# Metallacycle Transfer Routes to Main-Group Phosphacycles

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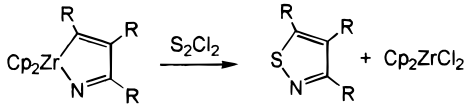
The employment of phosphazirconacycles in metallacycle transfer reactions is a facile method for the synthesis of main-group phosphacycles. Reactions of $Cp_2Zr(PPh)_3$ (**1**), $Cp_2Zr(P(R^*)C(Ph)=CPh)$ (**2**), and $Cp_2Zr(P(Mes)P(Mes)C(Ph)=CPh)$ (**3**) with various main-group dihalides results in cleavage of TM−MG bonds and formation of new MG−MG bonds. Triphosphanato complex **1** reacts with $PhPCl_2$ or $^tBu_2SnCl_2$ to yield $(PPh)_4$ (**4**) and $(t\text{-}Bu)_2Sn(PPh)_3$ (**7**), respectively. Reaction of phosphametallacyclobutene **2** with $PhPCl_2$ results in the formation of the unsymmetrically substituted 1,2-diphosphetene $P(Ph)P(R^*)C(Ph)=CPh$ (**5**), while reaction with $PhBCl_2$ yields $PH(C_6H_2\text{-}(2\text{-}CH_2C(CH_3)_2)\text{-}4,6\text{-}t\text{-}Bu_2)B(Ph)CPh=CPh$ (**8**), the product of ring expansion via C−H activation. Phosphametallacyclopentene **3** reacts with $PhPCl_2$ to furnish the unsymmetrically substituted 1,2,3-triphospholene $P(Ph)P(Mes)P(Mes)C(Ph)=CPh$ (**6**). Advantages to such metallacycle transfer reactions include (i) facile accessibility of main-group derivatives where conventional syntheses are laborious, tedious, and/or fraught with safety issues, (ii) selective control over molecular fragments, and (iii) new routes to novel main-group compounds.



## Introduction

Studies in our own laboratories have demonstrated the highly reactive nature of Zr−P bonds,[1−7] a trait which may be exploited in the preparation of organophosphorus compounds or new families of phosphazirconacycles. In the present paper, we describe the employment of phosphazirconacycles in metallacycle transfer reactions, a class of reaction that was discovered by Fagan and Nugent in 1988.[7] The scope of this transformation was subsequently extended by several research groups to include syntheses of numerous heteroles and other heterocycles of the group 13−16 elements.[8] Despite the thorough exploration of this chemistry, the reaction of the azazirconacycles $Cp_2Zr(N=C(R)C(R)=C(R))$ with $S_2Cl_2$ to give the isothiazoles $S(N=C(R)C(R)=C(R))$ are the only examples of metallacycle transfer resulting in the cleavage of a transition-metal (TM)−main-group (MG) bond and formation of a new MG−MG bond (eq 1).[8]




(1)

There are a number of potential advantages for main-group-compound synthesis offered by metallacycle transfer reactions. These include (i) facile accessibility of main-group derivatives where conventional syntheses are laborious, tedious, and/or fraught with safety issues, (ii) selective control over molecular fragments, and (iii) new routes to novel main-group compounds. In the present work, each of these attributes is illustrated by the use of phosphazirconacycles to access organophosphorus derivatives.

## Experimental Section

**General Data.** All preparations were performed under an atmosphere of dry, $O_2$-free $N_2$ by employing either Schlenk-line techniques or a Vacuum Atmospheres inert-atmosphere glovebox. Solvents were reagent grade and were distilled from the appropriate drying agents under $N_2$ and degassed by the freeze−thaw method at least three times prior to use. Organic reagents were purified by conventional methods. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AC-300 operating at 300 and 75 MHz, respectively. $^{31}P$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC-200 operating at 81 MHz. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$ and 85% $H_3PO_4$, respectively. Low- and high-resolution EI mass spectral data were obtained employing a Kratos Profile mass spectrometer outfitted with a $N_2$ glovebag enclosure for

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the inlet port. Combustion analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, or Schwarzkopf Laboratories, Woodside, NY. All reagents were purchased from either the Aldrich Chemical Co. or the Strem Chemical Co. $Cp_2Zr(PPh)_3$ (**1**),[9] $Cp_2\overline{Zr(P(R^*)C(Ph)=CPh)}$ (**2**),[6g] and $Cp_2\overline{Zr(P(Mes)P(Mes)C(Ph)=CPh)}$ (**3**)[6i] were prepared by literature methods. Throughout the paper Mes = $C_6H_2$-2,4,6-$Me_3$ and R* refers to $C_6H_2$-2,4,6-*t*-$Bu_3$.

