Hydrozirconation of Phospha-alkenes and Phosphaimines. Evidence for the Formation of P–C–Zr and P–N–Zr Three-membered Rings

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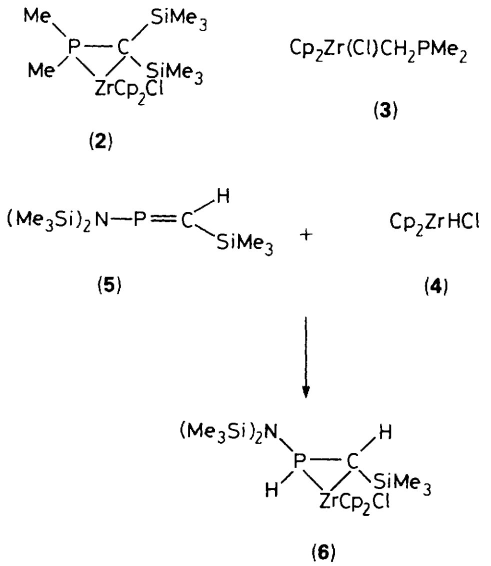
Addition of bis(η-cyclopentadienyl)zirconium hydride (Cp_2ZrHCl) to phospha-alkenes and phosphaimines leads either to a functionalized bis(η-cyclopentadienyl)zirconium phosphirane and azaphosphirane or to a protonated dico-ordinated phosphorus species.

Recently it has been demonstrated that the reaction of dimethylphosphinomethanide (**1**) $Li[Me_2PC(SiMe_3)_2]$ with Cp_2ZrCl_2 (Cp = cyclopentadienyl) leads to the first examples of Zr–P bonding in dimethylphosphinomethylzirconium(IV) complexes[1] (**2**) rather than to the corresponding 16 electron zirconium complex (**3**) as reported in a closely related reaction.[2] It has been postulated that steric hindrance at the carbanionic C atom of the ligand (**1**) favours the formation of this unique phosphorus–zirconium three membered ring. This communication reports a convenient access to the first functionalized bis(η-cyclopentadienyl)zirconium phosphirane (**6**) and zirconocene azaphosphirane (**12**) as well as the formation of a novel P-protonated phosphaimine or diphosphirane.

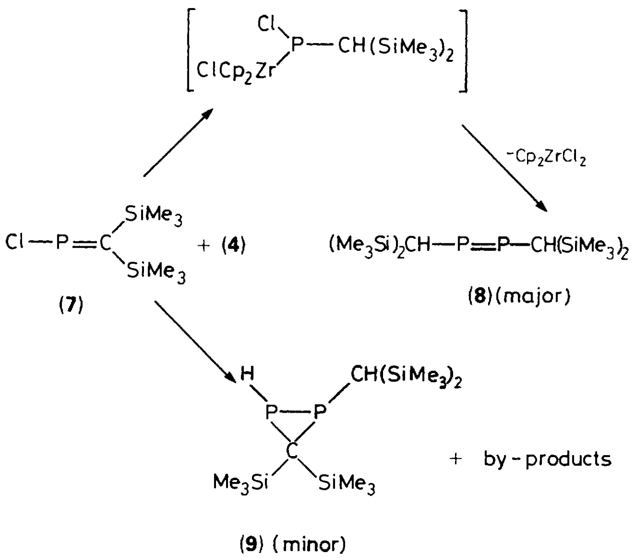
Addition of the hydride Cp_2ZrHCl (**4**) to a tetrahydrofuran (THF) solution of the phospha-alkene $(Me_3Si)_2N$–P = $CH(SiMe_3)$ (**5**) at −20 °C affords the metallated three membered ring (**6**) as a white powder in 95% yield (Scheme

$Li[Me_2PC(SiMe_3)_2]$

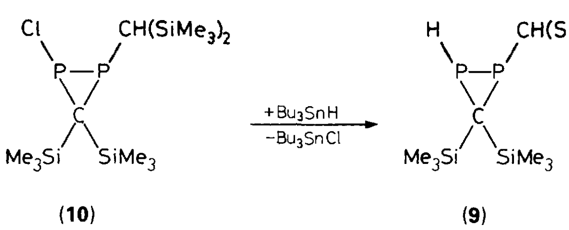
(**1**)



