMe_2]Cl$, ^{t}BuCOCl, or $HOSO_2CF_3$ leading to unsaturated phosphines $PhP(R)(CH_2)_2CH{=}CH_2$, **8** (R = CH_2NMe_2), **9** (R = C(O)^{t}Bu), or **10** (R = H), respectively. Hydrozirconation of 2,5-dihydrofuran (**12**) or 2,3-dihydrofuran (**13**) affords the acyclic zirconated species $Cp_2Zr(Cl)O(CH_2)_2CH{=}CH_2$ (**15**), which reacts with **4**, Ph_2PCl, $[CH_2{=}NMe_2]Cl$, PhCOCl, or $HOSO_2CF_3$ to give, via exchange reactions, the corresponding substituted olefines **16**−**20**. Treatment of **12** or **13** with 2 equiv of **2** leads to dizirconated compound $Cp_2Zr(Cl)O(CH_2)_4Zr(Cl)Cp_2$ (**21**) which reacts with Ph_2PCl (2 equiv) to give the phosphino−phosphinite $Ph_2PO(CH_2)_4PPh_2$ (**22**) isolated as its disulfide **23**. 2-Methyl-4,5-dihydrofuran (**24**) treated first with 2 equiv of **2** and then with 2 equiv of Ph_2PCl affords the phosphino−phosphinite $Ph_2PO(CH_2)_5PPh_2$ (**26**). Hydrozirconation of 2,5-dimethoxy-2,5-dihydrofuran (**28**) with 2 equiv of **2** gives rise to $Cp_2Zr(OMe)Cl$ (**31**) and $Cp_2Zr(Cl)O(CH_2)_2CH{=}CHOMe$ (**33**), which react further with Ph_2PCl (2 equiv) leading to phosphinites Ph_2POMe (**34**) and $Ph_2PO(CH_2)_2CH{=}CHOMe$ (**35**). Addition of **2** to 1-benzyl-3-pyrroline (**36**) allows the formation of the β-zirconated nitrogen five-membered ring $PhCH_2\overline{N(CH_2)_2CH(ZrCp_2Cl)CH_2}$ (**37**). **37** reacts with Ph_2PCl giving rise to the acyclic aminophosphine $Ph_2PN(CH_2Ph)(CH_2)_2CH{=}CH_2$ (**38**) and to a substitute pyrroline **39**. Derivative **37** also reacts with **4** to give the saturated nitrogen heterocycle **42**, while it reacts with PhCOCl or $HOSO_2CF_3$ to afford the corresponding linear species $PhC(O)N(CH_2Ph)(CH_2)_2CH{=}CH_2$ (**44**) or the amine $HN(CH_2Ph)(CH_2)_2CH{=}CH_2$ (**45**). Hydrozirconation of **38** followed by addition of Ph_2PCl and then addition of S_8 gives the aminophosphine−phosphine disulfide $Ph_2P(S)N(CH_2Ph)(CH_2)_4P(S)Ph_2$ (**46**). Hydrozirconation of oxygen six-membered rings such as 3,4-dihydro-2*H*-pyran (**53**) and 2-methoxy-3,4-dihydro-2*H*-pyran (**55**) is discussed as well as the hydrozirconation of a seven-membered ring, cis-dihydro-1,3-dioxepin (**62**). The behavior of 3-sila- (**47**) or 3-boracyclopentene (**48**) is also presented.

Introduction

Zirconium derivatives were found to be useful tools in organic and organometallic syntheses.[1] Among them $[Cp_2ZrHCl]_n$ proved to be one of the most effective reagents making unactivated methyl hydrogens accessible to substitution in linear systems and allowing carbon−carbon, carbon−hydrogen, carbon−halogen, or carbon−main group element bond formation.[2] Indeed, a number of different functionalities can be introduced by cleavage of the carbon−zirconium bond with electrophiles. Hydrozirconation of cyclic olefins[3] or unsaturated heterocycles[4] was also an attractive method to prepare various substituted ring systems without generally the help of catalysts. In contrast, the Schwartz reagent was rarely used as a mild reagent facilitating ring opening. To our knowledge, only hydrozirconation

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(1) Tetrahedron Symposia in print No. 57; Negishi, E., Guest Ed. *Tetrahedron* **1995**, *51*, 4255. For reviews see for example: (a) Annby, U.; Karlsson, S. *Acta Chem. Scand.* **1993**, *47*, 425. (b) Labinger, J. A. *Comprehensive Organic Chemistry*; Fleming, I., Ed.; Pergamon Press: London, 1991; Vol. 3, Chapter 3, p 667. (c) Negishi, E. *Ibid*, Paquette, L. A., Ed.; Vol. 9, Chapter 5, p 1163. (d) Ryabov, A. D. *Chem. Rev.* **1990**, 403. (e) Karlsson, S.; Hallberg, A.; Gronowitz, S. *J. Organomet. Chem.* **1991**, *403*, 133. (f) Erker, G.; Aulbach, M.; Mena, M.; Pfaff, R.; Sosna, F. *Chem. Scr.* **1989**, *29*, 451. (g) Negishi, E. *Ibid.* **1989**, *29*, 457. (h) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1. (i) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (j) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. (k) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. (l) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *6*, 333.

(2) See for example: (a) Wailes, P. C.; Weingold, H. *J. Organomet. Chem.* **1970**, *24*, 405. (b) Lipshutz, B. H.; Kato, K. *Tetrahedron Lett.* **1991**, *32*, 5647. (c) Tucker, C. E.; Knochel, P. *J. Am. Chem. Soc.* **1991**, *113*, 9888. (d) Venanzi, L. M.; Lehman, R.; Keil, R.; Lipshutz, B. H. *Tetrahedron Lett.* **1992**, *33*, 5857. (e) Godfrey, A. G.; Ganem, B. *Tetrahedron Lett.* **1992**, *33*, 7461. (f) Karlson, S.; Hallberg, A.; Gronowitz, S. *J. Organomet. Chem.* **1992**, *430*, 53. (g) Treilhou, M.; Fauve, A.; Pougny, J.-R.; Prome, J.-C.; Veschambre, H. *J. Org. Chem.* **1992**, *57*, 3203. (h) Hauske, J. R.; Dorff, P.; Julin, S.; Martinelli, G.; Bussolari, J. *Tetrahedron Lett.* **1992**, *33*, 3715. (i) Maeta, H.; Suzuki, K. *Tetrahedron Lett.* **1992**, *33*, 5969. (j) Maeta, H.; Suzuki, K. *Tetrahedron Lett.* **1992**, *34*, 341. (k) Schedler, D. J. A.; Godfrey, A. G.; Ganem, B. *Tetrahedron Lett.* **1993**, *34*, 5035. (l) Chemin, D.; Linstrumelle, G. *Synthesis* **1993**, *4*, 377. (m) Maeta, H.; Hasegawa, T.; Suzuki, K. *Synlett.* **1993**, *33*, 341.

(3) Wipf, P.; Śmitrovich, J. H. *J. Org. Chem.* **1991**, *56*, 6494.

(4) Cénac, N.; Zablocka, M.; Igau, A.; Majoral, J. P.; Pietrusiewicz, M. *Organometallics* **1994**, *13*, 5166.

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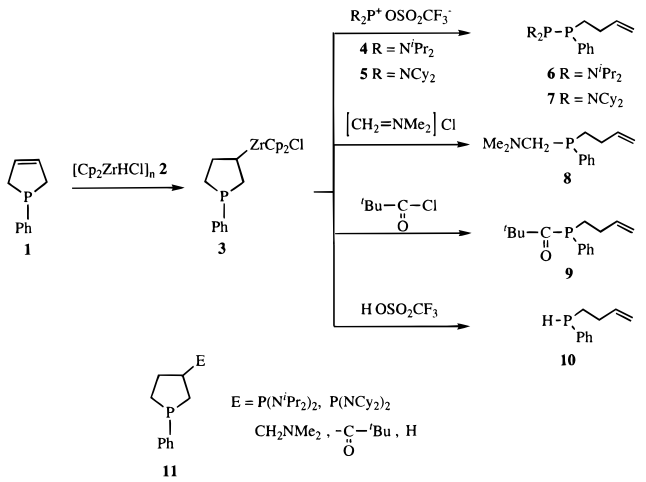
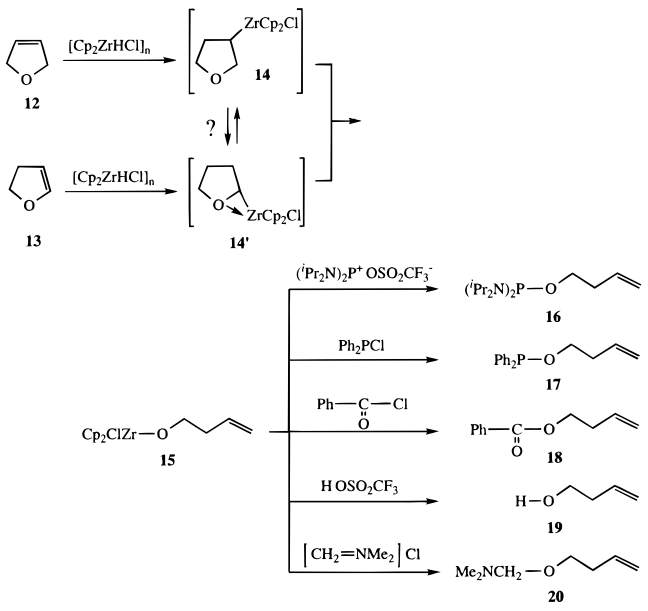
Scheme 1



Scheme 2



of dihydropyran leading to the acyclic compound $Cp_2Zr(Cl)O(CH_2)_3CH{=}CH_2$ was described[5] while ring-opening reactions using other zirconium species such as for example zirconium complexes of cyclic alkynes or zirconocene butene complex are well documented.[6]

In a preliminary communication[4] we reported the zirconium-promoted ring opening of nitrogen-, oxygen-, or phosphorus-containing unsaturated five-membered rings. Herein we present the scope and limitations of such a useful new methodology. It will be demonstrated that this reaction can be extended not only to various other five-membered rings provided that these compounds possess one donor heteroatom included in the ring but also to six- or seven-membered rings. The particular behavior of silacyclopentene and boracyclopentene will also be presented.

Results and Discussion

Five-Membered Rings. Phosphorus Heterocycles. Hydrozirconation of phospholene **1** is performed by adding the Schwartz reagent $[Cp_2ZrHCl]_n$ (**2**) to a solution of **1** in THF at −20 °C. The reaction proceeds smoothly giving rise to the isolated β-zirconated phospholane **3**.[4] Derivative **3** is stable at room temperature, and no equilibrium between **3** and its eventual acyclic isomer has been detected. Treatment of **3** with phosphenium salts $R_2P^+OSO_2CF_3^-$ (**4**, R = N^iPr_2; **5**, R = NCy_2) leads via elimination of $Cp_2Zr(Cl)(OSO_2CF_3)$ to new unsymmetrical unsaturated acyclic 1,1-diphosphines **6** or **7** (Scheme 1). The ^{31}P NMR spectra of **6** and **7** reveal the presence of two doublets at −48.3 and 71.7 ($^1J(PP)$ = 125.4 Hz) ppm for **6** and −47.6 and 78.9 ($^1J(PP)$ = 130.6 Hz) ppm for **7**. These values are in agrement with the proposed structures which are corroborated by other NMR data as well as by mass spectrometry. Similarly addition of organic electrophiles such as the Eschenmoser salt $[CH_2{=}NMe_2]Cl$, the acyl chloride ^{t}BuCOCl, or triflic acid to the metalated phospholane **3** afford the unsaturated phosphines **8**, **9**, and **10** arising from a clean and mild cleavage of the phospholane ring. No substitution reaction which would have resulted in the formation of β-substituted phospholanes **11** has been detected. Moreover, it can be noted that direct addition of an electrophile such as $[CH_2{=}NMe_2]Cl$ or $HOSO_2CF_3$ to phospholene **1** gives rise to the corresponding cyclic phosphonium salts $Ph(E)P^+CH_2CH{=}CHCH_2X^-$ (E = CH_2NMe_2, H; X = I, OSO_2CF_3) and not to ring-opening products. Furthermore, hydrozirconation of these salts does not take place.