**Synthesis of $(PPh)_4$ (4) and $(t\text{-}Bu)_2Sn(PPh)_3$ (7).** Compounds **4** and **7** were prepared through similar routes; thus, only one representative procedure is described. To a benzene solution (3 mL) of **1** (109 mg, 0.2 mmol) was added phenyldichlorophosphine (27.1 mL, 0.2 mmol). The reaction mixture stood for 1 h, resulting in the formation of a colorless solution. After filtration, the solvent was removed in vacuo and the product dissolved in hexane (2 mL). Colorless crystals formed over a 3-day period at room temperature and were isolated by filtration. **4**: yield 71 mg (82%). $^{31}$P NMR (25 °C, $C_6D_6$): $\delta$ −48.0 (s). $^1$H NMR and $^{13}C\{^1H\}$ NMR data were consistent with those reported in the literature.[10] **7**: yield 51 mg (46%). $^1$H NMR (25 °C, $C_6D_6$): $\delta$ 7.10−6.91 (m, 15H, Ph *H*), 1.42 ($|J_{P-Sn}|$ = 78.6 Hz, $|J_{P-Sn}|$ = 73.1 Hz, 9H, $^t$Bu), 0.89 ($|J_{P-Sn}|$ = 80.9 Hz, $|J_{P-Sn}|$ = 77.8 Hz, 9H, $^t$Bu). $^{13}C\{^1H\}$ NMR (25 °C, $C_6D_6$): $\delta$ 137.6 (m, quat), 131.7 (m, arom *C*−H), 130.9 (m, arom *C*−H), 128.3 (d, $|J|$ = 18.5 Hz, arom *C*−H), 128.1 (s, arom *C*−H), 127.6 (s, arom *C*−H), 126.3 (s, arom *C*−H), 42.7 (s, *C*($CH_3$)$_3$), 31.3 (s, C(*C*$H_3$)$_3$). $^{31}$P NMR (25 °C, $C_6D_6$): $\delta$ −51.3 (t, $|^1J_{P-P}|$ = 139.9 Hz), −70.5 (d, $|^1J_{P-P}|$ = 140.6 Hz, $|^1J_{P-Sn}|$ = 573.9 Hz). Anal. Calcd for $C_{26}H_{33}P_3Sn$: C, 56.05; H, 5.97. Found: C, 55.88; H, 5.84.

