Versatile Behaviour of the Phosphanyl Salt $(\mathrm{Pr^i_2N})_2\mathrm{P^+CF_3SO_3^-}$ towards Zirconocene Derivatives

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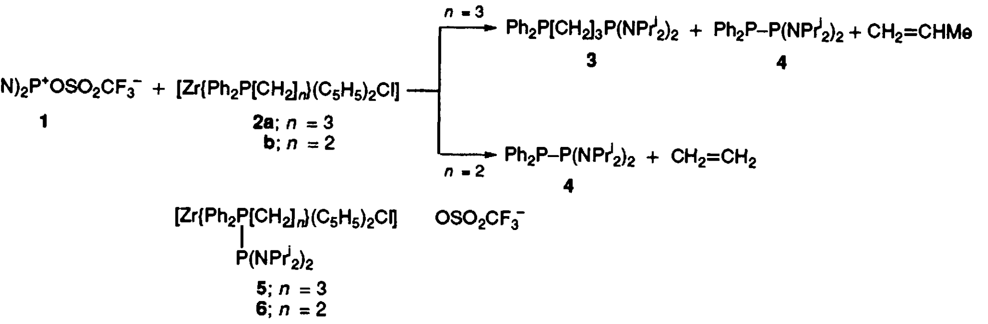
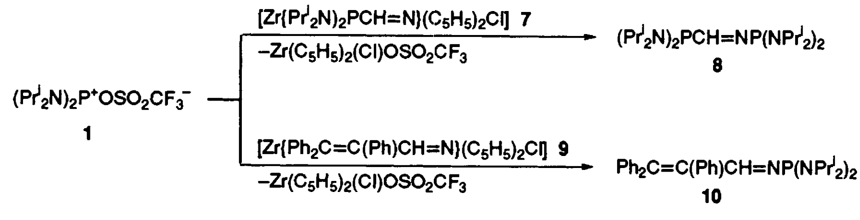
Transfer reactions of various groups ($\mathrm{Ph_2P[CH_2]_3}$–, $\mathrm{Ph_2C{=}CPh{-}CH{=}N}$–, $\mathrm{N_3}$, CN, Me, Cl, H) occurred from zirconium to phosphorus in reactions of the phosphanylium salt $(\mathrm{Pr^i_2N})_2\mathrm{P^+CF_3SO_3^-}$ with zirconocene derivatives; the crystal structure of $(\mathrm{Pr^i_2N})_2\mathrm{P{-}CH{=}N{-}P(NPr^i_2)_2}$ **8** has been determined.

Transmetallation of a variety of alkenyl and alkyl groups from zirconium to boron, phosphorus or other main group elements[1] are being actively investigated. Most of these reactions involved the halophilicity of zirconium species which were treated for example either with classical halogenated boranes[1a] and halogenated phosphanes[1d] or with low-coordinated phosphorus species such as the chlorophosphaalkenes $\mathrm{ClP{=}C(SiMe_3)_2}$, $\mathrm{(Me_3Si)_2NP{=}CCl_2}$ or the chlorophosphineimine $\mathrm{ClP{=}NAr}$ (Ar = $1,3,5\text{-}\mathrm{Bu^t_3C_6H_2}$).[2]

Another major property of zirconium derivatives, their oxophilicity, has been used in organic synthesis for the protection of functional groups (carboxylic acids, alcohols *etc.*)[3] but has not been taken into account in main group element chemistry. These observations prompted us to study the transfer of various functional groups from zirconium to phosphanylium salts, expecting that the presence of the triflate anion would facilitate such a transfer; the phosphanylium salt $\mathrm{R_2P^+CF_3SO_3^-}$, a six-electron species isoelectronic with silylene, possesses a vacant orbital and a lone electron pair which confer to these amphoteric cationic derivatives a great diversity of reactivity in organic and organometallic chemistry.