Therefore, it appears that the ring-opening process necessitates the preliminary β-zirconation of the phospholene. Concomitant attack of the electrophile on the phosphorus atom of the ring and nucleophilic attack of the anion X^- (X = Cl, OSO_2CF_3) on the Zr center may be ascribed for the ring opening,[7] the transient resulting β anionic cyclic system being highly unstable.

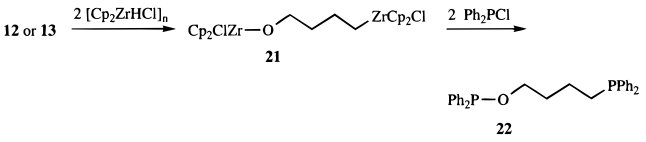
Oxygen Heterocycles. Apparently, the same type of ring opening occurs when oxygen-containing heterocycles such as 2,5-dihydrofuran (**12**) or 2,3-dihydrofuran (**13**) are submitted to hydrozirconation and then to the addition of electrophiles such as **4**, chlorodiphenylphosphine, benzoyl chloride, triflic acid, or *N*,*N*-dimethylmethyleneammonium chloride. Indeed, the expected acyclic compounds **16-20** coming from oxygen−carbon bond cleavage are isolated in excellent yields (60−90%) (Scheme 2). The transient zirconated ring systems **14** or **14′** are not observed. Due to the oxophilicity of zirconium, migration of the Cp_2ZrCl fragment rapidly occurs giving rise to the linear derivative **15**, which is isolated and fully characterized. Therefore, in the case of these heterocycles, ring-opening reactions are initiated by the Schwartz reagent and not by the addition of electrophiles. This is in marked contrast with what we have observed with the phosphorus-containing heterocycle **1**.

(5) Wipf, P.; Xu, W. *Synlett*. **1992**, *33*, 718.

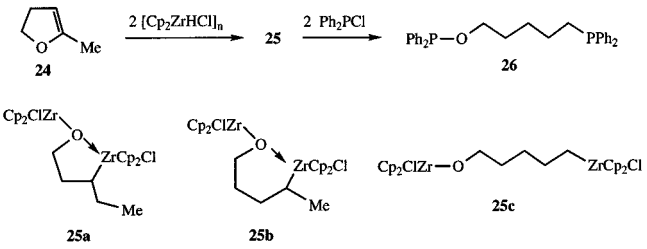
(6) (a) Hanzawa, Y.; Ito, H.; Ito, Taguchi, T. *Synlett* **1995**, *4*, 299. (b) Ito, H.;Ikeuchi, Y.; Taguchi, T.; Hanzawa, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5469−70. (c) Annby, U.; Karlsson, S.; Gronowitz, S.; Hallberg, A.; Alvhäll, Svenson, R. *Acta Chem. Scand.* **1993**, *47*, 425−33. (d) Cuny, G. D.; Buchwald, S. L. *Organometallics* **1991**, *10*, 363. (e) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *Organometallics* **1988**, *7*, 2324−28.

(7) Ring-opening reactions of cyclic phosphines are very rare. See: (a) Quin, L. D.; Hughes, A. N. In *The Chemistry of Organophosphorus Compounds*; Pataï, P., Series Ed.; Hartley, F. R., Ed.; John Wiley & Sons: New York, 1990; Vol. 1, Chapter 10. (b) Quin, L. D.; Roser, C. E. *J. Org. Chem.* **1974**, *23*, 3423.

Scheme 3



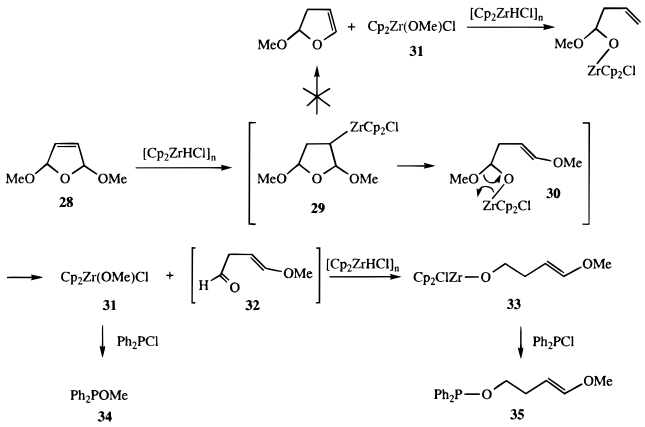
Scheme 4



Treatment of **12** or **13** with 2 equiv of $[Cp_2ZrHCl]_n$ leads directly to the dihydrozirconated species **21**. An easy exchange reaction takes place when **21** is reacted with 2 equiv of Ph_2PCl affording the phosphinito−phosphine **22** [$\delta(^{31}P)$ = 111.4 ($OPPh_2$), −15.6 ($CPPh_2$) ppm] isolated as its disulfide form **23** [$\delta(^{31}P)$ = 81.2 ($OP(S)Ph_2$), 42.5 ($CP(S)Ph_2$) ppm] (Scheme 3).[8] Thus, these reactions can be orientated, for example, depending on the ratio of reagents, to the one-pot synthesis either of a 1,5-diphosphorus species or of an unsaturated monophosphorus compound.

With a view to enhance the practical applications of such a methodology and to check if the presence of ring substituents does not interfer with the ring opening process, we further add **2** (2 equiv) to a THF solution of 2-methyl-4,5-dihydrofuran (**24**). Here also ring opening occurs leading to the stable acyclic dizirconated species **25** (Scheme 4). ^1H and ^{13}C 2D NMR experiments (GE-COSY, GE-HMQC ^1J, and GE-HMQCLR) allow one to choose unambiguously structure **25a** and to reject both structures **25b,c**. Compound **25a** does not exist in the isomeric form **25c** after heating 2 h at 55 °C. This unprecedented observation may be due to internal chelation of the zirconium fragment by the oxygen of the alkoxy group. Such a chelation was already observed in the hydrozirconation reaction of vinyldiphenylphosphine oxide.[9] Note that compound **25c** is independently prepared (see hereafter and Scheme 9). Nevertheless the reaction of **25** with 2 equiv of Ph_2PCl gives rise to the phosphinito−phosphine **26** (Scheme 4) demonstrating that the sequence of reversible β-hydrogen elimination and addition, which is basically the reason for the high regioselectivity within hydrozirconation, occurs in this case but *only during the exchange reaction*.

Scheme 5



The phosphinito−phosphine **26** [$\delta(^{31}P)$ = 111.4 ($OPPh_2$), −15.6 ($CPPh_2$) ppm] is isolated as its disulfide adduct **27** [$\delta(^{31}P)$ = 80.9 ($OP(S)Ph_2$), 42.0 ($CP(S)Ph_2$) ppm] in 50% yield after workup.[10]

Hydrozirconation of 2,5-dimethoxy-2,5-dihydrofuran (**28**) with 2 equiv of **2** gives rise to the two isolated zirconated species **31** and **33** in a 1/1 ratio (Scheme 5). It is reasonable to postulate that the first step of the reaction is hydrozirconation of the intracyclic carbon−carbon double bond of **29** followed by migration of Cp_2ZrCl with transient formation of **30**. Elimination of $Cp_2Zr(OMe)Cl$ (**31**) from **30** leads to the aldehyde **32**, which reacts as soon as formed with the second 1 equiv of **2** to give **33**. ^1H and ^{13}C NMR data unambiguously prove the structure of **33**. Further addition of Ph_2PCl (2 equiv) to the mixture **31** and **33** affords phosphinites **34** and **35** exclusively. Compound **34** can be separatively prepared by reacting $Cp_2ZrCl(OMe)$, prepared from a literature procedure,[11] with Ph_2PCl.

The foregoing results clearly show that ring opening of oxygen heterocycles easily occurs when they are submitted to hydrozirconation, the presence of substituents dramatically changing the orientation of the reaction. The resulting zirconated acyclic compounds react with chlorodiphenylphosphine as an example of the attack of electrophiles to give a variety of saturated or unsaturated phosphinites or phosphinito−phosphines. One can also conclude that hydrozirconation followed by the ring-opening process is faster than the hydrozirconation of the terminal alkene, which is not the case in the hydrozirconation reaction of dihydropyran.

Nitrogen Heterocycles. Hydrozirconation of 1-benzyl-3-pyrroline (**36**) gives rise univocally to the stable expected β-zirconated nitrogen five-membered ring **37** fully characterized by NMR. No ring opening was

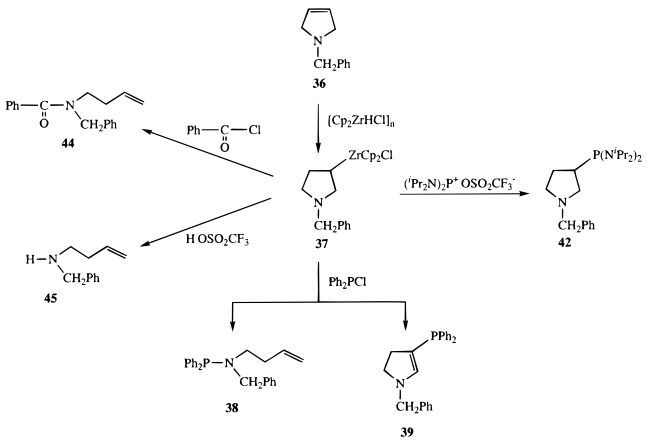
(8) $Ph_2PO(CH_2)_3CH_3$ ($\delta(^{31}P)$ = 111.4 ppm) isolated as its corresponding sulfide ($\delta(^{31}P)$ = 78.9 ppm) is also formed (15%). Its formation can be easily explained from partial hydrolysis of the C−Zr bond in **21**, giving $Cp_2Zr(Cl)O(CH_2)_3CH_3$ which reacts with Ph_2PCl. Selected data for $Ph_2P(S)O(CH_2)_3CH_3$ are as follows. It is a colorless oil isolated and chromatographed [silica gel eluted with 2/1 pentane/CH_2Cl_2 (R_f = 0.32, 15% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.9. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 13.5 (s, CH_3), 18.8 (s, CH_2), 32.2 (d, $^3J(CP)$ = 8.1, CH_2-CHOP), 64.5 (d, $^2J(CP)$ = 5.8, CH_2OP), 128.3 (d, $^3J(CP)$ = 13.6, *m*-Ph), 130.18 (d, $^2J(CP)$ = 11.6, *o*-Ph), 131.58 (s, *p*-Ph), *i*-Ph (not detected). ^1H NMR ($CDCl_3$): δ 0.87 (t, $^3J(HH)$ = 7.3, 3H, CH_3), 1.39 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 3.97 (td, $^3J(HH)$ = 6.5, $^3J(HP)$ = 7.9, 2H, CH_2OP), 7.34−7.42 and 7.78−7.87 (m, 10H, Ph). Mass spectrum: *m*/*z* 290, $[M]^+$. Anal. Calcd for $C_{16}H_{19}OPS$: C, 66.18; H, 6.59. Found: C, 66.12; H, 6.54.

(9) Zablocka, M.; Igau, A.; Majoral, J. P.; Pietrusiewicz, K. M. *Organometallics* **1993**, *12*, 603.