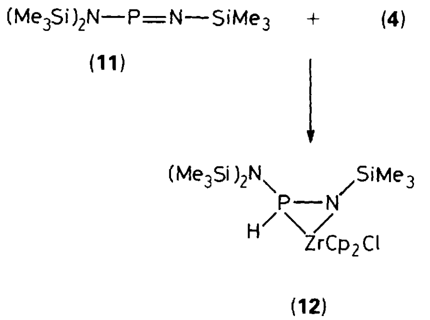
Scheme 1



Scheme 2



Scheme 3



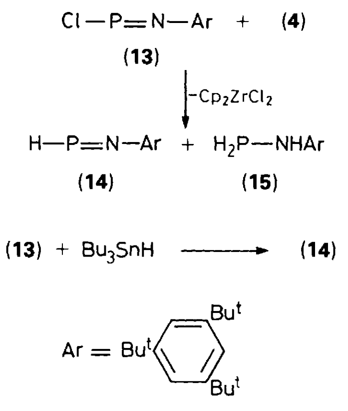
Scheme 4

1). The medium resolution mass spectrum (70 eV) exhibits a parent peak at *m*/*z* 533. The ^{31}P NMR chemical shift of (**6**) consists of a doublet (δ 42 p.p.m.) with a large P–H coupling constant ($^{1}J_{PH}$ 346 Hz) indicating P co-ordination. These data are in agreement with a cyclic structure and not with the corresponding linear form $(Me_3Si)_2NP(H)CH(SiMe_3)(ZrCp_2Cl)$ which would have presented similar ^{31}P NMR values; for example $(Me_3Si)_2NP(H)CH_2(SiMe_3)$ [δ(^{31}P) 3.2 p.p.m., $^{1}J_{PH}$ 209 Hz].[3] Indeed all the known secondary phosphines of $R_2NP(H)R$ (R = alkyl) type show $^{1}J_{PH}$ values smaller than 240 Hz. Moreover such a ^{31}P deshielding effect is reported in the literature[1] [$Me_2PCH_2ZrCp_2Cl$ δ −36.2 p.p.m.; $Me_2\overline{P{-}C(SiMe_3)_2Zr}Cp_2Cl$ δ 2.73 p.p.m.]. ^{1}H NMR (two doublets for the Cp groups at δ 5.74 and 5.81 with J_{HP} 2.4 and 1.9 Hz respectively† as well as ^{13}C NMR data (two singlets for the Cp groups) confirm our assignment for (**6**).

A 1,2-addition of Cp_2ZrHCl to the P=C double bond of (**5**) followed by cyclisation is a reasonable postulation to explain the formation of the cyclic adduct (**6**).

Treatment of the P-halogenated phospha-alkene (**7**) with (**4**) gives rise to the diphosphene (**8**)[4] (major compound), the diphosphirane (**9**), and some other by-products not yet identified. A reverse 1,2-addition of the zirconium hydride to the P–C double bond of (**7**) followed by Cp_2ZrCl_2 elimination might account for the formation of derivative (**8**) (Scheme 2). The diphosphirane (**9**) may also be prepared directly by reacting the corresponding halogenated diphosphirane (**10**)[5] with tributyltin hydride [(**9**) δ(^{31}P) −134.4 and −244.9 p.p.m., $^{1}J_{PP}$ 161.2, $^{1}J_{PH}$ 149 Hz] (Scheme 3).

The reaction of the phosphaimine (**11**) in THF with the hydride (**4**) under the same experimental conditions, leads only to a functionalized zirconium-containing phosphorus species (**12**) obtained as a white powder in near quantitative yield (Scheme 4). We have been unable to obtain suitable crystals for *X*-ray analysis. Nevertheless the following data suggest a cyclic structure for (**12**). ^{31}P NMR spectra exhibit a doublet at + 34 p.p.m. with a large coupling constant of 317 Hz‡ which falls in the expected range for a P–H metallated complex.[6] ^{1}H NMR (two doublets for the Cp groups at 5.85 and 6 with P–H coupling contants of 2.7 and 1.9 Hz respectively) and ^{13}C NMR data (two singlets for the Cp groups at δ 110.2 and 111.1) are in agreement with the proposed cyclic structure (**12**) (mass spectrum, *m*/*z* 534).



Scheme 5

On the other hand, reaction of the chlorophosphaimine (**13**) with (**4**) affords a mixture of the new phosphaimine (**14**) [δ(^{31}P) 84.4 p.p.m., $^{1}J_{PH}$ 208 Hz] and of the primary phosphine (**15**) [δ(^{31}P) −43.5 p.p.m., $^{1}J_{PH}$ 201 Hz) (Scheme 5). Compound (**14**) was also prepared directly by reacting (**13**) with tributyltin hydride. The formation of derivative (**15**) may involve a 1,2-addition to the P=N double bond, the Cp_2ZrCl group being linked to phosphorus, followed by bis(η-cyclopentadienyl)zirconium dichloride elimination and hydrogen abstraction from the solvent (THF) by the transient phosphinidene <P–NHAr. In this case no trace of the corresponding dimer, the diphosphene ArNH-P=P-NHAr, has been detected.

Work is in progress to demonstrate the mechanism of formation of these compounds and to extend these reactions not only to other phospha-alkenes and phosphaimines but also to various unsaturated phosphorus species.

Received, 13th December 1989; Com. 9/05322K

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† A similar small proton phosphorus coupling constant (J_{HP} 2 Hz) has been detected for the Cp groups in (**1**).[1]

‡ For comparison: $^{1}J_{PH}$ 210 Hz in $[(Me_3Si)_2N]_2P{-}H$.[3]