**Synthesis of $\overline{P(Ph)P(R^*)C(Ph)=CPh}$ 5 and $\overline{PH(C_6H_2\text{-}(2\text{-}CH_2C(CH_3)_2)\text{-}4,6\text{-}t\text{-}Bu_2)B(Ph)CPh=CPh}$ (8).** Compounds **5** and **8** were prepared through similar routes; thus, only one representative procedure is described. To a benzene solution (3 mL) of **2** (135 mg, 0.2 mmol) was added phenyldichlorophosphine (27.1 mL, 0.2 mmol). The reaction mixture stood for 8 h, resulting in the formation of a yellow solution. After filtration, the solvent was removed in vacuo and the product dissolved in pentane (2 mL). Pale yellow crystals formed over 12 h at room temperature and were isolated by filtration. **5**: yield 60 mg (53%). $^1$H NMR (25 °C, $C_6D_6$): $\delta$ 7.59 (m, 4H, Ph *H*), 7.34 (s, 2H, Ph *H*), 7.18 (m, 2H, Ph *H*), 6.86 (m, 9H, Ph *H*), 1.58 (s, 18H, *o*-$^t$Bu), 1.22 (s, 9H, *p*-$^t$Bu). $^{13}C\{^1H\}$ NMR (25 °C, $C_6D_6$): $\delta$ 159.4 (d, $|J|$ = 13.1 Hz, quat), 151.2 (s, quat), 142.2 (m, quat), 136.6 (m, quat), 135.9 (m, quat), 135.2 (s, quat), 134.8 (d, $|J|$ = 5.6 Hz, arom *C*−H), 134.6 (d, $|J|$ = 4.9 Hz, arom *C*−H), 131.1 (s, arom *C*−H), 122.0 (d, $|J|$ = 5.2 Hz, arom *C*−H), 39.1 (s, *o*-*C*($CH_3$)$_3$), 34.6 (s, *p*-*C*($CH_3$)$_3$), 33.5 (*AB* d, $|J_{AB}|$ = 5.5 Hz, *o*-C(*C*$H_3$)$_3$), 31.1 (s, *p*-C(*C*$H_3$)$_3$). $^{31}$P NMR (25 °C, $C_6D_6$): $\delta$ −23.1, −27.4 (*AB* q, $|J_{AB}|$ = 151.9 Hz). Anal. Calcd for $C_{38}H_{44}P_2$: C, 81.11; H, 7.88. Found: C, 81.33; H, 8.15. **8**: yield 51 mg (47%). $^1$H NMR (25 °C, $C_6D_6$): $\delta$ 8.03 (br d, $|J|$ = 7.5 Hz, 2H, Ph *H*), 7.85 (br d, $|J|$ = 3.7 Hz, 1H, Ph *H*), 7.58−7.44 (m, 5.5H, Ph *H* and P−*H*), 7.05−6.86 (m, 8H, Ph *H*), 6.35 (d, $|J|$ = 2.2 Hz, 0.5 H, P−*H*), 2.08 (br, 2H, C$H_2$), 1.76 (s, 3H, C$H_3$), 1.68 (s, 3H, C$H_3$), 1.24 (s, 9H, $^t$Bu), 1.06 (s, 9H, $^t$Bu). $^{13}C\{^1H\}$ NMR (25 °C, $C_6D_6$): $\delta$ 160.2 (d, $|J|$ = 14.6, quat), 154.8 (s, quat), 153.7 (s, quat), 139.2 (d, $|J|$ = 51.5 Hz, quat), 137.8 (s, quat), 133.2 (d, $|J|$ = 8.3 Hz, arom *C*−H), 131.2 (d, $|J|$ = 46.1 Hz, quat), 130.2 (s, arom *C*−H), 128.8 (s, arom *C*−H), 128.5 (s, arom *C*−H), 128.3 (d, $|J|$ = 3.6 Hz, arom *C*−H), 128.1 (s, arom *C*−H), 127.9 (d, $|J|$ = 2.2 Hz, arom *C*−H), 127.2 (s, arom *C*−H), 126.1 (d, $|J|$ = 3.5 Hz, arom *C*−H), 123.8 (d, $|J|$ = 10.4 Hz, arom *C*−H), 122.1 (d, $|J|$ = 6.4 Hz, arom *C*−H), 117.6 (d, $|J|$ = 21.8 Hz, quat), 42.0 (d, $|J|$ = 10.1 Hz, quat), 38.7 (s, Me), 37.1 (s, quat), 35.2 (s, quat), 34.7 (v br s, *C*$H_2$), 33.7 (s, Me), 33.3 (s, $^t$Bu), 31.0 (s, $^t$Bu). $^{31}$P NMR (25 °C, $C_6D_6$): $\delta$ −35.3 (dd, $|^1J_{P-H}|$ = 371.4 Hz, $|J|$ = 31.9 Hz). Anal. Calcd for $C_{38}H_{44}BP$: C, 84.13; H, 8.17. Found: C, 84.37; H, 7.97.