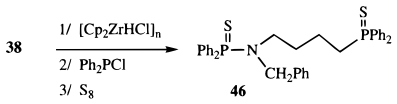
(10) $Ph_2PO(CH_2)_4CH_3$ ($\delta(^{31}P)$ = 111.4 ppm) isolated as its corresponding sulfide ($\delta(^{31}P)$ = 79.4 ppm) is also formed (20%). Its formation can be easily explained from partial hydrolysis of the C−Zr bond in **25**, giving $Cp_2Zr(Cl)O(CH_2)_4CH_3$ which reacts with Ph_2PCl. Selected data for $Ph_2P(S)O(CH_2)_4CH_3$, isolated by chromatography [silica gel eluted with 1/4 pentane/dichloromethane (R_f = 0.74)], are as follows. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 79.0. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 14.0 (s, CH_3), 22.5 (s, CH_2), 28.0 (s, CH_2), 30.3 (d, $^3J(CP)$ = 8.2, CH_2CH_2OP), 64.9 (d, $^2J(CP)$ = 5.7, CH_2OP), 128.3 (s, *m*-Ph), 131.4, (d, $J(CP)$ = 10.6, *o*-Ph), 131.6 (d, $J(CP)$ = 1.2, *p*-Ph), *i*-Ph (not detected). ^1H NMR (C_6D_6): δ 0.75 (m, 3 H, CH_3), 1.07−1.16 (m, 4H, CH_2), 1.45 (m, 2H, CH_2CH_2-OP), 3.96 (td, $^3J(HH)$ = 6.5, $^3J(HP)$ = 8.3, 2H, CH_2OP), 6.99−7.05 (m, 6H, Ph), 7.98−8.07 (m, 4H, Ph). Mass spectrum: *m*/*z* 304, $[M]^+$. Anal. Calcd for $C_{17}H_{21}OPS$: C, 67.08; H, 6,95. Found: C, 66.85; H, 7.02.

(11) Erker, G.; Schlund, R.; Albrecht, M.; Sarter, C. *J. Organomet. Chem.* **1988**, *353*, C27.

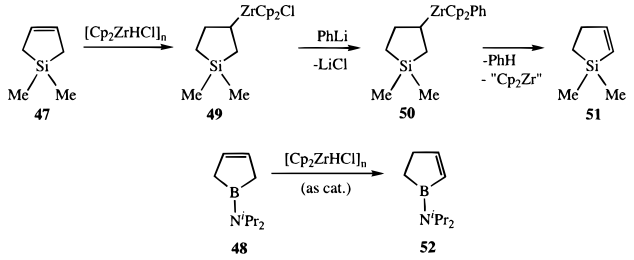
Scheme 6



Scheme 7



Scheme 8



observed. However, the versatile behavior of **37** toward electrophiles can be pointed out. Addition of chlorodiphenylphosphine to **37** in THF solution leads to two main products: the new acyclic aminophosphine **38** (50% yield) and the unexpected 1-benzyl-3-(diphenylphosphino)-2-pyrroline (**39**) (40% yield) (Scheme 6). Derivatives **38** and **39** were isolated as their corresponding sulfides **40** and **41**. The ^{31}P NMR spectra of **38** (δ = 65.1 ppm) or **40** (δ = 68.1 ppm) are typical for aminodiphenylphosphine or aminodiphenylphosphine sulfide. The presence of a homoallyl substituent on nitrogen in **38** is clearly shown by ^{1}H and ^{13}C NMR, and mass spectrometry corroborates such an assignment. The formation of **38** can be explained with the same mechanism proposed for the ring opening of the β-zirconated phospholane **3**, while that of **39** may involve the following steps: β hydride elimination to give 1-benzyl-2-pyrroline and then electrophilic addition of Ph_2PCl to the enamine followed by loss of H^+. The HCl produced could then consume $[Cp_2ZrHCl]_n$ formed in the process. Compounds **39** and **41** are also fully characterized by NMR, mass spectrometry, and elemental analyses. For example, the ^{31}P NMR spectrum of **39** or **41** consists of one singlet at −20.5 ppm (**39**) or at +32.7 ppm (**41**), these chemical shifts being characteristic of phosphine or phosphine sulfide with a $C-PPh_2$ linkage.

Again surprising is the reaction of the phosphenium salt **4** with the cyclic β-zirconated species **37**: no ring opening is detected here, and only the product **42** arising from a direct exchange reaction between $(^iPr_2N)_2P^+$ and the $ZrCp_2Cl$ fragment is isolated (85% yield after workup)! Addition of sulfur to **42** affords the corresponding sulfide **43**.

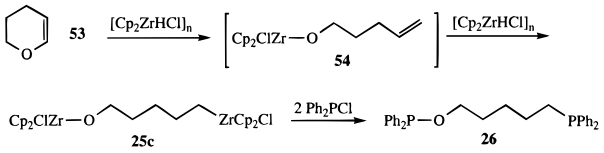
Indeed treatment of **37** with Ph_2PCl or $(^iPr_2N)_2P^+$ points out the different behavior of the β-zirconated nitrogen five-membered ring in comparison with β-zirconated phosphorus five-membered ring (see above). This might be due to the difference of nucleophilicity of phosphorus and nitrogen, phosphines being generally better nucleophiles than amines. Reactions are slower with pyrroline derivatives than with phospholane allowing competitive reactions, such as exchange reaction, to take place.

However, an electrophile as benzoyl chloride leads to the ring-opening product **44** (60% yield) when it is reacted with **37**. Such an intracyclic carbon−nitrogen bond cleavage is also observed when **37** is treated with triflic acid to give the expected homoallylamine **45**. The very poor yield of **45** (5%) may be explained by the formation of oligomers coming from the polymerization of **45** in the reaction conditions. Last, it is of interest to note that hydrozirconation of **38** followed by addition of Ph_2PCl and of S_8 affords the new aminophosphine−phosphine disulfides **46** (65% yield) fully characterized by NMR and mass spectrometry (Scheme 7). Such a disubstitution process was already observed with the corresponding 2,5- or 2,3-dihydrofurans **12** or **13** (see above).

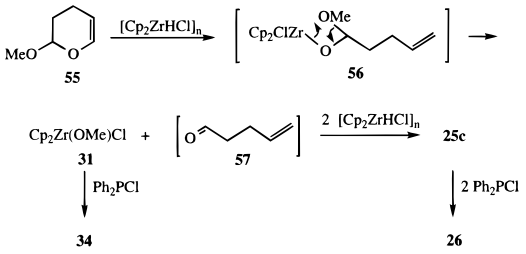
Silicon and Boron Heterocycles. To gain some insight into the mechanism of the reaction, we turn our attention toward the behavior of sila- or boracyclopentenes. Hydrozirconation of silacyclopentene **47** or of the corresponding boron derivative **48** followed by addition of Ph_2PCl is further investigated in order to check if the replacement of a donor heteroatom by an electron-deficient heteroatom included in the ring does not prevent such ring-opening reactions. Hydrozirconation of **47** in solution in THF gives rise quantitatively to the β-zirconated silacyclopentane **49** as indicated by ^{1}H, ^{13}C, and ^{29}Si NMR. **49** is found to be thermally stable after heating 1 h at 40 °C and does not isomerize into the 2-zircona isomer. **49** is also unreactive toward a variety of electrophiles such as **4**, Ph_2PCl, and even PCl_3 in the presence or not of $AlCl_3$! The reasons for such a lack of reactivity are not clear at present (presence of a Si−Cl−Zr bridge?). Addition of phenyllithium to **49** leads to the metalated silacyclopentane **50** which slowly evolves to the 2-silacyclopentene **51** (Scheme 8). **50** is stable enough to be fully characterized by NMR. Intramolecular elimination of benzene (detected in the resulting mixture) can be postulated; final zirconium species have not been identified. Therefore, it can be concluded that no ring opening of 3-silacyclopentene occurs here, in marked contrast with phosphorus, oxygen, or nitrogen heterocycles: isomerization into 2-silacyclopentene is only observed. Isomerization of 3-boracyclopentene **48** into 2-boracyclopentene **52** is also found when **48** is treated with even a catalytic amount of **2**. Such a catalytic isomerization was already observed using the rhodium complex $[RhCl(C_2H_4)_2]$ instead of **2**.[12] However, hydrozirconation of **48** is never detected and hydrozirconation of **52** does not take place. Additional experiments have to be done to rationalize the formation of **51** and **52**; it appears anyway that a

(12) Herberich, G. E.; Boveleth, W.; Hessner, B.; Hostalek, M.; Köffer, D. P. J.; Ohst, H.; Söhnen, D. *Chem. Ber.* **1986**, *119*, 420.

Scheme 9



Scheme 10



ring-opening process occurs *only* with five-membered rings possessing an intracyclic donor heteroatom. As a supplementary proof, the zirconium-promoted ring opening of cyclopentene is found to proceed inefficiently.

Six-Membered Rings. It is of particular interest in a synthetic context that zirconium-promoted ring-opening reactions can be extended to six-membered rings. Indeed hydrozirconation of 3,4-dihydro-2*H*-pyran (**53**) occurs when a THF solution of this compound (1 equiv) and **2** (1 equiv) are stirred overnight at room temperature or heated at 50 °C for 2 h. Nevertheless the final product is not the unsaturated species **54** but the dizirconated acyclic compound **25c**, half of the starting pyran **53** being recovered. The same reaction performed with **53** and **2** in a 1/2 ratio leads exclusively to **25c** (Scheme 9). These results can be easily explained if one considers that hydrozirconation of the six-membered ring is slower than that of the acyclic unsaturated species **54**. This can be compared with hydrozirconation of 2,5-dihydrofuran (**12**) or 2,3-dihydrofuran (**13**) (see above), which necessitates only 15 mn of stirring at 25 °C to go to completion.

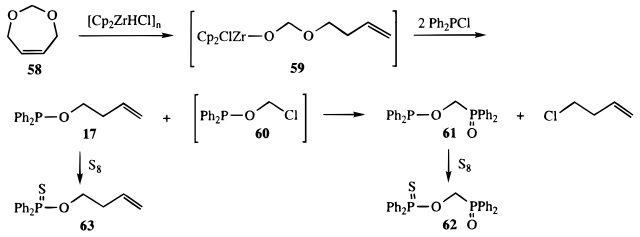
Treatment of **25c** with Ph_2PCl (2 equiv) affords the phosphinito−phosphine **26** (80% yield); the phosphinite $Ph_2PO(CH_2)_4CH_3$ is also obtained as a byproduct (10% yield).

Ring opening of 2-methoxy-3,4-dihydro-2*H*-pyran (**55**) via hydrozirconation proceeds as with the corresponding five-membered ring **28**. Three equivalents of the Schwartz reagent **2** for 1 equiv of **55** are necessary to obtain a clean reaction with the formation of Cp_2Zr(OMe)Cl and $Cp_2Zr(Cl)O(CH_2)_5(Cl)ZrCp_2$ (**25c**) in a 1/1 ratio (Scheme 10). It is also reasonable to postulate here that the first step of the reaction is the ring opening affording the acyclic metalated compound **56**, which gives further Cp_2Zr(OMe)Cl and the transient aldehyde **57**. Hydrozirconation of **57** with 2 equiv of **2** affords **25c**. Compound **55** is partially recovered if hydrozirconation is conducted with 1 or 2 equiv of **2** instead of 3 equiv.

Addition of 3 equiv of chlorodiphenylphosphine to the 1/1 mixture of Cp_2Zr(OMe)Cl and **25c** results in the formation of the expected phosphinite Ph_2POMe and of the phosphinito−phosphine $Ph_2PO(CH_2)_5PPh_2$ (**26**) (Scheme 10).