Scheme 1



Scheme 2

We report here the convenient new preparation of some phosphanes and diphosphanes as well as the X-ray structure determination of one of these species, the imine-bis phosphine $(Pr^i_2N)_2P{-}CH{=}N{-}P(NPr^i_2)_2$ **8**. Extension of these reactions to the formation of various phosphanes *via* easy transfer of methyl, cyano and azido groups or the proton and chlorine is also illustrated.

A transfer reaction easily took place when a tetrahydrofuran (thf) solution of the phosphane $[Zr\{Ph_2P[CH_2]_3\}(C_5H_5)_2Cl]$ **2a**† was added dropwise to a solution of the bis(diisopropylamino)phosphanylium salt **1** in dichloromethane at 0 °C. The expected diphosphane **3**‡ (75% yield) was formed as well as the diphosphane $(Pr^i_2N)_2PPPh_2$ **4**, and propene. Addition of **1** to the phosphane $[Zr\{Ph_2P[CH_2]_2\}(C_5H_5)_2Cl]$ **2b**[4] under the same conditions led exclusively to compound **4**‡ and ethylene. The unexpected formation of **4** in these two reactions (Scheme 1) can be explained *via* the transient generation of the phosphinophosphonium salts **5** or **6**[4] which rearranged into **4** with loss of propene or ethylene respectively. Attempts to detect salts **5** or **6** by ^{31}P NMR spectroscopy failed even at low temperature.

On the other hand, the oxophilicity of zirconium allowed the transfer of imine groups. Indeed, addition of **1** to a dichloromethane solution of the zirconyl-imine $[Zr\{(Pr^i_2N)_2PCH{=}N\}(C_5H_5)_2Cl]$ **7** led quantitatively to the *trans*-bisphosphino imine **8**.[1d] The molecular structure of **8**§ (Fig. 1) showed the quasi-symmetry of this molecule with similar bond lengths between P(1)C(1) and P(2)N(1) (1.749 and 1.796 Å respectively) and a pyramidal environment around phosphorus [sum of angles 316° at P(1), 312° at P(2)]. Similarly, treatment of a thf solution of the zirconyl-imine $[Zr\{Ph_2C{=}C(Ph)CH{=}N\}(C_5H_5)_2Cl]$ **9**¶ with the carbenoid species **1** gave the expected phosphane **10** in 95% yield|| (Scheme 2).

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† Phosphines **2a** and **2b** were easily prepared by the reaction of the corresponding vinyl or allyl phosphines $Ph_2PCH{=}CH_2$ or $Ph_2PCH_2CH{=}CH_2$ with $[Zr(C_5H_5)_2(H)(Cl)]$ in thf.

‡ *Selected NMR data*: **3** ^{31}P NMR (C_6D_6) δ 46.00 (s, PN) and −16.97 (s, P–Ph); ^{13}C NMR (C_6D_6) δ 23.28 (dd, $^2J_{CP}$ 26.7 and 16.9 Hz, CH_2), 24.70 (d, $^3J_{CP}$ 6.4 Hz, CH_3), 24.89 (d, $^3J_{CP}$ 7.3 Hz, CH_3), 30.95 (dd, J_{CP} 15.4 and 13.2 Hz, CH_2P) and 31.08 (dd, J_{CP} 11.6 and 6.14 Hz, CH_2P); **4** ^{31}P NMR ($CDCl_3$) δ 71.2 (d, $^1J_{PP}$ 120.8 Hz, PN) and −36.3 (d, $^1J_{PP}$ 120.8 Hz, P–Ph); ^1H NMR ($CDCl_3$) δ 0.82 (d, $^3J_{HH}$ 6.6 Hz, 12H, CH_3), 1.20 (d, $^3J_{HH}$ 6.7 Hz, 12H, CH_3), 3.64 (m, 4H, CH–CH_3) and 7.01–7.10, 8.00–8.06 (m, 10H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 24.90 (d, $^3J_{CP}$ 5.7 Hz, CH_3), 25.05 (d, $^3J_{CP}$ 6.1 Hz, CH_3), 49.41 (br s, CH), 128.56 (d, J_{CP} 7.8 Hz, *m*-C_{Ph}), 129.41 (s, J_{CP} 7.8 Hz, *p*-C_{Ph}), 137.10 (dd, J_{CP} 20.6, J_{CP} 7.9 Hz, *o*-C_{Ph}) and 138.84 (dd, J_{CP} 16.4, J_{CP} 17.9 Hz, *ipso*-C_{Ph}).