**Synthesis of $\overline{P(Ph)P(Mes)P(Mes)C(Ph)=CPh}$ (6).** To a benzene solution (3 mL) of **3** (140 mg, 0.2 mmol) was added phenyldichlorophosphine (27.1 mL, 0.2 mmol). The reaction mixture stood for 4 h, resulting in the formation of a pale yellow solution. After filtration, the solvent was removed in vacuo and the product dissolved in hexane (2 mL). Colorless crystals formed over 12 h at room temperature and were isolated by filtration. Yield: 54 mg (46%). $^1$H NMR (25 °C, $C_6D_6$): $\delta$ 7.65 (m, 2H, Ph *H*), 7.48 (m, 2H, Ph *H*), 7.06−6.51 (m, 15H, Ph *H*), 2.90 (s, 6H, *o*-C$H_3$), 2.77 (br s, 3H, C$H_3$), 2.29 (br s, 3H, C$H_3$), 2.08 (s, 3H, C$H_3$), 1.95 (s, 3H, C$H_3$). $^{13}C\{^1H\}$ NMR (25 °C, $C_6D_6$): $\delta$ 150.3 (dd, $|J|$ = 25.5 Hz, $|J|$ = 4.5 Hz, quat), 146.3 (m, quat), 145.6 (br d, $|J|$ = 13.5 Hz, quat), 145.1 (s, quat), 144.5 (m, quat), 140.7 (d, $|J|$ = 19.5 Hz, quat), 140.2 (s, quat), 139.9 (s, quat), 139.6 (d, $|J|$ = 12.8 Hz, quat), 139.3 (br s, quat), 132.2 (m, arom *C*−H), 130.3 (s, arom *C*−H), 130.2 (br s, arom *C*−H), 130.0 (s, arom *C*−H), 129.4 (br d, $|J|$ = 6.8 Hz, arom *C*−H), 129.1 (s, arom *C*−H), 128.3 (d, $|J|$ = 4.5 Hz, arom *C*−H), 128.2 (s, arom *C*−H), 126.8 (d, $|J|$ = 12.8 Hz, arom *C*−H), 24.0 (m, *C*$H_3$), 20.8 (s, *C*$H_3$). $^{31}$P NMR (25 °C, $C_6D_6$): $\delta$ 33.7 (d, $|^1J_{P-P}|$ = 252.0 Hz), 15.6 (d, $|^1J_{P-P}|$ = 230.8 Hz), −58.2 (dd, $|^1J_{P-P}|$ = 247.2 Hz, $|^1J_{P-P}|$ = 237.3 Hz. Anal. Calcd for $C_{38}H_{37}P_3$: C, 77.80; H, 6.36. Found: C, 78.08; H, 6.58.

**Crystal Structure Determination.** X-ray-quality crystals of **4**−**8** were obtained directly from the preparation as described above. The crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, $O_2$-free environment for each crystal. Diffraction experiments were performed on a Rigaku AFC6 diffractometer equipped with graphite-monochromatized Mo K$\alpha$ radiation. Crystal data and details associated with data collection for **4**−**8** are given in Tables 1 and S1 (Table S1 is in the Supporting Information). The data were processed using the TEXSAN crystal solution package operating on a SGI Challenger mainframe with remote X-terminals. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[11,12] Atom positions were determined using direct methods and successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and $F_o$ and $F_c$ are the observed and calculated structure factor amplitudes. The P−H hydrogen atom of **8** was located in a difference Fourier map, and its contribution was included but not refined in subsequent least-squares calculations. The final values of *R*, $R_w$, and the maximum $\Delta/\sigma$ on any of the parameters in the final cycles of the refinements are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Crystallographic details, positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

## Results and Discussion

**Facile Synthesis.** Triphosphanato metallacycles such as $Cp_2Zr(PPh)_3$ (**1**)[9,13] have been known for 25

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**Table 1. Crystallographic Data**

| | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|
| formula | $C_{24}H_{20}P_4$ | $C_{38}H_{44}P_2$ | $C_{38}H_{37}P_3$ | $C_{52}H_{66}P_3Sn_2$ | $C_{38}H_{44}BP$ |
| fw | 432.06 | 562.71 | 586.63 | 1114.32 | 542.55 |
| *a* (Å) | 11.757(4) | 26.327(7) | 11.468(2) | 30.583(9) | 17.00(1) |
| *b* (Å) | 12.612(7) | 10.211(7) | 14.627(2) | 8.482(3) | 13.496(4) |
| *c* (Å) | 7.558(3) | 26.918(7) | 10.374(2) | 21.566(5) | 29.56(1) |
| α (deg) | | | 98.21(1) | | |
| *β* (deg) | | 106.37(2) | 109.52(1) | | 102.13(4) |
| *γ* (deg) | | | 81.23(1) | | |
| space group | $P2_12_12$ | *C*2/*c* | $P\bar{1}$ | $Pca2_1$ | *C*2/*c* |
| *V* (Å$^3$) | 1120.8(7) | 6826(5) | 1613.2(5) | 5594(7) | 6630(5) |
| $D_{calcd}$ (g cm$^{-3}$) | 1.12 | 1.10 | 1.21 | 1.32 | 1.09 |
| Z | 8 | 8 | 2 | 4 | 8 |
| abs coeff, $\mu$ (cm$^{-1}$) | 0.70 | 1.50 | 2.09 | 10.95 | 1.06 |
| temp (°C) | 24 | 24 | 24 | 24 | 24 |
| no. of data collected | 1174 | 6377 | 5689 | 5556 | 6101 |
| no. of data, $F_o^2 > 3\sigma(F_o^2)$ | 590 | 1044 | 2668 | 2717 | 1114 |
| no. of variables | 67 | 171 | 370 | 280 | 166 |
| *R* (%)[a] | 6.0 | 10.4 | 5.6 | 7.5 | 9.5 |
| $R_w$ (%)[a] | 4.4 | 8.4 | 4.7 | 6.8 | 7.5 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma(|F_o| - |F_c|)^2|/\Sigma|F_o|^2]^{0.5}$

