

Insertion of Zirconocene into the Carbon–Halogen Bond of 2-Halophosphinines

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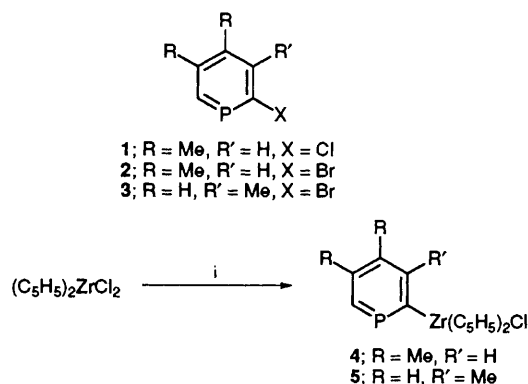
Insertion of zirconocene into the C–X bond of 2-halophosphinines (X = Cl, Br) takes place between –80 and 20 °C in tetrahydrofuran (THF); the X-ray crystal structure analysis of such an insertion product shows a normal geometry at zirconium and a highly delocalised phosphinine ring with all C=C and the two P=C bonds being strictly equal at 1.395 and 1.726 Å, respectively; protonation, deuteration and halogenation of these products lead to the expected phosphinines by cleavage of Zr–C bond.

Since classical methods for the functionalization of aromatic heterocycles that contain oxygen, nitrogen, or sulfur, such as electrophilic substitution and metallation reactions do not work for phosphinines,¹ the introduction of phosphinine rings into complex structures is presently difficult. Recently, several attempts have been made to circumvent this limitation using

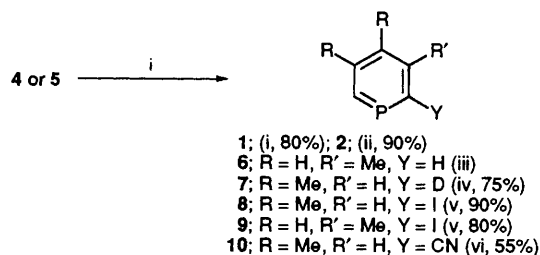
synthetic equivalents of 2-lithiophosphinines. These are accessible from 2-bromophosphinines after protection of phosphorus by sulfurization or complexation.² Non-protected 2-iodophosphinines give organozinc derivatives directly, but these organometallic compounds display a poor reactivity.³ A straightforward access to reactive organometallic derivatives

of phosphinines was therefore desirable and the insertion of zirconocene into the C–X bond of the readily available 2-halophosphinines^{2,4} represented a possible solution. Zirconocene, obtained *in situ* from n-butyllithium and zirconocene dichloride,⁵ inserts quantitatively into the C–X bond of 2-halophosphinines between –80 and +20 °C according to ³¹P NMR analysis of the crude mixtures. (Scheme 1).

Complexes **4** and **5** were characterized by ¹H and ³¹P NMR spectroscopy.† Curiously, the same complex **4** appears to be formed from phosphinines **1** and **2**. The X-ray crystal structure analysis of **4**‡ showed that it includes a Zr–Cl bond which, in the case of **2**, presumably results from metathesis of the first-formed Zr–Br bond with chloride ions from the initial reduction of the zirconocene dichloride. The geometry at zirconium (Fig. 1) appears to be normal when compared with the analogous –C(Ph)=CMe₂⁶ and –CH=CH–SiMe₃⁷ (C₅H₅)₂ZrCl-complexes. Both the Zr–C(2) and Zr–Cl bonds at 2.313(4) and 2.4780(9) Å are very similar in length to the corresponding bonds in their alkenyl counterparts. The Cl–Zr–C(2) angle [100.4(1)°] lines between those recorded for the –C(Ph)=CMe₂ [100.8(1)°] and the –CH=CHSiMe₃ [96.6(2)°] complexes. The main surprise comes from the structure of the phosphinine ring, where the two P–C bonds are strictly equal at 1.724(4) and 1.729(4) Å in spite of the



Scheme 1 Reagents and conditions: i, BuⁿLi, (2 equiv.) THF, –80 °C, 1 h, then add the phosphinine 1–3 and back to 20 °C in 2 h



Scheme 2 Conditions: THF, 10 °C, 10 min; Reagents: i, *N*-chlorosuccinimide; ii, *N*-bromosuccinimide; iii, H₂O; iv, D₂O; v, I₂; vi, –80 °C, BrCN (2 equiv.). Phosphinines **6**, **7** and **10**† have not been described in the literature previously.