Seven-Membered Ring. Ring opening induced by the Schwartz reagent is not limited to five- or six-membered rings. This reaction can also be applied to seven-membered rings. As an example, addition of a THF solution of *cis*-dihydro-1,3-dioxepin (**58**) (1 equiv) to a suspension of **2** (1 equiv) in THF followed by treatment of the resulting mixture with 2 equiv of Ph_2PCl led to two compounds: the diphosphorus species **61** [$\delta(^{31}P) = 124.8$ (d, $^3J(PP) = 30.6$ Hz, $OPPh_2$), 23.4 (d, $^3J(PP) = 30.6$ Hz, $CH_2P(O)Ph_2$) ppm] and 4-chlorobutene ($Cl(CH_2)_2CH{=}CH_2$). Derivative **61** is isolated as its sulfide **62** [$\delta(^{31}P) = 85.8$ (d, $^3J(PP) = 32.2$ Hz ($OP(S)Ph_2$)), 23.8 (d, $^3J(PP) = 32.2$ Hz ($CH_2P(O)Ph_2$) ppm]. The following mechanism can be proposed to explain these quite surprising results (Scheme 11). The first step should be hydrozirconation of the carbon−carbon double bond of **58** followed by ring opening as expected. Addition of chlorodiphenylphosphine affords the phosphorus derivatives **17** and **60**, and then an Arbusov type reaction between **17** and **60** gives rise to **61** and 4-chlorobutene. Such a mechanism is corroborated by several observations: (i) two singlets at 115.4 and 111.8 ppm are observed in ^{31}P NMR at low temperature besides the doublet of doublet due to the diphosphorus species **61**. This is consistent with the transient formation of compounds **17** and **60** (the observed $\delta(^{31}P)$ are in the expected range for such trivalent species), which react one with another to give **61**. (ii) **17** is trapped by adding sulfur, and the corresponding sulfide **63** is isolated and fully characterized. (iii) 4-Chlorobutene is characterized by gas chromatography in the resulting mixture.

Scheme 11



Although it is not possible to isolate the phosphinite **60**, it seems that the proposed mechanism is plausible but deserves of course other experiments to be corroborated without any doubt.

Nevertheless once again the zirconium-promoted ring opening can be observed for a seven-membered ring.

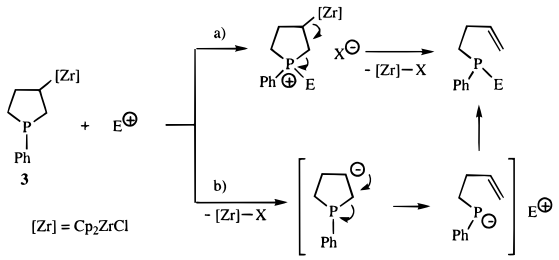
Conclusion

Several main features of this useful ring opening methodology can be emphasized.

(1) Zirconium-promoted ring opening generally occurs with mono-unsaturated heterocycles possessing one donor heteroatom whatever the size of the given heterocycle: five-, six-, or seven-membered rings. However the behavior of 1-benzyl-3-pyrroline is more versatile.

(2) Nucleophilicity of the donor heteroatom plays a decisive role. Ring opening of oxygen heterocycles [2,5-dihydrofuran (**12**), 2,3-dihydrofuran (**13**), 2-methyl-4,5-dihydrofuran (**24**), 2,5-dimethoxy-2,5-dihydrofuran (**28**), 3,4-dihydro-2*H*-pyran (**53**), 2-methoxy-3,4-dihydro-2*H*-pyran (**55**), *cis*-dihydro-1,3-dioxepin (**58**)] is induced by hydrozirconation. In contrast, ring opening of phosphorus heterocycles such as the phospholene **1** necessitates addition of an electrophile *following* that of the Schwartz

Scheme 12



reagent **2**; as for oxygen heterocycles, ring opening is quantitative. Due to the lower nucleophilicity of the nitrogen of 1-benzyl-3-pyrroline (**36**), competitive reactions take place when **36** is submitted first to hydrozirconation and then to addition of an electrophile:ring opening but also exchange reactions with ring retention occur.

(3) The presence of ring substituents (methyl, methoxy groups) does not prevent the ring opening of oxygen-containing heterocycles.

(4) No ring opening occurs with silicon- or boron-containing heterocycles such as **47** or **48**. Only isomerization of 3-silacyclopentene **47** into 2-silacyclopentene **51** and isomerization of 3-boracyclopentene **48** into 2-boracyclopentene **52** are detected.

(5) The ratio of heterocycle derivatives versus $[Cp_2ZrHCl]_n$ used in these reactions and therefore the number of equivalents of electrophiles such as Ph_2PCl dramatically directs the reaction either to the formation of unsaturated (or not) phosphines and phosphinites or to the formation of 1,1-diphosphines or 1,2-, 1,5-, or 1,6-phosphinito−phosphines, some of them being new or difficult to obtain via more classical procedures.

How can the mechanism of the electrophile inducing the ring opening of the β-zirconated phospholane **3** be seen? The key point is to determine if it is the addition of the electrophile on the phosphorus atom which induces the ring-opening process (Scheme 12, path a) or the attack of the anion on the metal fragment to give a negative charge on β position to the cyclic heteroatom, the last step being the isomerization of the resulting compound into the linear derivative (Scheme 12, path b). This last mechanism seems, in a first approach, more likely as it has already demonstrated that a negative charge at the β position on a cyclic heteroatom provokes the ring-opening process.[13] However such a ring-opening process should be applied to the silacyclopentene **47**; but as demonstrated, no ring-opening reaction occurred in that case. Therefore one might postulate for the ring opening of **3** path a and not path b. Nevertheless additional experiments have to be perform to elucidate without any doubt this mechanism.

Extension of this useful methodology to more elaborated systems such as polycyclic or macrocyclic species is underway.

Experimental Section

All manipulations were carried out under an argon atmosphere, either on a high-vacuum line using standard Schlenk techniques or in a Braun MB 200-G drybox. Solvents were freshly distilled from dark purple solutions of sodium/benzophenone ketyl (THF, diethyl ether), lithium aluminium hydride (pentane), or CaH_2 (CH_2Cl_2). C_6D_6, CD_2Cl_2, and $CDCl_3$ were treated respectively with $LiAlH_4$ and CaH_2, distilled, and stored under argon. 2,5-Dihydrofuran (**12**), 2,3-dihydrofuran (**13**), 2-methyl-4,5-dihydrofuran (**24**), 2,5-dimethoxy-2,5-dihydrofuran (**28**), 1-benzyl-3-pyrroline (**36**), 3,4-dihydro-2*H*-pyran (**53**), 2-methoxy-3,4-dihydro-2*H*-pyran (**55**), and *cis*-dihydro-1,3-dioxepin (**58**) were purchased from Aldrich and used without further purification. $[Cp_2ZrHCl]_n$ (Schwartz's reagent) (**2**) was synthesized by the method of Buchwald et al.[14] **47**[15] and **48**[12] were prepared according to the literature procedure.

Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on Bruker AMX 400, WM-250, AC-200, and AC-80 Fourier transform spectrometers. Chemical shifts are expressed in ppm upfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Coupling constants (J) are given in hertz. The ^{13}C NMR assignments were confirmed by proton-decoupled and/or selective heteronuclear-decoupled spectra. In the case of compound **25a**, NMR experiments were recorded on a Bruker AMX 400 using UXNMR Bruker software. 1D ^1H with integration (F2, sw2 = 7.22, TD2 = 32 K for the acquisition) and $^{13}C\{^1H\}$ (F2, sw2 = 236, TD2 = 32 K for the acquisition) spectra were obtained in C_6D_6 at 300 K and then Fourier transformed. The following correlations were done on the same sample. (a) $\delta(^1H)-\delta(^1H)$ (GE-COSY): acquisition parameters F2 dimension (sw2 = 3.72, TD2 = 4 K, D1 = 15 s), F1 dimension (sw1 = 3.72, TD1 = 256 w); processing parameters F2, TD2 = SI2 = 4 K, F1, TD1 zero filled to 1 K, square sine bell filter in both dimensions and then Fourier transformed. (b) $\delta(^1H)-\delta(^{13}C)\{^{13}C\}$ (GE-HMQC ^1J, D2 = 3.5 ms): acquisition parameters F2 dimension (sw2 = 6.15, TD2 = 4 K, D1 = 1 s), F1 dimension (sw1 = 131, TD1 = 256 w); processing parameters F2 (TD2 = SI2 = 4 K, exponential filter (LB = 1)), F1 (TD1 zero filled to 1 K, exponential filter (LB = 7)) and then Fourier transformation in both dimensions. (c) $\delta(^1H)-\delta(^{13}C)\{^{13}C\}$ (GE-HMQC LR, D2 = 50 ms): acquisition parameters and processing parameters identical to those in (b). Chemical analyses were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS. Mass spectra were obtained on a Nermag R10-10H. Melting point were determined in evacuated capillaries and were corrected and calibrated.

$PhPCH_2CH(ZrCp_2Cl)CH_2CH_2$ (3). To a magnetically stirred solution of **1** (0.146 g, 0.9 mmol) in THF (5 mL) cooled at −20 °C was added a suspension of $[Cp_2ZrHCl]_n$ (**2**) (0.232 g, 0.9 mmol) in THF (5 mL). The mixture was stirred for 15 min at −20 °C and then allowed to warm slowly at room temperature and stirred for 3 h. During this time, the solution turned dark brown and became homogeneous. Evaporation of THF gave quantitatively **3** as a dark brown powder. $^{31}P\{^1H\}$ NMR (THF): δ −10.3. $^{13}C\{^1H\}$ NMR ([D8]THF): δ 30.7 (d, $^1J(CP)$ = 11.8 Hz, PCH_2CH_2), 39.2 (d, $^2J(CP)$ = 1.3 Hz, PCH_2CH_2), 40.2 (d, $^1J(CP)$ = 16.9 Hz, PCH_2CH), 66.2 (d, $^2J(C,P)$ = 6.6 Hz, CHZr), 115.4 (s, Cp), 127.8 (s, *p*-Ph), 129.2 (d, $^3J(C,P)$ = 6.8 Hz, *m*-Ph), 131.5 (d, $^2J(C,P)$ = 14.8 Hz, *o*-Ph), 145.4 (d, $^1J(C,P)$ = 25.7 Hz, *i*-Ph).