§ *Crystal data* for **8**: $P_2N_5C_{25}H_{57}$, $M_r = 489$, triclinic, $P\bar{1}$, $a = 9.587(9)$, $b = 11.853(7)$, $c = 7.578(9)$ Å, $\alpha = 102.4(1)$, $\beta = 73.9(2)$, $\gamma = 76.3(1)°$, $V = 767$ Å^3, $Z = 1$, $F(000) = 272$, μ(Mo-Kα) = 1.6 cm^{-1}, $T = 193$ K, λ(Mo-Kα) = 0.71069 Å, Final $R = 0.0518$, $R_w = 0.0459$ for 2478 observed reflections, 286 variables.

Unit cell parameters, space group and data collection were obtained on an Enraf-Nonius CAD4 automatic diffractometer. Accurate cell dimensions and an orientation matrix were obtained from least-squares refinements of the setting angles of 25 well-centred reflections ($2\theta < 25°$). Computations were performed using the CRYSTALS system from Oxford University adapted to a mini super calculator ALLIANT VFX80. Most atoms were localized by direct methods (SHELXS86, G. Sheldrick). Hydrogen atoms were located by difference Fourier techniques, then all hydrogen atoms were fixed at 1 Å from their carbon atoms. They were not further refined in the final stages of calculation. No important residue in the final difference map.

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

¶ The zirconyl-imine **9** was obtained in near quantitative yield by hydrozirconation of triphenyl acrylonitrile.

|| **10**, *selected NMR data*: ^{31}P NMR ($CDCl_3$) δ 84.9; ^1H NMR ($CDCl_3$) δ 1.15 (d, $^3J_{HH}$ 6.5 Hz, 12H, CH_3), 1.29 (d, $^3J_{HH}$ 6.5 Hz, 12H, CH_3), 3.32 (m, 4H, CH–CH_3), 7.01–7.31 (m, 15H, C_6H_5) and 8.73 (d, $^3J_{HP}$ 21.6 Hz, 1H, CH=N); ^{13}C NMR ($CDCl_3$) δ 24.18 (d, $^3J_{CP}$ 6 Hz, CH_3), 24.32 (d, $^3J_{CP}$ 8 Hz, CH_3), 45.83 (d, J_{CP} 12.03 Hz, CH) and 163.55 (d, J_{CP} 12.03 Hz, CH=N).

15 *selected NMR data*: ^{31}P NMR ($CDCl_3$) δ 38.7; ^1H NMR ($CDCl_3$) 1.25 (d, J_{HH} 6.75 Hz, 12H, CH_3), 1.29 (d, J_{HH} 6.75 Hz, 12H, CH_3), 1.28 (d, J_{HP} 10 Hz, 3H, P–CH_3) and 3.38 (m, 4H, CH); ^{13}C NMR ($CDCl_3$) δ 15.57 (d, $^1J_{CP}$ 11.2 Hz, CH_3–P), 24.21 (d, $^3J_{CP}$ 6.0 Hz, CH_3), 24.34 (d, $^3J_{CP}$ 7.8 Hz, CH_3) and 46.53 (d, $^2J_{CP}$ 10.1 Hz, CH).

