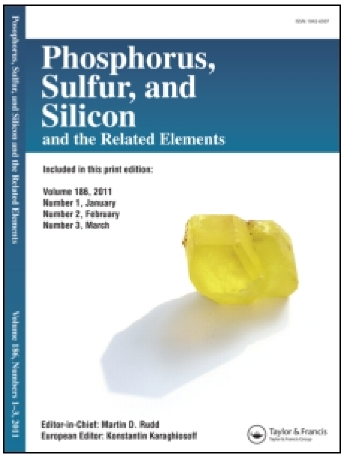

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ZIRCONOCENE PHOSPHINIDENE COMPLEX TRAPPING REACTIONS

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Communication

ZIRCONOCENE PHOSPHINIDENE COMPLEX TRAPPING REACTIONS

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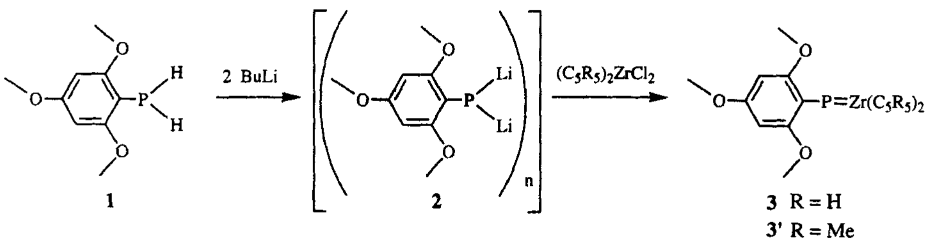
Reactions of a zirconocene phosphinidene like complex, **3**, with the dichlorophosphine 2,4,6-$(^tBu_3)C_6H_2PCl_2$, the Eschenmoser's salt $[H_2C{=}NMe_2][Cl]$, the phospha-imine $(Me_3Si)_2N{-}P{=}N{-}SiMe_3$ or ^tBuOH lead, respectively, to the diphosphene 2,4,6-$(MeO)_3C_6H_2{-}P{=}P{-}$2,4,6-$(^tBu)_3C_6H_2$, the phosphine 2,4,6-$(MeO)_3C_6H_2{-}P(CH_2NMe_2)_2$, the diphosphino metallacycle 2,4,6-$(MeO)_3C_6H_2{-}P{-}P(N(SiMe_3)_2){-}N(SiMe_3){-}ZrCp_2$ or the metallated phosphine 2,4,6-$(MeO)_3C_6H_2{-}P(H){-}Zr{-}Cp_2(OtBu)$.

Key words: Zirconocene phosphinidene complex, [2+2] Cycloaddition.

A few papers concerning the preparation and the reactivity of phosphinidene complexes have been published to date in spite of the synthetic interest of such compounds.[1-10] In an elegant work, Stephan *et al.*[4-8] recently reported the generation and the trapping of some very unstable zirconocene phosphinidenes $R{-}P{=}ZrCp_2$. In one case, the structure of a bent terminal phosphinidene derivative stabilized by a mole of PMe_3 was solved by X-ray diffraction studies.[9] These results prompted us to report our investigations in this field[11] which are related to the general study of the interactions between main group elements (essentially phosphorus, boron, silicon derivatives) and group 4 elements.[12] We describe here the synthesis of zirconocene complex, **3**, reacting formally as a free zirconocene phosphinidene 2,4,6-$(MeO)_3C_6H_2{-}P{=}ZrCp_2$. Three trapping reactions of **3** will be presented: i) exchange reactions with formation either of phosphorus-phosphorus double bond or phosphorus carbon single bonds, ii) [1,2] addition on the formal phosphorus-zirconium double bond, iii) [2+2] cycloaddition leading to a new phosphametallacycle.