$(^iPr_2N)_2PP(Ph)(CH_2)_2CH{=}CH_2$ (6). To a solution of chlorobis(diisopropylamino)phosphine (0.267 g, 1.0 mmol) in 15 mL of dichloromethane at −78 °C was added trimethylsilyl triflate (193 μL, 1.0 mmol). The mixture was stirred at room temperature for 1 h and then cooled to −40 °C. To this solution was added the β-zirconated phospholane **3** (0.420 g, 1.0 mmol) in 5 mL of THF. The resulting mixture was stirred for 10 min at −40 °C and then for 1 h at 25 °C. Removal of the solvents followed by extraction with pentane (4 × 10 mL) gave **6** as a yellow oil (95% yield from **3**). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −48.3 (d, $^1J(PP)$ = 125.4, PPh), 71.7 (d, $^1J(PP)$ = 125.4, PN^iPr). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 24.3, 24.4, 24.5, 24.7 (s, CH_3), 27.2 (dd,

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^1J(CP) = 27.6, ^2J(CP) = 16.3, CH_2P), 32.0 (dd, ^2J(CP) = 14.7, ^3J(CP) = 9.9, CH_2CH=), 48.9 (dd, ^2J(CP) = 8.5, ^3J(CP) = 8.5, CHN), 114.3 (s, =CH_2), 128.2 (s, *p*-Ph), 128.6 (s, *m*-Ph), 136.1 (dd, ^2J(CP) = 19.0, ^3J(CP) = 7.7, *o*-Ph), 137.6 (dd, ^1J(CP) = 17.6, ^2J(CP) = 8.3, *i*-Ph), 139.5 (d, ^3J(CP) = 11.5, CH=) ppm. ^{1}H NMR (δ) 0.73 (d, ^3J(HH) = 6.6, 3H, CH_3), 1.06 (d, ^3J(HH) = 6.8, 3H, CH_3), 1.15 (d, ^3J(HH) = 6.6, 3H, CH_3), 1.17 (d, ^3J(HH) = 6.7, 6H, CH_3), 1.22 (d, ^3J(HH) = 5.1 3H, CH_3), 1.26 (d, ^3J(HH) = 5.2, 6H, CH_3), 1.85−2.35 (m, 4H, CH_2), 3.60 (m, 4H, HCN), 4.96 (m, 2H, =CH_2), 5.88 (m, 1H, CH=), 7.06−7.93 (m, 5H, Ph). Mass spectrum: *m*/*z* 394, $[M]^+$. Anal. Calcd for $C_{22}H_{40}N_2P_2$: C, 66.98; H, 10.22. Found: C, 66.91; H, 10.16.

$(Cy_2N)_2PP(Ph)(CH_2)_2CH$=$CH_2$ (7). In a procedure analogous to that given for **6**, treatment of **3** (0.420 g, 1.0 mmol) with **5** [$(Cy_2N)_2PCl$ (0.427 g, 1.0 mmol) and trimethylsilyl triflate (193 μL, 1.0 mmol)] gave **7** as a yellow oil (95% yield from **3**). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −47.6 (d, ^1J(PP) = 130.6, PPh), 78.9 (d, ^1J(PP) = 130.6, PNCy). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 25.4−28.6 and 34.2−37.2 (m, CH_2), 59.6 (m, CH_{cy}), 114.7 (s, =CH_2), 128.6 (s, *p*-Ph), 129.6 (s, *m*-Ph), 137.0 (dd, ^2J(CP) = 18.8, ^3J(CP) = 7.9, *o*-Ph), 138.7 (dd, ^1J(CP) = 21.7, ^2J(CP) = 11.9, *i*-Ph), 140.0 (d, ^3J(CP) = 11.0, CH=). ^{1}H NMR (C_6D_6): δ 1.01−2.05 (m, 40H, CH_2), 3.22 (m, 4H, HCN), 4.95 (m, 2H, =CH_2), 5.87 (m, 1H, CH=), 7.10−7.16 (m, 2H, Ph) 7.87−7.91 (m, 3H, Ph). Mass spectrum: *m*/*z*, 555 $[M]^+$. Anal. Calcd for $C_{34}H_{56}N_2P_2$: C, 73.61; H, 10.18. Found: C, 73.44; H, 10.11.

$Me_2NCH_2P(Ph)(CH_2)_2CH$=CH_2 (8). To a suspension of $[CH_2$=$NMe_2]Cl$ (0.094 g, 1.0 mmol) in 5 mL of THF was added the β-zirconated phospholane **3** (0.420 g, 1.0 mmol) in solution in 5 mL of THF at −78 °C. The resulting mixture was allowed to warm to room temperature and then stirred for 2 h at 25 °C. Evaporation of the solvent followed by several washings of the crude product with 2 × 20 mL of ether gave **8** as a colorless oil (80% yield). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −39.5. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 26.5 (d, ^1J(CP) = 7.8, CH_2P), 29.7 (d, ^2J(CP) = 16.1, CH_2CH=), 44.3 (d, ^3J(CP) = 6.5, NCH_3), 59.2 (d, ^1J(CP) = 20.1, NCH_2P), 115.3 (s, =CH_2), 129.3 (d, ^3J(CP) = 8.5, *m*-Ph), 130.7 (s, *p*-Ph), 133.3 (d, ^2J(CP) = 20.8, *o*-Ph), 137.8 (d, ^3J(CP) = 12.6, CH=), *i*-Ph (not detected). ^{1}H NMR (CD_2Cl_2): δ 2.12 (m, 4H, CH_2), 2.68 (d, ^4J(HP) = 4.4, 3H, NCH_3), 2.87 (d, ^4J(HP) = 4.5, 3H, NCH_3), 3.54 (d, ^2J(HP) = 2.8, 2H, NCH_2P), 5.02 (m, 2H, =CH_2), 5.84 (m, 1H, CH=), 7.45−7.75 (m, 5H, Ph). Mass spectrum: *m*/*z* 222, $[M + 1]^+$. Anal. Calcd for $C_{13}H_{20}NP$: C, 70.56; H, 9.11. Found: C, 70.41; H, 8.98.

^{t}BuC(O)P(Ph)$(CH_2)_2CH$=CH_2 (9). To a solution of the β-zirconated phospholane **3** (0.420 g, 1 mmol) in 5 mL of THF at −78 °C was added ^{t}BuCOCl (123 μL, 1.0 mmol). After the mixture was stirred for 20 min at −78 °C and then for 2 h at room temperature, the solvent was evaporated and the residue extracted with 2 × 40 mL of pentane. **9** was obtained as a yellow oil (80% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −7.1 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 26.0 (d, ^1J(CP) = 8.7, CH_2P), 27.4 (d, ^3J(CP) = 5.6, CCH_3), 28.2 (d, ^2J(CP) = 21.9, CCH_3), 30.8 (d, ^2J(CP) = 18.5, CH_2CH=), 115.2 (s, =CH_2), 129.4 (d, ^3J(CP) = 8.6, *m*-Ph), 130.2 (s, *p*-Ph), 135.4 (d, ^2J(CP) = 20.3, *o*-Ph), 139.3 (d, ^3J(CP) = 13.1, CH=), 144.6 (d, ^1J(CP) = 86.0, *i*-Ph), 168.5 (d, ^1J(CP) = 49.9, CO). ^{1}H NMR (C_6D_6): δ 1.01 (s, 9H, CH_3), 2.08 (m, 2H, CH_2), 2.31 (m, 2H, CH_2), 4.94 (m, 2H, =CH_2), 5.76 (ddt, $^3J(HH_{trans})$ = 17.0, $^3J(HH_{cis})$ = 10.1, ^3J(HH) = 5.8, 1H, CH=), 7.00−7.50 (m, 5H, Ph). Mass spectrum: *m*/*z* 249, $[M + 1]^+$. Anal. Calcd for $C_{15}H_{21}OP$: C, 72.55; H, 8.52. Found: C, 72.42; H, 8.44.

HP(Ph)$(CH_2)_2CH$=CH_2 (10). To a solution of the β-zirconated phospholane **3** (0.420 g, 1.0 mmol) in 5 mL of dichloromethane at −78 °C was added triflic acid (88 μL, 1.0 mmol). The resulting solution was stirred for 20 min at −78 °C and then for 1 h at room temperature. Evaporation of the solvent followed by extraction with 40 mL of ether gave **10** as a colorless oil (90% yield). ^{31}P NMR (CD_2Cl_2): δ −53.0 (d, ^1J(PH) = 211.4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 23.2 (d, ^1J(CP) = 13.0, CH_2P), 32.5 (d, ^2J(CP) = 7.4, CH_2CH=), 115.4 (s, =CH_2), 128.7 (s, *p*-Ph), 129.1 (d, ^3J(CP) = 5.8, *m*-Ph), 134.3 (d, ^2J(CP) = 15.7, *o*-Ph), 139.0 (d, ^3J(CP) = 7.3, CH=), *i*-Ph (not detected). ^{1}H NMR (CD_2Cl_2): δ 2.04 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 4.89 (m, 2H, =CH_2), 5.57 (m, 1H, CH=), 7.05−7.47 (m, 5H, Ph). Mass spectrum: *m*/*z* 164, $[M]^+$. Anal. Calcd for $C_{10}H_{13}P$: $C_{10}H_{13}P$: C, 73.15; H, 7.98. Found: C, 73.01; H, 7.90.

$Cp_2Zr(Cl)O(CH_2)_2CH$=CH_2 (15). To a suspension of $[Cp_2ZrHCl]_n$ (0.258 g, 1.0 mmol) in 5 mL of THF was added 2,3- or 2,5-dihydrofuran (76 μL, 1.0 mmol) at 0 °C. After the mixture was stirred for 2 h at room temperature and evaporation of the resulting yellow solution, the yellow residue was characterized. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 38.7 (s, CH_2CH=), 75.3 (s, CH_2OZr), 113.9 (s, Cp), 116.8 (s, =CH_2), 136.6 (s, CH=). ^{1}H NMR (C_6D_6): δ 2.09 (tdt, ^3J(HH) = 6.5, ^3J(HH) = 6.5, ^4J(HH) = 1.3, 2H, CH_2CH=), 3.86 (t, ^3J(HH) = 6.5, 2H, CH_2OZr), 5.06 (m, 2H, =CH_2), 5.75 (m, 1H, CH=), 5.99 (s, 10H, Cp).

$(^iPr_2N)_2PO(CH_2)_2CH$=CH_2 (16). To a solution of the phosphenium $(^iPr_2N)_2P^+OSO_2CF_3^-$ obtained from $(^iPr_2N)_2PCl$ (0.267 g, 1.0 mmol) and trimethylsilyl triflate (193 μL, 1.0 mmol) (see preparation of **6**) in 5 mL of dichloromethane at −40 °C was added a solution of $Cp_2Zr(Cl)O(CH_2)_2CH$=CH_2 (**15**) (0.328 g, 1.0 mmol) in 5 mL of THF. After the solution was stirred 24 h at room temperature, the solvent was evaporated and the residue extracted with pentane (2 × 40 mL) to give **16** as a yellow oil (75% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 122.1. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 24.4, 24.5, 25.0, 25.2 (s, CH_3), 37.1 (d, ^3J(CP) = 8.7, CH_2CH=), 45.5 (d, ^2J(CP) = 13.0, HCN), 64.6 (d, ^2J(CP) = 21.8, CH_2OP), 116.6 (s, =CH_2), 136.4 (s, CH=). ^{1}H NMR (C_6D_6): δ 1.18, 1.22 (d, ^3J(HH) = 6.8, 12H, CH_3), 2.32 (m, 2H, CH_2CH=), 3.51 (d sept, ^3J(HP) = 10.6, ^3J(HH) = 6.8, 4H, CHN), 3.61 (dt, ^3J(HH) = 6.8, ^3J(HP) = 6.8, 2H, CH_2OP), 5.04 (m, 2H, =CH_2), 5.87 (m, 1H, CH=). Mass spectrum: *m*/*z* 303, $[M + 1]^+$. Anal. Calcd for $C_{16}H_{35}N_2OP$: C, 63.54; H, 11.67. Found: C, 63.44; H, 11.55.