† Spectroscopic data for **4**: δ ³¹P (THF) 224.4; ¹H NMR (C₄D₈O): δ 2.21 (d, *J*_{H–P} 3.39 Hz, 3H, Me), 2.24 (s, 3H, Me), 6.36 (s, 10H, C₅H₅), 7.89 (d, ³*J*_{H–P} 14.79 Hz, 1H, 3-H), 8.30 (d, ²*J*_{H–P} 35.13 Hz, 1H, 6-H). **5**: δ ³¹P (THF) 219.4.

6: δ ³¹P (THF) 206.8; ¹H NMR (CDCl₃): δ 2.49 (s, Me), 6.52 (ddt, 1H, ²*J*_{H–P} 24.50, ³*J*_{H–H} 8.36 Hz, ⁴*J*_{H–H}: not observed; 6-H), 7.36 (m, 1H, ³*J*_{H–H} 8.36 Hz, 4-H), 7.80 (dt, 1H, ³*J*_{H–P} 10.8, ³*J*_{H–H} 8.36 Hz, 6-H), 8.52 (d, 1H, ²*J*_{H–P} 37.59 Hz, 2-H).

7: δ ³¹P (CDCl₃) 190.0; ¹H NMR (CDCl₃): δ 2.45 (d, *J*_{H–P} 3.62 Hz, 3H, Me); 2.51 (s, 3H, Me), 7.81 (d, ³*J*_{H–P} 8.49 Hz, 1H, 3-H), 8.56 (d, ²*J*_{H–P} 36.81 Hz, 1H, 6-H). (**7**) W(CO)₅: δ ³¹P (CDCl₃) 156.2, ¹*J*_{31P–183W} 258.1 Hz; ¹H NMR (CDCl₃): δ 2.43 (d, *J*_{H–P} 6.22 Hz, 3H, Me), 2.61 (s, 3H, Me), 7.78 (d, ³*J*_{H–P} 23.28 Hz, 1H, 3-H), 8.22 (d, ²*J*_{H–P} 23.97 Hz, 1H, 6-H).

9: δ ³¹P (CH₂Cl₂) 236.65; ¹H NMR (CDCl₃): δ 2.61 (s, 3H, Me), 7.44 (dd, 1H, ³*J*_{H–H} 7.98 Hz, ⁴*J*_{H–P} 3.75 Hz, 4-H), 7.82 (dd, 1H, ³*J*_{H–H} 7.98 Hz, ³*J*_{H–H} 9.89 Hz, ³*J*_{H–P}: not observed, 5-H), 8.16 (dd, 1H, ²*J*_{H–P} 38.84 Hz, ³*J*_{H–H} 9.89 Hz, 6-H); ¹³C NMR (CDCl₃): δ 32.73 (s, Me), 130.60 (d, ¹*J*_{C–P} 74.76 Hz, C₂), 132.02 (d, *J*_{C–P} 19.39 Hz, C₄ or C₅), 134.23 (d, *J*_{C–P} 13.6 Hz, C₅ or C₄), 147.68 [d, ²*J*_{C–P} 15.32 Hz, C₃ (Me)], 157.74 (d, ¹*J*_{C–P} 57.64 Hz, C₆); Mass (EI, 70 eV): *m/z* 236 (M⁺, 100%).

10: δ ³¹P (CDCl₃) 212.63; ¹H NMR (CDCl₃): δ 2.41 (d, 3H, *J*_{H–P} 3.64 Hz, Me), 2.50 (d, 3H, *J*_{H–P} = 0.44 Hz, Me), 8.00 (d, 1H, ³*J*_{H–P} 3.42 Hz, 3-H), 8.57 (d, 1H, ²*J*_{H–P} 40.90 Hz, 2-H); ¹³C NMR (CDCl₃): δ 22.68 (s, Me), 24.28 (d, *J*_{C–P} 4.18 Hz, Me), 121.13 (d, ²*J*_{C–P} 30.27 Hz, C≡N), 134.00 (d, ¹*J*_{C–P} 46 Hz, C₂), 140.9 (d, *J*_{C–P} 16.32 Hz, C₄ or C₅), 142.21 (d, ²*J*_{C–P} 12.0 Hz, C₃), 147.67 (d, *J*_{C–P} 14.57 Hz, C₅ or C₄), 155.68 (d, ¹*J*_{C–P} 52.25 Hz, C₄); Mass (EI, 70 eV): *m/z* 149 (M⁺, 100%).