Our strategy for the generation of terminal phosphinidene species involves one of the most basic non-hindered primary phosphine 2,4,6-$(MeO)_3C_6H_2{-}PH_2$[13] (**1**), which was lithiated with 2 equiv. of BuLi then reacted with Cp_2ZrCl_2 (Scheme I). We anticipated that donor effects of the methoxy groups may contribute to the stabilization of the expected zirconocene-phosphinidene compound. Dilithiation of **1** with 2 equiv. of BuLi in the presence of crown ether in THF gave a compound **2** readily insoluble which was nevertheless detected by ^{31}P NMR [**2** $\delta^{31}P = -238.7$ ppm (br. s.)][14] and by its reaction with the Eschenmoser salt $[H_2C{=}NMe_2][Cl]$ (**4**) which leads to the phosphine **5** ($\delta^{31}P = -67.3$ ppm). These observations are in

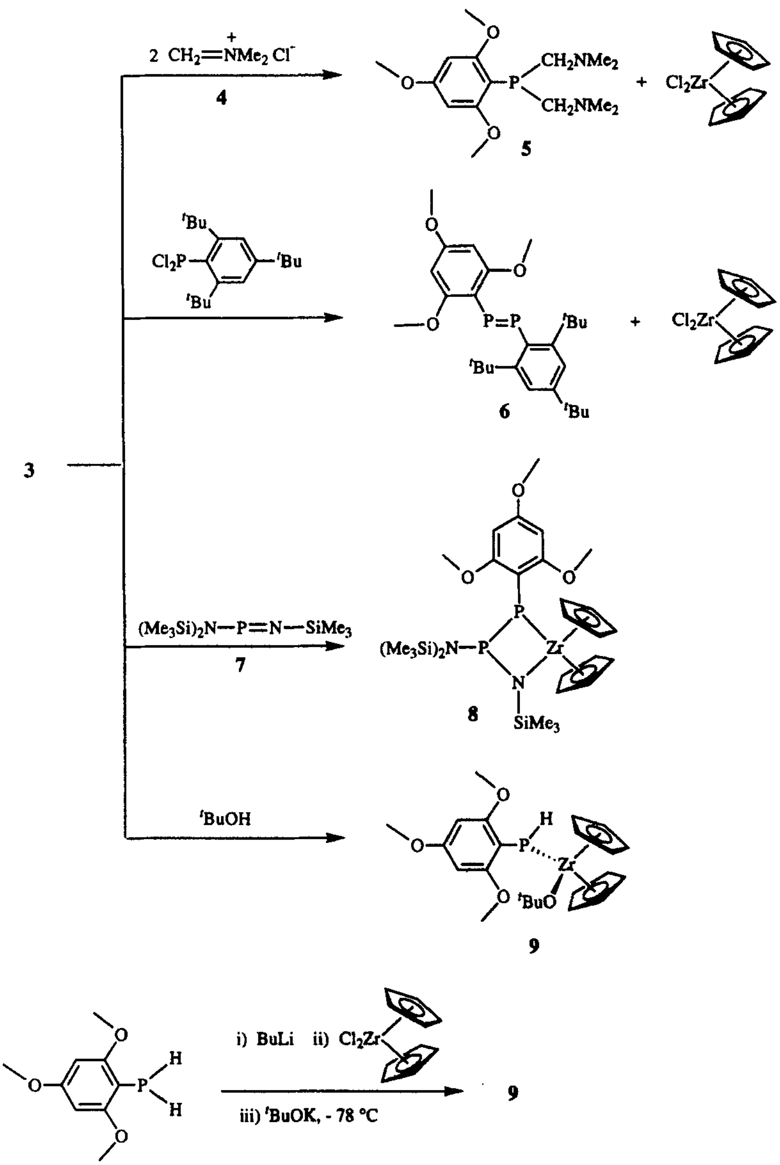


SCHEME I

agreement with the formation of monomeric or more probably oligomeric dilithiated species reacting as 2,4,6-$(MeO)_3C_6H_2$—PLi_2. It can be noted that **1** does not react with **4** in the same experimental conditions. Reaction of **2** with Cp_2ZrCl_2 affords the complex **3**. ^{31}P NMR spectrum of **3** consists in a singlet at 465.2 ppm which might be consistent with a zirconocene phosphinidene structure 2,4,6-$(MeO)_3C_6H_2$—P=$ZrCp_2$; nevertheless the corresponding dimeric (or polymeric) formulation(s) cannot be totally ruled out. No PH coupling is detected. Similar ^{31}P chemical shifts were found for transient zirconocene-phosphinidene[7] (2,4,6-$Me_3C_6H_2$—P=$ZrCp_2$ 526 ppm; 2,4,6-$(^tBu)_3C_6H_2$—P=$ZrCp_2$ 478 ppm, Cy—P=$ZrCp_2$ 498.9 ppm etc.). The shielding effect observed for **2** can be explained by the presence of methoxy groups. Such a shielding effect was already detected for the starting primary phosphines (2,4,6-$Me_3C_6H_2$—PH_2 − 160 ppm; 2,4,6-$(^tBu)_3C_6H_2$—PH_2 − 129.9 ppm, Cy-PH_2 − 111.7 ppm, but 2,4,6-$(MeO)_3C_6H_2$—PH_2 − 174 ppm). The ^{13}C NMR spectrum exhibits two singlets for the ortho- and meta-carbon atoms of the phenyl group (159.4 and 159.0 *o*-$\underline{C}$-OMe; 92.6 and 91.1 *m*-$\underline{C}$-OMe ppm), and one singlet is detected for each methoxy group (56.0, 55.8, 55.3 ppm). Because of the instability of **3** mass spectrometry measurements or molecular weight determinations do not address the question of oligomerization. The same experiment conducted with **2** and $Cp^*_2ZrCl_2$ leads to an analogous complex **3'**.