$Ph_2PO(CH_2)_2CH$=CH_2 (17). To a solution of $Cp_2Zr(Cl)O(CH_2)CH$=CH_2 (**15**) (0.328 g, 1.0 mmol) in 5 mL of THF at −78 °C was added chlorodiphenylphosphine (179 μL, 1.0 mmol). After the solution was stirred for 12 h at room temperature and evaporation of the solvent, the residue was extracted with pentane (2 × 40 mL) to give **17** as a yellow oil (75% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 111.8 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 36.7 (d, ^3J(CP) = 7.8, CH_2CH=), 69.9 (d, ^2J(CP) = 19.6, CH_2OP), 117.4 (s, =CH_2), 129.0 (d, ^3J(CP) = 6.8, *m*-Ph), 129.9 (s, *p*-Ph), 131.1 (d, ^2J(CP) = 21.8, *o*-Ph), 135.4 (s, CH=), 143.5 (d, ^1J(CP) = 18.7, *i*-Ph). ^{1}H NMR (C_6D_6): δ 2.26 (dt, ^3J(HH) = 6.7, ^3J(HH) = 6.7, 2H, CH_2CH=), 3.77 (dt, ^3J(HH) = 6.7, ^3J(HP) = 9.1, 2H, CH_2OP), 4.96 (m, 2H, =CH_2), 5.76 (ddt, $^3J(HH_{trans})$ = 16.9, $^3J(HH_{cis})$ = 10.6, ^3J(HH) = 6.7, 1H, CH=), 6.96−7.64 (m, 10H, Ph). Mass spectrum: *m*/*z* 256, $[M]^+$. Anal. Calcd for $C_{16}H_{17}OP$: C, 74.98; H, 6.69. Found: C, 74.72; H, 6.57.

PhC(O)O$(CH_2)_2CH$=CH_2 (18). To a suspension of $[Cp_2ZrHCl]_n$ (0.258 g, 1.0 mmol) in 5 mL of THF at 0 °C was added 2,3- or 2,5-dihydrofuran (76 μL, 1.0 mmol) in 5 mL of THF. The resulting mixture was stirred until all $[Cp_2ZrHCl]_n$ was dissolved (2 h). To this new solution maintained at −78 °C was added PhCOCl (116 μL, 1.0 mmol). The resulting mixture was stirred for 20 min at −78 °C and then for 2 h at 25 °C. Evaporation of the solvent and extraction with pentane (40 mL) gave **18** as a colorless oil (60% yield). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 33.8 (s, CH_2CH=), 64.3 (s, CH_2O), 117.5 (s, =CH_2), 128.9 (s, *m*-Ph), 130.3 (s, *o*-Ph), 131.1 (s, *i*-Ph), 133.3 (s, *p*-Ph), 135.4 (s, CH=), 166.6 (s, CO). ^{1}H NMR (C_6D_6): δ 2.18 (dt, ^3J(HH) = 6.6, ^3J(HH) = 6.6, 2H, CH_2CH=), 4.15 (t, ^3J(HH) = 6.6, 2H, CH_2O), 4.96 (m, 2H, =CH_2), 5.63 (m, 1H, CH=), 6.81−8.14 (m, 5H, Ph). Mass spectrum: *m*/*z* 176, $[M]^+$. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.91; H, 6.81.

HO$(CH_2)_2CH$=CH_2 (19). To a solution of **15** (0.328 g, 1.0 mmol) in 2 mL of C_6D_6 at 0 °C was added triflic acid (88 μL, 1.0 mmol). After the solution was stirred for 20 min at 0 °C and then for 2 h at room temperature, **19** was isolated in 90% yield from the zirconated residue by trap to trap vacuum

transfer. Coinjection with a commercially available sample of **19** proved its structure.

$Me_2NCH_2O(CH_2)_2CH{=}CH_2$ (20). To a suspension of $[Cp_2ZrHCl]_n$ (0.258 g, 1.0 mmol) in 5 mL of THF at 0 °C was added 2,3- or 2,5-dihydrofuran (76 μL, 1.0 mmol). After stirring until the solution was clear, the solvent was evaporated and the residue dissolved in 2 mL of C_6D_6. To this new solution was added $[CH_2{=}NMe_2]Cl$ (0.094 g, 1.0 mmol) as a powder. The resulting mixture was stirred for 2 h at room temperature, and **20** was isolated as a colorless oil by trap to trap distillation (90% yield). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 36.1 (s, $CH_2CH{=}$), 41.9 (s, NCH_3), 68.4 (s, CH_2O), 89.9 (s, OCH_2N), 116.9 (s, $=CH_2$), 136.2 (s, $CH{=}$). ^1H NMR (C_6D_6): δ 2.22 (m, 2H, $CH_2CH{=}$), 2.25 (s, 6H, NCH_3), 3.31 (t, $^3J(HH) = 6.7$, 2H, CH_2O), 3.86 (s, 2H, OCH_2N), 5.02 (m, 2H, $=CH_2$), 5.79 (m, 1H, $CH{=}$). Mass spectrum: m/z, 129 $[M]^+$. Anal. Calcd for $C_7H_{15}NO$: C, 65.07; H, 11.70. Found: C, 64.94; H, 11.49.

$Cp_2Zr(Cl)O(CH_2)_4ZrCp_2Cl$ (21). To a suspension of $[Cp_2ZrHCl]_n$ (0.258 g, 1.0 mmol) in 5 mL of THF at 0 °C was added 2,3- or 2,5-dihydrofuran (38 μL, 0.5 mmol). The resulting solution was stirred for 2 h at room temperature and the solvent evaporated to give quantitatively **21** as a yellow oil. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 30.9 (s, CH_2), 40.6 (s, CH_2), 54.9 (s, CH_2Zr), 75.7 (s, CH_2OZr), 113.1 (s, Cp), 113.9 (s, Cp). ^1H NMR (C_6D_6): δ 1.11 (m, 2H, CH_2), 1.49 (m, 2H, CH_2), 1.72 (m, 2H, CH_2), 3.99 (t, $^3J(HH) = 4.0$, 2H, CH_2OZr), 5.92 (s, 10H, Cp), 6.07 (s, 10H, Cp).

$Ph_2PO(CH_2)_4PPh_2$ (22). To a solution of **21** (0.586 g, 1.0 mmol) prepared as above, in 10 mL of THF at −78 °C, was added chlorodiphenylphosphine (358 μL, 2.0 mmol). After the solution was stirred for 12 h at room temperature, the solvent was evaporated and the residue dissolved in 10 mL of CH_2Cl_2. **22** was identified by $^{31}P\{^1H\}$ NMR [$\delta(^{31}P)$ = 111.4 ($OPPh_2$), −15.6 ($CPPh_2$) ppm]. Sulfur (0.190 g, 6.0 mmol) was added, and the resulting mixture was stirred for 12 h. $Ph_2P(S)O(CH_2)_4P(S)Ph_2$ (**23**) was chromatographed [silica gel eluted with pentane/CH_2Cl_2 (1/2) ($R_f = 0.25$)] and isolated (60% yield) as a colorless oil. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.5 (s, $Ph_2P(S)C$), 81.2 (s, $Ph_2P(S)O$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.5 (s, CH_2), 30.5 (dd, $^3J(CP) = 8.1$, $^3J(CP) = 16.6$, CH_2CH_2O), 31.6 (d, $^1J(CP) = 57.0$, CH_2P), 63.4 (d, $^2J(CP) = 5.1$, CH_2OP), 128.3 (d, $^3J(CP) = 11.3$, *m*-Ph); 128.5 (d, $^3J(CP) = 10.6$, *m*-Ph), 131.0 (d, $^2J(CP) = 9.4$, *o*-Ph), 131.3 (s, *p*-Ph), 131.7 (s, *p*-Ph), *i*-Ph (not detected). ^1H NMR ($CDCl_3$): δ 1.76 (m, 4H, CH_2), 2.45 (m, 2H, CH_2P), 3.96 (td, $^3J(HH) = 5.8$, $^3J(HP) = 7.8$, 2H, CH_2OP), 7.31−7.43 and 7.73−7.82 (m, 20H, Ph). Mass spectrum: m/z 507, $[M + 1]^+$. Anal. Calcd for $C_{28}H_{28}OP_2S_2$: C, 66.39; H, 5.57. Found: C, 66.27; H, 5.51.

Formation of 25a from 24 and 2. To a suspension of $[Cp_2ZrHCl]_n$ (0.258 g, 1.0 mmol) in 5 mL of THF at room temperature was added 2-methyl-4,5-dihydrofuran (46 μL, 0.5 mmol). The solution was stirred for 2 h at 55 °C. Evaporation of the solvent gave an oily residue which was washed with pentane (2 × 20 mL) to give the dizirconated product **25a** (80% yield). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.6 (s, CH_3), 32.0 (s, CH_2CH_3), 38.0 (s, OCH_2CH_2), 62.5 (s, CHZr), 74.9 (s, CH_2OZr), 109.9 (s, Cp), 110.7 (s, Cp). ^1H NMR (C_6D_6): δ 1.32 (m, 1H, CHZr), 1.35 (m, 3H, CH_3), 1.48 (m, $^2J(HH) = 12.3$, 1H, OCH_2CH_2), 1.65 (m, 2H, CH_2CH_3), 2.16 (m, $^2J(HH) = 12.3$, 1H, OCH_2CH_2), 3.14 (m, $^2J(HH) = 9.3$, 1H, OCH_2), 3.55 (m, $^2J(HH) = 9.3$, 1H, OCH_2), 5.75 (s, 5H, Cp), 5.79 (s, 5H, Cp).

$Ph_2PO(CH_2)_5PPh_2$ (26). To a solution of **25a** (0.300 g, 0.5 mmol) in 5 mL of THF at −78 °C was added chlorodiphenylphosphine (180 μL, 1.0 mmol). After the mixture was stirred for 12 h at room temperature, the solvent was evaporated and the residue dissolved in 5 mL of dichloromethane to give **26**. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 111.4 ($OPPh_2$), −15.6 ($CPPh_2$). To this new solution was added sulfur (0.190 g, 6.0 mmol). After the mixture was stirred 12 h at room temperature, $Ph_2P(S)O(CH_2)_5P(S)Ph_2$ (**27**) was isolated by chromatography [silica gel eluted with pentane/dichloromethane 4/1 ($R_f = 0.42$)] in 50% yield. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 80.9 (s, $Ph_2P(S)O$), 42.0 (s, $Ph_2P(S)C$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 22.4 (d, $J(CP) = 2.5$, CH_2), 27.4 (d, $J(CP) = 16.8$, CH_2), 30.4 (d, $J(CP) = 7.8$, CH_2), 32.9 (d, $^1J(CP) = 56.6$, CH_2P), 65.0 (d, $^2J(CP) = 5.8$, CH_2OP), 128.9 (d, $^3J(CP) = 13.8$, *m*-Ph), 129.1 (d, $^3J(CP) = 12.3$, *m*-Ph), 131.5 (d, $^2J(CP) = 10.1$, *o*-Ph), 131.6 (d, $^2J(CP) = 11.3$, *o*-PH), 131.9 (d, $^4J(CP) = 2.9$, *p*-Ph), 132.3 (d, $^4J(CP) = 2.9$, *p*-Ph), *i*-Ph (not detected). ^1H NMR (C_6D_6): δ 1.22 (m, 4H, CH_2), 1.61 (m, 2H, CH_2), 2.08 (m, 2H; CH_2), 3.82 (td, $^3J(HH) = 6.1$, $^3J(HP) = 8.3$, 2H, CH_2OP), 7.40−7.87 (m, 20H, Ph). Mass spectrum: m/z 521, $[M + 1]^+$. Anal. Calcd for $C_{29}H_{30}OP_2S_2$: C, 66.90; H, 5,81. Found: C, 66.78; H, 5,92.