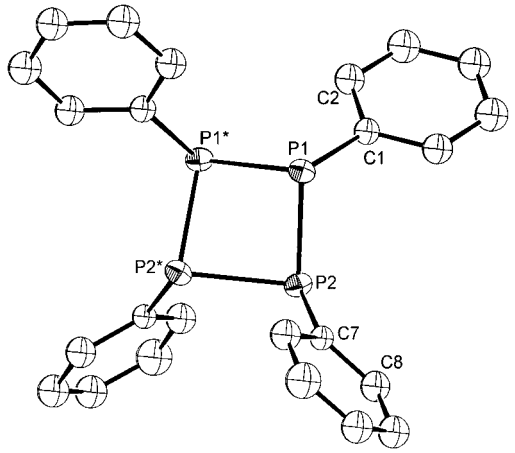
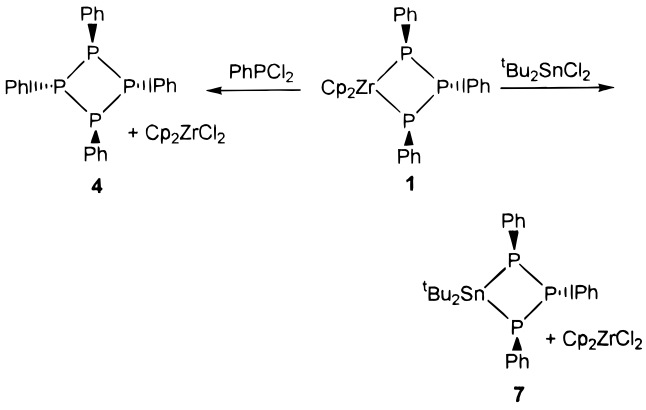



**Figure 1.** ORTEP drawing of **4** (30% thermal ellipsoids are shown). Selected bond distances (Å) and angles (deg) are as follows: P(1)−P(1)*, 2.218(6); P(1)−P(2), 2.240(4); P(2)−P(2)*, 2.232(6); P(1)*−P(1)−P(2), 84.6(1); P(1)−P(2)−P(2)*, 84.2(1).

**Scheme 1**




years, yet little is known about their reactivity. Much of our recent published work illustrates the reactive nature of Zr−P bonds; thus, we inferred that the four-membered metallacycle **1** would be susceptible to metallacycle transfer reactions. As surmised, compound **1** reacted cleanly with phenyldichlorophosphine in solution at 25 °C to yield $Cp_2ZrCl_2$ and the known phosphacycle $(PPh)_4$ (**4**),[10] the latter in 82% isolated yield. The identity of **4** was established by comparison of the spectral data to the literature data as well as a crystallographic structural study (Figure 1), which confirmed the previously predicted "all-*trans*" conformation. The present synthesis of **4** offers several advantages over the previously reported synthesis, which involved reaction of $K_2(PPh)_3$ or $(Me_3Si)_2(PPh)_3$ with phenyldichlorophosphine. This metallacycle transfer reaction of **1** is an exceptionally facile route to **4**; furthermore, starting material **1** is accessible through straightforward and high-yielding preparations.[9]

**Fragment Control.** Conventional organic routes to 1,2-diphosphetenes[14] and 1,2,3-triphospholenes[14dhi,15] have been known for some time. Ring contraction of 1,2,3-triphospholenes is a reliable route to 1,2-diphosphetenes,[14d,h] while reaction of *cis*-1,2-dichloroalkenes with $(PR)_3$ dianions or reaction of cyclopolyphosphines with alkynes yield the triphospholenes.[14d,h,15] These methods do not permit control of the P substitution pattern. In contrast, additions of [RP] to phosphirenes[14i] and the present metallacycle transfer reactions offer routes to unsymmetrically substituted diphosphatenes.