[13] Compound **3'** is more stable than **3** but not enough to be unambiguously characterized by mass spectroscopy or by X-ray diffraction studies.

Direct evidence for the structure of **3** has been found when this compound was reacted with a variety of reagents (Scheme II). A clean exchange reaction occurs when **3** is treated with the bulky dichlorophosphine 2,4,6-$(^tBu)_3C_6H_2$—PCl_2 at −78°C; the diphosphene **6** was formed in 90% yield. Derivative **6** exhibits classical NMR data for such a compound. For example, the ^{31}P NMR spectrum consists of two doublets at low field (520.6 and 435.0 ppm) with a large $^1J_{PP}$ coupling constant (546 Hz).

An easy exchange reaction takes place when the Eschenmoser's salt $[H_2C{=}NMe_2][Cl]$ (2 equiv.) is added to **3**: the phosphine **5** is isolated in near quantitative yield. Addition of the phospha-imine **7** to a THF solution of **3** maintained at −78°C leads to the new diphosphinometallacycle **8**[13] which is the first isolated [2+2] cycloadduct formed from a zirconocene-phosphinidene like species.[15] The ^{31}P NMR spectra of **8** shows two doublets at 105.2 [P—$N(SiMe_3)_2$] and −72.5 [P—2,4,6-$(OMe)_3C_6H_2$] ppm with $^1J_{PP}$ = 267 Hz. ^{1}H NMR (two Cp groups at 6.41 (d, $^3J_{HP}$ = 1.5 Hz) ppm and 6.02 (s) ppm)[16] and ^{13}C NMR data (two Cp



SCHEME II

groups at 114.4 (d, $^{2}J_{CP}$ = 5.2 Hz) ppm and 114.8 (s) ppm) are in agreement with the proposed cyclic structure.

On the other hand, direct addition of ᵗBuOH on **3** at −78°C leads to the adduct **9**[13] which can be more cleanly prepared by treatment of the primary phosphine **1** with 1 equiv. of BuLi, then addition of Cp_2ZrCl_2 followed by that of ᵗBuOK. **9** appears to be extremely unstable giving rise to **1** and the corresponding diphosphine 2,4,6-$(MeO)_3C_6H_2$—P(H)—(H)P—2,4,6-$(MeO)_3C_6H_2$ (**10**).

Cycloaddition reactions involving **3** or other zirconocene-phosphinidene species and a variety of unsaturated phosphorus, boron or silicon derivatives are underway.