$Cp_2Zr(OMe)Cl$ (31) and $Cp_2Zr(Cl)O(CH_2)_2CH{=}CHOMe$ (33). To a suspension of $[Cp_2ZrHCl]_n$ (0.258 g, 1.0 mmol) in 5 mL of THF at 0 °C was added 2,5-dimethoxy-2,5-dihydrofuran (**28**) (61 μL, 0.5 mmol). The solution was stirred for 2 h at 25 °C and became yellow. Removal of the solvent gave an oily residue characterized as it was and by coinjection with $Cp_2Zr(OMe)Cl$. **31**: 50% yield; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 63.9 (s, CH_3O), 114.7 (s, Cp); ^1H NMR (C_6D_6) δ 3.67 (s, 3H, CH_3O), 6.01 (s, 10H, Cp). **33**: 50% yield; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 32.9 (s, $CH_2CH{=}$), 56.0 (s, CH_3O), 76.8 (s, CH_2OZr), 114.0 (s, Cp), 99.8 (s, $=CH$), 149.4 (s, $=CHOMe$); ^1H NMR (C_6D_6) δ 2.00 (tdd, $^3J(HH) = 6.4$, $^3J(HH) = 6.4$, $^4J(HH) = 1.1$, 2H, $CH_2CH{=}$), 3.18 (s, 3H, CH_3O), 3.84 (t, $^3J(HH) = 6.4$, 2H, CH_2OZr), 4.72 (dt, $^3J(HH) = 12.7$, $^3J(HH) = 7.4$, 1H, $CH{=}$), 5.97 (s, 10H, Cp), 6.37 (dt, $^3J(HH) = 12.7$, $^4J(HH) = 1.1$, 1H, $=CHOMe$).

Ph_2POMe (34) and $Ph_2PO(CH_2)_2CH{=}CHOMe$ (35). To the mixture of **31** and **33** (see above) in 5 mL of THF at −40 °C was added chlorodiphenylphosphine (180 μL, 1.0 mmol). The resulting solution was stirred for 2 h at room temperature and then the solvent evaporated to dryness. **34** (50% yield) and **35** (40% yield) were separated by successive extractions with pentane (2 × 30 mL). **34**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 116.4; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 56.8 (d, $^2J(CP) = 19.7$, CH_3OP), 129.1 (s, *m*-Ph), 129.9 (s, *p*-Ph), 131.2 (d, $^2J(CP) = 21.6$, *o*-Ph), *i*-Ph (not detected); ^1H NMR (C_6D_6) δ 3.39 (d, $^3J(HP) = 13.9$, 3H, CH_3OP), 7.01−7.16 and 7.53−7.68 (m, 10H, Ph). **35**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 111.7; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 30.9 (s, $CH_2CH{=}$), 55.7 (s, CHO), 71.6 (d, $^2J(CP) = 19.4$, CH_2OP), 98.5 (s, $CH{=}$), 129.1 (s, *m*-Ph), 129.9 (s, *p*-Ph), 131.2 (d, $^2J(CP) = 21.6$, *o*-Ph), 149.7 (s, $=CHOMe$), *i*-Ph (not detected); ^1H NMR (C_6D_6) δ 2.16 (tdd, $^3J(HH) = 6.8$, $^3J(HH) = 6.8$, $^4J(HH) = 1.1$, 2H, $CH_2CH{=}$), 3.09 (s, 3H, CH_3O), 3.75 (td, $^3J(HH) = 6.8$, $^3J(HP) = 9.3$, 2H, CH_2OP), 4.54 (td, $^3J(HH) = 7.4$, $^3J(HH) = 12.7$, 1H, $CH{=}$), 6.22 (dt, $^3J(HH) = 12.7$, $^4J(HH) = 1.1$, 1H, $=CHOMe$), 7.01−7.16 and 7.53−8.01 (m, 10H, Ph). Mass spectrum (m/z): 286; 201; 84, $[M]^+$.

$PhCH_2\overline{NCH_2CH(ZrCp_2Cl)CH_2CH_2}$ (37). To a suspension of $[Cp_2ZrHCl]_n$ (0.258 g, 1.0 mmol) in 5 mL of THF at 0 °C was added 1-benzyl-3-pyrroline (190 μL, 1.0 mmol). The solution became yellow and was stirred for 2 h at room temperature. Evaporation of the solvent gave **37** as a yellow oil which was characterized without further purification. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 35.9 (s, NCH_2CH_2), 56.9 (s, NCH_2CH_2), 60.6 (s, CHZr), 61.3 (s, CH_2), 63.1 (s, CH_2), 113.0 (s, Cp), 113.1 (s, Cp), 127.4 (s, *p*-Ph), 129.0 (s, *m*-Ph), 129.4 (s, *o*-Ph), 141.4 (s, *i*-Ph). ^1H NMR (C_6D_6): δ 1.88 (m, 2H, NCH_2CH_2), 2.31 (m, 2H, NCH_2CH_2), 2.73 (m, 2H, NCH_2CHZr), 3.59 (m, 3H, $PhCH_2N$ and CHZr), 5.89 (s, 5H, Cp), 5.92 (s, 5H, Cp), 7.11−7.45 (m, 5H, Ph).

$PhCH_2N(PPh_2)(CH_2)_2CH{=}CH_2$ (38) and $PhCH_2\overline{NCH{=}C(PPh_2)CH_2CH_2}$ (39). To a solution of **37** (see above) in 5 mL of THF at −78 °C was added chlorodiphenylphosphine (180 μL, 1.0 mmol). The resulting mixture was stirred for 20 min at −78 °C and then for 2 h at room temperature. Evaporation of the solvent gave a residue from which a clear oil was extracted with pentane (2 × 40 mL). The pentane solution was evaporated and the resulting oil dissolved in 5 mL of dichloromethane. Compounds **38** and **39** were identified by ^{31}P NMR ($\delta(^{31}P)$ = 65.1 and −20.5, respectively). To this new

solution was added sulfur (0.190 g, 6.0 mmol). After being stirred for 12 h at room temperature, the mixture was chromatographed [silica gel eluted with pentane/CH_2Cl_2 (7/3) for $PhCH_2N[P(S)Ph_2](CH_2)_2CH{=}CH_2$ (**40**) (R_f: 0.52) and with dichloromethane for $PhCH_2NCH{=}C[P(S)Ph_2]CH_2CH_2$ (**41**) (R_f: 0.66)] giving rise to **40** (50% yield) and **41** (40% yield). **40**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 68.6; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 33.2 (s, $CH_2CH{=}$), 47.5 (s, CH_2N), 51.0 (s, CH_2N), 116.7 (s, $={=}CH_2$), 128.7 (s, *p*-Ph and *p*-Bz), 129.0 (s, *m*-Ph and *m*-Bz), 129.4 (s, *o*-Bz), 131.8 (s, CH=), 133.0 (d, $^2J(CP) = 11.1$, *o*-Ph), 136.0 (s, *i*-Bz), *i*-Ph (not detected); ^1H NMR (C_6D_6) δ 2.12 (td, $^3J(HH) = 8.0$, $^3J(HH) = 8.0$, 2H, $CH_2CH{=}$), 3.01 (m, 2H, CH_2NP), 4.23 (m, 2H, $PhCH_2N$), 4.70 (m, 2H, $={=}CH_2$), 5.25 (ddt, $^3J(HH_{trans}) = 16.1$, $^3J(HH_{cis}) = 10.6$ Hz, $^3JJ(HH) = 6.9$, 1H, CH=), 6.99−8.19 (m, 5H, Ph). Mass spectrum: *m*/*z* 378, [M + 1]. Anal. Calcd for $C_{23}H_{24}NPS$: C, 73.12; H, 6.36. Found: C, 73.01; H, 6.27. **41**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 32.7; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 31.2 (d, $^2J(CP) = 7.4$, CH_2), 53.3 (d, $^3J(CP) = 8.1$, CH_2N), 55.5 (s, $PhCH_2N$), 99.1 (d, $^1J(CP) = 109.6$, =CP), 128.1 (s, *p*-Bz), 128.6 (s, *m*-Bz), 128.7 (s, *o*-Bz), 129.1 (d, $^3J(CP) = 7.5$, *m*-Ph), 132.4 (d, $^4J(CP) = 2.5$, *p*-Ph), 132.4 (d, $^2J(CP) = 11.3$, *o*-Ph), 135.6 (d, $^1J(CP) = 87.4$, *i*-Ph), 137.8 (s, *i*-Bz), 155.4 (d, $^2J(CP) = 20.2$, =CH); ^1H NMR (C_6D_6) δ 2.45 (m, 2H, CH_2), 2.85 (t, $^3J(HH) = 9.8$, 2H, CH_2N), 3.51 (s, 2H, $PhCH_2N$), 6.68 (d, $^3J(HP) = 6.5$, 1H, =CH), 6.94−7.99 (m, 15H, Ph). Mass spectrum: *m*/*z* 376, [M + 1]. Anal. Calcd for $C_{23}H_{22}NPS$: C, 73.57; H, 5.91. Found: C, 73.48; H, 5.88.

$PhCH_2NCH_2CH[P(N^iPr_2)]CH_2CH_2$ (42). To a solution of chlorobis(diisopropylamino)phosphine (0.267 g, 1.0 mmol) in 15 mL of dichloromethane at −78 °C was added trimethylsilyl triflate (193 μL, 1.0 mmol). The mixture was stirred at room temperature and then cooled to −40 °C. To this solution was added **37** (0.417 g, 1.0 mmol). After the solution was stirred for 20 min at −40 °C and then for 2 h at room temperature, the solvent was evaporated and the residue was washed with pentane (2 × 40 mL). The pentane solution was evaporated to give **42** as a colorless oil (85% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 53.7. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 25.1 (s, CH_3), 22.2 (s, CH_3), 29.7 (d, $^1J(CP) = 25.0$, NCH_2CHP), 33.8 (s, NCH_2CH_2), 47.2 (d, $^2J(CP) = 9.9$, CHN), 47.3 (d, $^2J(CP) = 9.9$, CHN), 55.8 (d, $^3J(CP) = 4.4$, NCH_2CH_2), 59.2 (d, $^2J(CP) = 29.9$ Hz, NCH_2CH_2), 61.4 (s, $PhCH_2N$), 127.4 (s, *p*-Ph), 128.8 (s, *m*-Ph), 129.4 (s, *o*-Ph), 140.9 (s, *i*-Ph). ^1H NMR (C_6D_6): δ 1.03 (d, $^3J(HH) = 6.7$, 6H, CH_3), 1.08 (d, $^3J(HH) = 6.7$, 6H, CH_3), 1.18 (d, $^3J(HH) = 6.7$, 6H, CH_3), 1.19 (d, $^3J(HH) = 6.7$, 6H, CH_3), 1.86 (m, 2H, CH_2), 2.44 (m, 3H, CH_2N and CHP), 2.72 (m, 4H, CH_2N), 3.20 (d sept, $^3J(HP) = 9.7$, $^3J(HH) = 6.7$, 4H, CHN), 7.10−7.47 (m, 5H, Ph). Mass spectrum: *m*/*z* 392, $[M + 1]^+$. Anal. Calcd for $C_{23}H_{42}N_3P$: C, 70.55; H, 10.81. Found: C, 70.46; H, 10.89.

$PhCH_2NCH_2CH[P(S)(N^iPr_2)_2]CH_2CH_2$ (43). A solution of **42** (0.391 g, 1.0 mmol) and sulfur (0.190 g, 6.0 mmol) in 5 mL of dichloromethane was stirred overnight. Filtration and evaporation of the solvent gave a brown oil. Extraction with pentane (2 × 10 mL) gave **43** as a colorless oil (85% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 78.4. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 23.8 (s, CH_3), 24.1 (s, CH_3), 26.1 (s, NCH_2CH_2), 36.5 (d, $^1J(CP) = 100.6$, NCH_2CHP), 47.7 (d, $^2J(CP) = 10.6$, CHN), 53.2 (s, NCH_2), 54.9 (s, NCH_2), 58.0 (s, $PhCH_2N$), 128.9 (s, *m*-Ph), 129.2 (s, *p*-Ph), 130.1 (s, *o*-Ph), 138.5 (s, *i*-Ph). Mass spectrum: *m*/*z* 424, [M + 1]. Anal. Calcd for $C_{23}H_{42}N_3PS$: C, 65.20; H, 9.99. Found: C, 65.04; H, 9.84.