‡ X-ray structure determination for **4**: Hexane was slowly diffused at –25 °C in a crude solution of the compound containing LiCl. The brownish–yellow hygroscopic crystals so obtained were handled under a layer of silicone oil. Data were collected at –150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallises in space group C2/c, *a* = 14.093(1), *b* = 7.247(1), *c* = 31.987(3) Å, β = 97.21(1)°; *V* = 3240.9(1.1) Å³; *Z* = 8; *D*_c = 1.557 g cm^{–3}; Mo–Kα radiation (λ = 0.71073 Å), graphite monochromator; μ = 9.2 cm^{–1}; *F*(000) = 1536. A total of 4703 unique reflections recorded in the range 2 ≤ 2θ ≤ 60.0° of which 1097 were considered as unobserved [*F*² < 3.0σ (*F*²)], leaving 3606 for solution and refinement. The position of the zirconium atom was obtained from a Patterson map. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a *p* factor equal to 0.08. The final agreement factors were *R* = 0.044, *R*_w = 0.085, GOF = 1.81.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

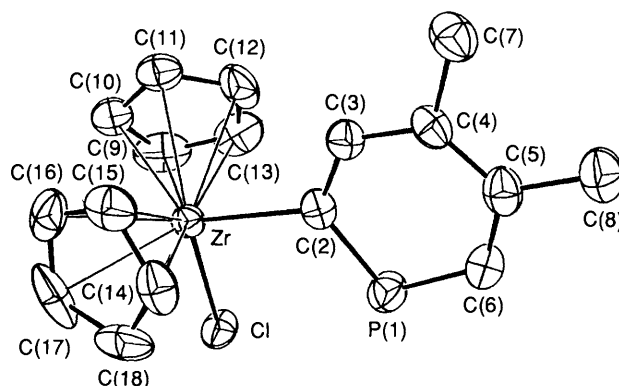


Fig. 1 Crystal structure of **4**: ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity. Important bond distances (Å) and angles (°): Zr–Cl 2.4780(9), Zr–C(2) 2.318(4), P(1)–C(2) 1.724(4), P(1)–C(6) 1.729(4), C(2)–C(3) 1.395(6), C(8)–C(4) 1.396(6), C(4)–C(5) 1.398(6), C(5)–C(6) 1.392(6); Cl–Zr–C(2) 100.4(1), C(2)–P(1)–C(6) 102.7(2), Zr–C(2)–P(1) 114.6(2), Zr–C(2)–C(3) 125.2(3), P(1)–C(2)–C(3) 120.1(3), C(2)–C(3)–C(4) 127.5(4), C(3)–C(4)–C(5) 122.8(4), C(4)–C(5)–C(6) 119.7(4), P(1)–C(6)–C(5) 127.2(3). Angle between the two C₃H₅ mean planes 128.34(14).

dissymmetry of the substitution scheme. Besides, the alternation between long (*ca* 1.41 Å) and short (*ca* 1.39 Å) C–C bonds which is characteristic of the phosphinine nucleus¹ completely disappears in **4**: the four C–C bonds are equal at 1.392(6)–1.398(6) Å, suggesting a better electronic delocalization in **4** than in non-metallated phosphinines.

We also carried out a preliminary investigation of the chemistry of **4** and **5**. The Zr–C bonds of **4** and **5** display a normal reactivity and can be cleaved by water, halogens, and cyanogen bromide to give the phosphinines shown in Scheme 2.

We have checked that, under our experimental conditions, $(C_5H_5)_2Zr$ does not insert into the C-Br bonds of bromobenzene and 2-bromopyridine. Hence, the phosphorus atoms of **1-3** must play a role in the reaction. Gell and Schwartz⁸ have shown that phosphines (L) induce the elimination of alkane from $(C_5H_5)_2Zr(H)R$, R = alkyl and give $(C_5H_5)_2ZrL_2$ complexes. Thus, very probably, the reaction of phosphinines **1-3** with zirconocene starts by a complexation of the phosphorus lone pairs, followed by an intramolecular insertion of the $[(C_5H_5)_2Zr]$ unit into the C-X bonds.

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