ACKNOWLEDGEMENT

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13. Selected data. (**1**) ^{31}P NMR (δ, C_6D_6): −174.0 (t,${}^{1}J_{PH}$ = 203 Hz). ^{1}H NMR (δ, C_6D_6): 6.05 (d, ${}^{4}J_{HP}$ = 1.9 Hz, 2H, H-aryl), 4.12 (d, ${}^{1}J_{HP}$ = 203 Hz, 2H, PH_2), 3.36 (s, 3H, *p*-OCH_3), 3.30 (s, 6H, *o*-OCH_3). ^{13}C{^{1}H} NMR (δ, C_6D_6): 162.0 (s, *p*-$\underline{C}$H), 162.2 (s, *o*-$\underline{C}$H), 91.0 (s, *m*-$\underline{C}$H), 55.2 (s, *o*-$\underline{C}H_3O$), 54.8 (s, *p*-$\underline{C}H_3O$), *i*-$\underline{C}$P not detected. (**3**) ^{31}P NMR (δ, THF-d_8): 465.2. ^{1}H NMR (δ, THF-d_8): 6.15 (s, 2H, H-aryl), 5.61 (s, 10H, Cp), 3.70 (s, 3H, *p*-OMe), 3.63 (s, 6H, *o*-OMe). ^{13}C{^{1}H} NMR (δ, THF-d_8): 163.1 (s, *i*-C-aryl), 159.0 (s, *p*-$\underline{C}$OMe), 158.4 (s, *o*-$\underline{C}$OMe), 104.1 (s, Cp), 107.8 (s, Cp), 93.9 (s, *m*-CH), 57.0 (s, *p*-OMe), 56.0 (s, *o*-OMe). (**3′**) ^{31}P (δ, C_6D_6): 438.4. ^{1}H NMR (δ, C_6D_6): 6.31 (d, ${}^{4}J_{HP}$ = 1.9 Hz, 1H, H-aryl), 6.19 (d, ${}^{4}J_{HP}$ = 1.9 Hz, 1H, H-aryl), 3.38 (s, 6H, *o*-OMe), 3.37 (s, 3H, *p*-OMe), 2.01 (s, 30H, CCH_3). ^{13}C{^{1}H} NMR (δ, C_6D_6): 159.4, 159.0 (s, *o*-$\underline{C}$OMe), 154.3 (s, *p*-$\underline{C}$OMe), 117.8 (s, $\underline{C}CH_3$), 92.6, 91.1 (s, *m*-CH), 56.0, 55.8, 55.3 (s, OMe), 12.7 (s, $C\underline{C}H_3$), *i*-$\underline{C}$P not detected. (**5**) ^{31}P NMR (δ, CD_2Cl_2): −67.3. ^{1}H NMR (δ, CD_2Cl_2): 6.13 (d, ${}^{4}J_{HP}$ = 1.6 Hz, 2H, H-aryl), 3.83 (s, 9H, OMe), 3.20 (m, 4H, PCH_2), 2.41 (s, 12H, NCH_3). ^{13}C{^{1}H} NMR (δ, CD_2Cl_2): 164.7 (d, ${}^{2}J_{CP}$ = 7.6 Hz, *o*-$\underline{C}$OMe), 163.8 (s, *p*-$\underline{C}$OMe), 91.1 (s, *m*-CH), 58.8 (d, ${}^{1}J_{CP}$ = 4.5 Hz, PCH_2), 55.9 (s, *o*-OMe), 55.4 (s, *p*-OMe), 45.2 (d, ${}^{3}J_{CP}$ = 10.0 Hz, CH_3), *i*-$\underline{C}$P not detected. (**6**) ^{31}P NMR (δ, C_6D_6): 520.6 (d, ${}^{1}J_{PP}$ = 546 Hz, P^{t}Bu), 435.0 (d, ${}^{1}J_{PP}$ = 546 Hz, POMe). ^{1}H NMR (δ, C_6D_6): 7.63 (s, 2H, H-aryl), 7.37 (s, 2H, H-aryl), 3.45 (s, 3H, *p*-OMe), 3.35 (s, 6H, *o*-OMe), 1.67 (s, 6H, *o*-^{t}Bu), 1.35 (s, 3H, *p*-^{t}Bu). ^{13}C{^{1}H} NMR (δ, C_6D_6): 164.1 (s, *p*-$\underline{C}$OMe), 161.5 (d, ${}^{2}J_{CP}$ = 6.4 Hz, *o*-$\underline{C}$OMe), 