The phosphametallacyclobutene $Cp_2\overline{Zr(P(R^*)C(Ph)=CPh)}$ (**2**; R* = $C_6H_2$-2,4,6-*t*-$Bu_3$) reacts with 1 equiv of phenyldichlorophosphine to yield the yellow crystalline product **5** in 65% yield along with $Cp_2ZrCl_2$. The AB quartet observed in the $^{31}P$ NMR spectrum of **5** supports its formulation as the first unsymmetrically substituted 1,2-diphosphetene ring, $\overline{P(Ph)P(R^*)C(Ph)=CPh}$ (Scheme 1). The X-ray crystallographic study (Figure 2) of **5** shows a *transoid* disposition for the substituents on P with respect to the four-membered ring. The general structural features correlate well with those previously described for the related 1,2,3,4-tetraphenyl-1,2-diphosphetene.[14d]

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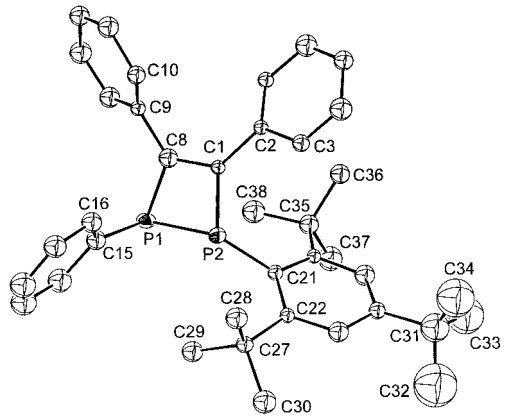



**Figure 2.** ORTEP drawing of **5** (30% thermal ellipsoids are shown). Selected bond distances (Å) and angles (deg) are as follows: P(1)−P(2), 2.253(9); P(1)−C(8), 1.79(2); P(2)−C(1), 1.76(2); P(2)−P(1)−C(8), 73.8(8); P(1)−P(2)−C(1), 76.1(8).

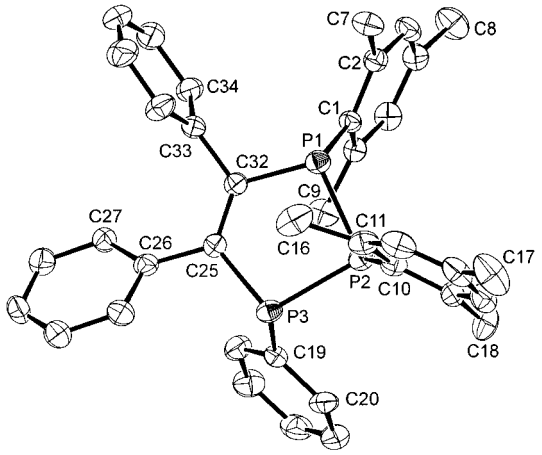
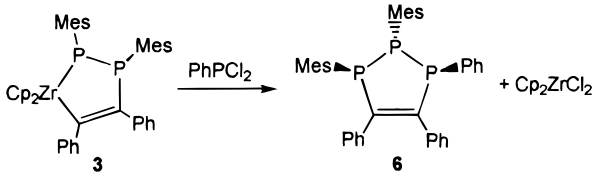



**Figure 3.** ORTEP drawing of **6** (30% thermal ellipsoids are shown). Selected bond distances (Å) and angles (deg) are as follows: P(1)−P(2), 2.200(2); P(2)−P(3), 2.207(3); P(1)−C(32), 1.818(7); P(3)−C(25), 1.838(6); P(2)−P(1)−C(32), 99.0(2); P(2)−P(3)−C(25), 99.4(2).

The related reaction of the diphosphametallacyclopentene $Cp_2Zr$(P(Mes)P(Mes)C(Ph)=CPh) (**3**; Mes = $C_6H_2$-2,4,6-$Me_3$) with phenyldichlorophosphine yielded $Cp_2ZrCl_2$ and product **6** in 46% yield (eq 2). The P−P-




**(2)**

coupled signals in the $^{31}P$ NMR spectrum at 33.7, 15.6, and −58.2 ppm and the $^1H$ and $^{13}C\{^1H\}$ NMR data were consistent with the formulation of the product as the 1,2,3-triphospholene P(Ph)P(Mes)P(Mes)C(Ph)=CPh (**6**). The X-ray crystallographic study of **6** represents the first such data for an uncomplexed triphospholene (Figure 3). The structural parameters of **6** are comparable to those of the related 1,2,3-triphenyl-1,2,3-triphosphaindane.[16] The mesityl group on P(2) is *transoid* to both the mesityl group on P(1) and the phenyl group on P(3). The nonplanarity of the metallacycle is indicated by the P(1)−P(2)−P(3)−C(25) and P(3)−P(2)−P(1)−C(32) torsion angles of 11.8(2) and −12.8(2)°, respectively. The P−P bond lengths of 2.200(2) and 2.207(3) Å are analogous to those of 1,2,3-triphenyl-1,2,3-triphosphaindane.