$PhCH_2N(COPh)(CH_2)_2CH{=}CH_2$ (44). To a solution of **37** (0.417 g, 1.0 mmol) in 5 mL of THF at −78 °C was added PhCOCl (116 μL, 1.0 mmol). The solution was stirred for 2 h at room temperature, and then the solvent was evaporated to give a residue from which was extracted **44** with pentane (2 × 30 mL). **44** was obtained as white crystals (80% yield). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 32.81 (s, CHCH=), 48.0 (s, CH_2N), 53.4 (s, NCH_2Ph), 117.3 (s, $={=}CH_2$), 127.6 (s, *m*-Ph and *m*-Bz), 128.0 (s, *o*-Bz), 128.4 (s, *p*-Ph and *p*-Bz), 129.3 (s, *o*-Bz), 129.7 (s, CH=), 138.0 (s, *i*-Bz), 171.9 (s, CO), *i*-Ph not detected. Mass spectrum: *m*/*z* 265, $[M]^+$. Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22. Found: C, 81.28; H, 7.18.

$PhCH_2NH(CH_2)_2CH{=}CH_2$ (45). To a solution of **37** (0.417 g, 1.0 mmol) in 5 mL of dichloromethane at −78 °C was added triflic acid (88 μL, 1.0 mmol). After the solution was stirred for 20 min at −78 °C and then for 1 h at room temperature, the solvent was carefully evaporated from the resulting orange solution. Extraction with pentane (40 mL) gave **45** (5% yield) as a colorless oil, all the other products forming an intractable material. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 35.3 (s, $CH_2CH{=}$), 49.2 (s, CH_2N), 54.5 (s, CH_2N), 116.3 (s, $={=}CH_2$), 127.4 (s, *p*-Ph), 128.7 (s, *m*-Ph), 128.9 (s, *o*-Ph), 137.5 (s, CH=), 141.8 (s, *i*-Ph). ^1H NMR (C_6D_6): δ 2.09 (td, $^3J(HH) = 6.8$; $^3J(HH) = 6.8$, 2H, $CH_2CH{=}$), 2.49 (t, $^3J(HH) = 6.8$, 2H, CH_2N), 3.58 (s, 2H, $PhCH_2N$), 5.00 (m, 2H, $={=}CH_2$), 5.70 (ddt, $^3J(HH_{trans}) = 17.1$, $^3J(HH_{cis}) = 10.2$, $^3J(HH) = 6.8$, 1H, CH=), 7.06−7.31 (m, 5H, Ph), N−H (undetermined). Mass spectrum: *m*/*z* 161, $[M]^+$. Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38. Found: C, 81.84; H, 9.24.

$PhCH_2N[P(S)Ph_2](CH_2)_4P(S)Ph_2$ (46). To a suspension of $[Cp_2ZrHCl]_n$ (0.516 g, 2.0 mmol) in 5 mL of THF at 0 °C was added the crude solution of **38** (2.0 mmol) (for preparation see above) in 5 mL of THF. After the solution was stirred for 3 h at room temperature, chlorodiphenylphosphine (359 μL, 2.0 mmol) was added to the resulting limpid solution. The new solution was stirred for 12 h at room temperature, and then sulfur (0.768 g, 24.0 mmol) was added on the reaction mixture. After the solution was stirred for 12 h at room temperature, the solvent was removed. Chromatography (silica gel eluants 1/1 pentane/CH_2Cl_2) allowed us to obtain **46** as an oil (65% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 42.2 (s, $Ph_2P(S)CH_2$), 69.6 (s, $Ph_2P(S)N$). ^1H NMR ($CDCl_3$): δ 1.30 (m, 2H, CH_2), 1.51 (m, 2H, CH_2), 2.09 (m, 2H, CH_2P), 2.83 (m, 2H, CH_2NP), 4.14 (d, $^3J(HP) = 9.2$, 2H, $PhCH_2N$), 7.26−7.44 and 7.64−8.04 (m, 20H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 19.4 (s, CH_2CH_2N), 28.4 (d, $^2J(CP) = 18.4$, CH_2CH_2P), 31.7 (d, $^1J(CP) = 56.3$, CH_2P), 46.3 (s, CH_2N), 50.2 (s, CH_2N), 127.3, 128.2, 128.3, 128.4, 128.5 (Ph), 130.8 (d, $J(CP) = 10.1$, Ph), 131.4 (d, $J(CP) = 13.0$, Ph), 132.0 (d, $J(CP) = 10.5$, Ph), *i*-Ph (not detected). Mass spectrum: *m*/*z* 595, $[M]^+$. Anal. Calcd for $C_{35}H_{35}NP_2S_2$: C, 70.56; H, 5.92. Found: C, 70.44; H, 5.87.

Preparation of $Me_2SiCH_2CH(ZrCp_2Cl)CH_2CH_2$ (49). To a suspension of $[Cp_2ZrHCl]_n$ (0.258 g, 1.0 mmol) in 5 mL of THF at room temperature was added the silacyclopentene **47** (0.112 g, 1.0 mmol). After the solution was stirred for 3 h at room temperature, the solvent was evaporated and the yellow oil was used as it was. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ 21.3. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 1.3 (s, CH_3Si), 1.9 (s, CH_3Si), 16.3 (s, $SiCH_2CH_2$), 30.4 (s, $SiCH_2CHZr$), 42.1 (s, $SiCH_2CH_2$), 71.8 (s, CHZr), 112.3 (s, Cp), 112.8 (s, Cp). ^1H NMR (C_6D_6): δ −0.07 (s, 3H, CH_3Si), 0.22 (s, 3H, CH_3Si), 0.42 (m, 1H, CH_2Si), 0.77 (ddt, $J(HH) = 14.2$, $J(HH) = 6.5$, $J(HH) = 1.9$, 1H, CH_2Si), 1.05 (m, 1H, CH_2Si), 1.49 (dd, $J(HH) = 10.8$, $J(HH) = 6.5$, 1H, CH_2Si), 2.00 (m, 3H, $SiCH_2CH_2$ and CHZr), 5.86 (s, 5H, Cp), 5.91 (s, 5H, Cp).

Preparation of $Me_2SiCH_2CH(ZrCp_2Ph)CH_2CH_2$ (50). To a solution of **49** (0.370 g, 1.0 mmol) in 5 mL of THF at −78 °C was added 2 M phenylithium (500 μL, 1.0 mmol). After the solution was stirred 20 min at −78 °C and then for 3 h at room temperature, the solvent was evaporated and the residue was dissolved in 1 mL of C_6D_6. Centrifugation allowed us to remove lithium chloride. The resulting solution was characterized by NMR as **50**. **50** was not stable in solution and was transformed into silacyclopentene **51** characterized by coinjection with a sample prepared by a known method.[16] $^{13}C\{^1H\}$ NMR (C_6D_6): δ 2.1 (s, CH_3Si) 2.3 (s, CH_3Si), 16.4 (s, $SiCH_2CH_2$), 30.5 (s, $SiCH_2CHZr$), 39.7 (s, $SiCH_2CH_2$), 73.2 (s,

(16) Manuel, G.; Mazerolles, P.; Darbon, J. M. *J. Organomet. Chem.* **1973**, *59*, C7.

$SiCH_2CHZr$), 111.1 (s, Cp), 111.6 (s, Cp), 125.5 (s, *p*-Ph), 127.6 (s, *m*-Ph), 136.8 (s, *o*-Ph), *i*-Ph (not detected).

Preparation of $Cp_2Zr(Cl)O(CH_2)_5ZrCp_2Cl$ (25c) from 53. To a suspension of $[Cp_2ZrHCl]_n$ (0.258 g, 1.0 mmol) in 5 mL of THF at room temperature was added 3,4-dihydro-2*H*-pyran (**53**) (46 μL, 0.5 mmol). After the solution was stirred for 2 h at 50 °C, the dark red solution was evaporated giving **25c** (85% yield). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 33.3 (s, CH_2), 34.2 (s, CH_2), 34.71 (s, CH_2), 55.5 (s, CH_2Zr), 76.5 (s, CH_2OZr), 113.6 (s, Cp), 114.3 (s, Cp). ^1H NMR (C_6D_6): δ 1.20−1.61 (m, 8H, CH_2), 3.99 (t, $^3J(HH) = 6.2$, 2H, CH_2OZr), 5.86 (s, 10H, Cp), 6.04 (s, 10H, Cp).

The procedure leading to **26** from **25c** and 2 equiv of chlorodiphenylphosphine is analogous to that of **24** with chlorodiphenylphosphine (see Scheme 4 and above).

$Ph_2P(S)OCH_2P(O)Ph_2$ (62) and $Ph_2P(S)O(CH_2)_2CH{=}CH_2$ (63). To a suspension of $[Cp_2ZrHCl]_n$ (**2**) (0.258 g, 1.0 mmol) in 4 mL of THF was added a solution of *cis*-4,7-dihydro-1,3-dioxepin (0.100 g, 1.0 mmol) in 4 mL of THF. The mixture was stirred for 30 min at room temperature. During this time, the solution turned yellow and became homogeneous. The mixture was cooled to −40 °C, and chlorodiphenylphosphine (0.220 g, 1.0 mmol) was added. The resulting mixture was kept 15 min at −40 °C and then allowed to warm slowly to room temperature to give **17** [$\delta(^{31}P)\{^1H\}$ NMR (C_6D_6) 111.8 ppm] and **61** [$\delta(^{31}P)\{^1H\}$ NMR (C_6D_6) 124.8 (d, $^3J(PP) = 30.6$ Hz, $OPPh_2$), 23.4 (d, $^3J(PP) = 30.6$ Hz, $CH_2P(O)Ph_2$) ppm]. Sulfur (0.095 g, 3.0 mmol) was added and the mixture stirred for 3 h. Evaporation of the solvent gave the two phosphorus derivatives which were isolated by column chromatography using hexane/CH_2Cl_2 (3/1) as eluents. **62**: 40% yield; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 85.8 (d, $^3J(PP) = 32.2$, $Ph_2P(S)O$), 23.8 (d, $^3J(PP) = 32.2$, $Ph_2P(O)CH_2$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 61.3 (d, $^1J(CP) = 85.7$, $^2J(CP) = 7.4$, CH_2), 128.7, 128.9, 131.5, 131.7, 131.8, 132.1, 135.3 (Ph). Anal. Calcd for $C_{25}H_{22}O_2P_2S$: C, 66.96; H, 4.94. Found: C, 66.84; H, 4.92. **63**: 35% yield; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 79.9; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 35.0 (d, $^3J(CP) = 8.0$, $CH_2CH{=}$), 64.0 (d, $^2J(CP) = 5.4$, CH_2OP), 117.3 (s, $={=}CH_2$), 128.4 (d, $^3J(CP) = 13.4$, *m*-Ph), 131.5 (d, $^2J(CP) = 7.5$, *o*-Ph), 131.6 (s, *p*-Ph), 134.3 (s, $CH{=}$), 135.8 (d, $^1J(CP) = 110.0$, *i*-Ph); ^1H NMR (C_6D_6) δ 2.16 (dt, $^3J(HH) = 6.6$, $^3J(HH) = 6.6$, 2H, $CH_2CH{=}$), 3.96 (dt, $^3J(HP) = 8.5$, $^3J(HH) = 6.6$, 2H, CH_2P), 4.94 (m, 2H, $={=}CH_2$), 5.59 (m, 1H, $CH{=}$), 7.94−8.05 (m, 5H, Ph). Anal. Calcd for $C_{16}H_{17}OPS$: C, 66.65; H, 5.94. Found: C, 66.58; H, 5.91.

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