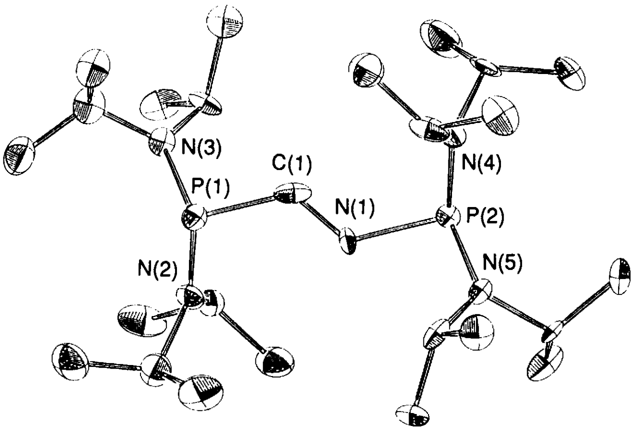
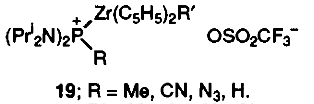


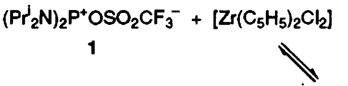
Fig. 1 Molecular structure of $(Pr^i_2N)_2PCH{=}NP(NPr^i_2)_2$ **8**. Selected bond distances (Å) and angles (°): P(1)–C(1) 1.749(1), P(1)–N(2) 1.646(6), P(1)–N(3) 1.680(4), C(1)–N(1) 1.271(4), P(2)–N(1) 1.796(9), P(2)–N(4) 1.707(3), P(2)–N(5) 1.711(9); N(2)–P(1)–N(3) 112.2(4), N(2)–P(1)–C(1) 105.6(1), C(1)–P(1)–N(3) 98.2(1), N(4)–P(2)–N(5) 108.7(5), N(1)–P(2)–N(4) 105.1(5), N(1)–P(2)–N(5) 97.8(4).

$[Zr(C_5H_5)_2XY]$
11; X = Y = Me
12; X = Y = CN
13; X = Y = N_3
14; X = H, Y = Cl

$(Pr^i_2N)_2PX$
15; X = Me
16; X = CN
17; X = N_3
18; X = H


$(Pr^i_2N)_2\overset{+}{P}(R)Zr(C_5H_5)_2R'\quad OSO_2CF_3^-$

19; R = Me, CN, N_3, H.
R′ = Me, CN, N_3, Cl



Scheme 3

This type of transfer appeared to be general since methyl, cyano and azide groups, and hydride can be easily transfered from the corresponding zirconium derivatives $[Zr(C_5H_5)_2Me_2]$ **11**, $[Zr(C_5H_5)_2(CN)_2]$ **12**, $[Zr(C_5H_5)_2(N_3)_2]$ **13**, and $[Zr(C_5H_5)_2(H)(Cl)]$ **14**, to the R_2P^+ moieties: the phosphanes $(Pr^i_2N)_2PMe$ **15**,‖ $(Pr^i_2N)_2PCN$ **16**,[5] $(Pr^i_2N)_2PN_3$ **17**[6] and $(Pr^i_2N)_2PH$ **18**[7] were obtained respectively, in excellent yields (>85%). The presence of a vacant orbital and a lone electron pair in **1** confers to this salt the ability to activate, for example, C–H and C–C bonds. A number of reactions involving insertion reactions (oxidative addition) into C–H, C–C or N–N bonds have been reported.[4] Nevertheless, we never detected, in our case, even at low temperature, phosphonium salts of type **19** which would result from an insertion into a Zr–R bond. If they are eventually formed they would rearrange very quickly to give the corresponding phosphane and $[Zr(C_5H_5)_2(R)(OSO_2CF_3)]$.

Competition between oxophilicity and halophilicity of zirconium occurred when **1** was treated with $[Zr(C_5H_5)_2Cl_2]$ in dichloromethane. ^{31}P NMR spectra at room temperature of the resulting mixture consisted of a broad signal at δ +205, compared with that of **1** (δ +300) and of bis(diisopropylamino)chlorophosphane **20** (δ +135 ppm). Moreover, the signal at δ +205 is shifted to δ +263 at −80 °C and to δ +239 at −20 °C. Such results suggest the equilibrium in Scheme 3. To our knowledge, this is the first example of a transfer of a chlorine atom from zirconium to a main group element species: up to now the reverse transfer had only been observed.[1,2]

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