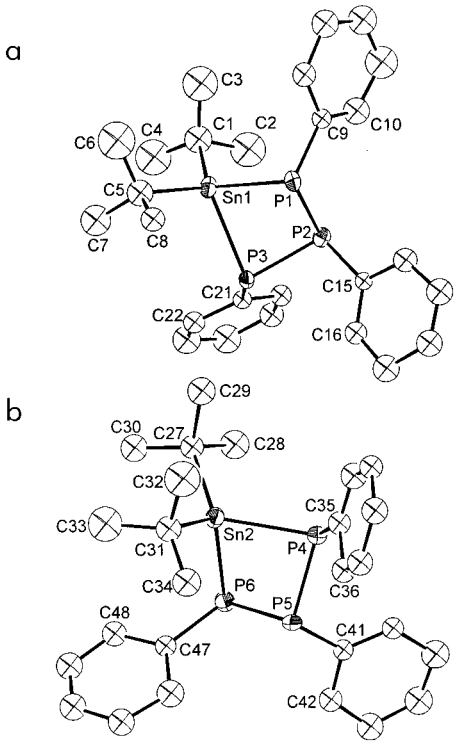



**Figure 4.** ORTEP drawings of the two molecules of **7** in the asymmetric unit (30% thermal ellipsoids are shown). Selected bond distances (Å) and angles (deg) are as follows: (a) Sn(1)−P(1), 2.538(8); Sn(1)−P(3), 2.549(7); Sn(1)−P(1)−P(2), 83.3(3); Sn(1)−P(3)−P(2), 83.1(3); P(1)−P(2)−P(3), 92.2(4); (b) Sn(2)−P(4), 2.533(8); Sn(2)−P(6), 2.538(8); Sn(2)−P(4)−P(5), 83.0(3); Sn(2)−P(6)−P(5), 82.4(3); P(4)−P(5)−P(6), 92.4(4).

The above metallacycle transfer reactions yield compounds **5** and **6**, the first examples of unsymmetrically substituted 1,2-diphosphetenes and 1,2,3-triphospholenes, respectively. The synthetic potential of such reactions is illustrated by the stepwise incorporation of main-group fragments, which permits some control over the substitution pattern.

**Novel Synthesis.** Conventional syntheses of tin−phosphorus[17] and boron−phosphorus[18] heterocycles involve halide ion metathesis reactions employing phosphorus nucleophiles. For example, the species $Et_2Sn$(P-*t*-Bu)$_3$ is obtained in low yield, one of a host of products derived from the reaction of K($^t$Bu)P−P(*t*-Bu)K with $Et_2SnCl_2$.[17c] Metallacycle transfer reactions offer an alternative synthetic approach.

The reaction of **1** with 1 equiv of di-*tert*-butyltin dichloride yielded compound **7**, which exhibited a $^{31}P$ NMR spectrum consisting of a triplet at −51.3 ppm and a doublet at −70.5 ppm ($|J_{P-P}|$ = 140 Hz), the latter resonance exhibiting tin satellites. The NMR data supported the formulation of **7** as (*t*-Bu)$_2$Sn(PPh)$_3$,

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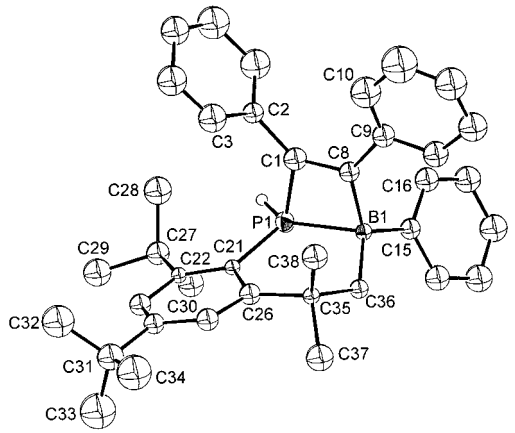
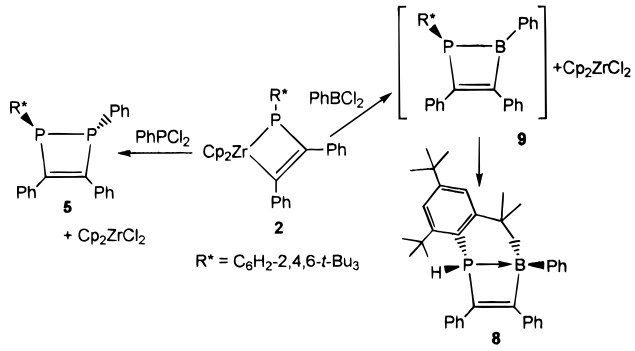