154.2 (d, ${}^{2}J_{CP}$ = 8.7 Hz, *o*-$\underline{C}$^{t}Bu), 149.9 (s, *p*-$\underline{C}$^{t}Bu), 122.7 (s, *m*-$\underline{C}$^{t}Bu), 91.8 (s, *m*-$\underline{C}$OMe), 55.6 (s, *o*-OMe), 55.5 (s, *p*-OMe), 39.3, 37.2 (s, *o*-$\underline{C}CH_3$), 35.0, 32.3 (s, *o*-$C\underline{C}H_3$), 32.0 (s, *p*-$C\underline{C}H_3$), 29.8 (s, *p*-$\underline{C}CH_3$), *i*-$\underline{C}$P not detected. (**8**) ^{31}P NMR (δ, C_6D_6) 105.2 (d, ${}^{1}J_{PP}$ = 267 Hz, PN), −72.5 (d, ${}^{1}J_{PP}$ = 267 Hz, PAr). ^{1}H NMR (δ, C_6D_6): 6.41 (d, ${}^{3}J_{HP}$ = 1.5 Hz, 5H, Cp), 6.02 (s, 5H, Cp), 5.78 (d, ${}^{4}J_{HP}$ = 1.9 Hz, 2H, H-aryl), 3.43 (s, 3H, *p*-OMe), 3.31 (s, 6H, *o*-OMe), 0.76 (s, 9H, $SiMe_3$), 0.62 (s, 9H, $SiMe_3$), 0.13 (s, 9H, $SiMe_3$). ^{13}C{^{1}H} NMR (δ, C_6D_6): 163.1 (s, *o*-$\underline{C}$OMe), 161.8 (s, *p*-$\underline{C}$OMe), 114.8 (s, Cp), 114.4 d, ${}^{2}J_{CP}$ = 5.2 Hz, Cp), 91.8 (s, *m*-CH), 55.6 (s, *o*-OMe), 55.3 (s, *p*-OMe), 7.3, 6.4, 4.5 (s, $SiMe_3$), *i*-$\underline{C}$P not detected. (**9**) ^{31}P NMR (δ, C_6D_6): −120.5 (d, ${}^{1}J_{PH}$ = 196 Hz). ^{1}H NMR (δ, THF-d_8): 6.26 (d, ${}^{4}J_{HP}$ = 1.9 Hz, 2H, H-aryl), 6.25 (s, 10H, Cp), 4.68 (d, ${}^{1}j_{HP}$ = 196.0 Hz, HP), 3.69 (s, 3H, *p*-OMe), 3.68 (s, 6H, *o*-OMe), 1.17 (s, 9H, *t*Bu). ^{13}C{^{1}H} NMR (δ, THF-d_8): 163.4 (s, *p*-$\underline{C}$OMe), 163.1 (s, *o*-$\underline{C}$OMe), 114.5 (s, Cp), 93.9 (s, *m*-CH), 56.4 (s, *p*-OMe), 55.8 (s, *o*-OMe), 32.7 (s, $\underline{C}CH_3$), 32.0 (s, $C\underline{C}H_3$), *i*-$\underline{C}$P not detected.

14. To be compared with the spectral data for **1** [δ ^{31}P = -174.4 ppm (t, $^{1}J_{PH}$ = 214 Hz)] and 2,4,6-$(MeO)_3C_6H_2$—P(H)Li[$\delta^{31}P$ = -190.0 ppm (d, $^{1}J_{PH}$ = 190 Hz)].
15. A [2+2] cycloaddition of MeCN to the transient phosphinidene 2,4,6-$Me_3C_6H_2$—P=ZrCp$^*_2$ with subsequent insertion of a second equiv. of MeCN into the Zr—P bond was postulated[8] in order to explain the formation of the metallacycle 2,4,6-$Me_3C_6H_2$—P(N=CMe)$_2$ZrCp$^*_2$ but the product of the initial cycloaddition was not detected.
16. Similar small proton phosphorus coupling constants (J_{HP} ≈ 2 Hz) have been detected for the Cp groups in three membered phosphorus metallacycles.[11k]