**Figure 5.** ORTEP drawing of **8** (30% thermal ellipsoids are shown). Selected bond distances (Å) and angles (deg) are as follows: P(1)−B(1), 1.99(2); P(1)−C(1), 1.80(2); B(1)−C(8), 1.62(2); B(1)−C(36), 1.65(2); C(1)−P(1)−B(1), 78.8(8); C(21)−P(1)−B(1), 117.0(7); P(1)−B(1)−C(8), 79(1); P(1)−B(1)−C(36), 102(1).

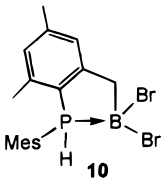
which was confirmed by a crystallographic study (Figure 4). Although some tin−phosphorus heterocycles have been synthesized in the past,[6f,17] very few have been structurally characterized. The Sn−P distances of **7** (ca. 2.54 Å) compare well to those of the related heterocycle $(t\text{-}Bu_2SnPR^*)_2$.[6f] Similar to the case in **4**, steric congestion in **7** is minimized by an alternating "*trans*" arrangement of the phenyl substituents. The present metallacycle transfer route to **7** is logistically facile, clean, and high yield (82%).

The analogous reaction of **2** with dichlorophenylborane furnished $Cp_2ZrCl_2$ and the yellow crystalline product **8**. The $^{31}P$ NMR spectrum of **8** consisted of a P−H-coupled doublet of doublets at −35.3 ppm ($|^1J_{P-H}| = 371.4$ Hz, $|J| = 31.9$ Hz), while $^1H$ and $^{13}C\{^1H\}$ NMR spectra both indicated that only two *tert*-butyl groups remained intact on the supermesityl substituent. C−H bond activation of the remaining *tert*-butyl group was indicated by resonances corresponding to two inequivalent methyl groups and a methylene fragment in the NMR spectra. These data lead to the formulation of **8** as $PH(C_6H_2\text{-}(2\text{-}CH_2C(CH_3)_2)\text{-}4,6\text{-}t\text{-}Bu_2)B(Ph)CPh{=}CPh$, which was subsequently confirmed crystallographically (Figure 5). The structure of **8** consists of a five- and a four-membered ring, fused via a P(1)−B(1) dative bond. The P(1)−B(1) bond length of 1.99(2) Å is comparable to that in adducts such as $H_3P{\cdot}BH_3$ and $Me_3P{\cdot}BH_3$ (ca. 1.93 Å).[19] The location of the P−H hydrogen establishes the pseudo-tetrahedral geometry at this site; similarly, the geometry about boron is best described as a distorted tetrahedron. The formation of **8** is likely to proceed through metallacycle transfer to boron, resulting in the formation of intermediate **9**, which is analogous to **5**,

**Scheme 2**




and 1 equiv of $Cp_2ZrCl_2$ as the byproduct. Subsequent C−H activation of the *o-tert*-butyl group effects the ring expansion (Scheme 2). A similar process has been observed in the attempted synthesis of $Br_2BPMes_2$, in which C−H activation of one of the *o*-methyl groups of a mesityl substituent led to the formation of heterocycle **10**.[20]




**10**

## Summary

In conclusion, these studies demonstrate that transfer reactions employing metallacycles offer viable synthetic approaches to main-group derivatives. The examples described herein demonstrate the accessibility of known, new, and in some cases unprecedented main-group heterocycles. In addition, this methodology offers a level of synthetic control heretofore unavailable, as well as logistical advantages of mild, safe reaction conditions and relatively high yields. These studies augur well for the future of such TM−MG compounds as reagents. Synthetic routes to readily accessible phosphametallacycles continue to be actively investigated in our laboratories with a view to broadening the scope and utility of their chemistry. Significant advances are expected as this area of research matures.

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**Supporting Information Available:** Text giving a full description of crystallographic details and tables of crystallographic parameters, atom is positional parameters, thermal parameters, and bond distances and angles for **4**−**8** (28 pages). Ordering information is given on any current masthead page.

OM960941D

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