



Scheme 2 Reagents and conditions: i, 1 equiv. of MeOSO₂CF₃, THF; ii, Bu^tNC then 1 equiv. of MeOSO₂CF₃

$\nu_{\text{CF}_3\text{SO}_3}$ absorption (1280 cm⁻¹) in the IR spectrum, clearly indicates the presence of the triflate anion. Absorption due to covalently bonded triflate cannot be clearly identified because of the presence of other absorptions in the relevant area (1370–1390 cm⁻¹). Nevertheless, the FABMS shows a well-defined molecular ion, with indication of a covalent zirconium–oxygen bond. These observations prompted us to explore the structure of **5a** in more depth, and a single crystal X-ray diffraction study was carried out. The structure of the cation is shown in Fig. 1 and demonstrates clearly that **5a** is a monocation in the solid state.¶ Therefore, two different processes occur when 2 equiv. of methyltrifluoromethane sulfonate are added to **4a**: alkylation on phosphorus and substitution on zirconium with the formation of a Zr–O bond.

Evidence is found by conductimetric measurements for the generation of a dicationic species **6a**|| on dissolution of **5a** in acetonitrile. Indeed, the conductance of **6a**, measured on a 10⁻³ mol dm⁻³ solution at 25 °C, is 321 Ω⁻¹ cm² mol⁻¹. This value is in agreement with values given for other 2:1 electrolytes (220–300 Ω⁻¹ cm² mol⁻¹)⁴ and not those for a 1:1 electrolyte, for which values between 120 and 160 Ω⁻¹ cm² mol⁻¹ are commonly measured. Under the same experimental conditions, a value of 177 Ω⁻¹ cm² mol⁻¹ is found for the monocation **7**, obtained by treatment of the vinylphosphine **1** with methyltrifluoromethane sulfonate. To our knowledge, compound **6a** is the first example of a stable phosphorus–zirconium dication. As the acetonitrile allows the dissociation of the Zr–O covalent bond, it is reasonable to assume that it

plays a part in the stabilisation of **6a**. No signal due to complexed acetonitrile is seen in the ¹H NMR spectrum, though this can be explained if the coordination to the zirconium centre is weak, and in solution there is an equilibrium set up eqn. (1), for which the equilibrium constant is very large.

Evaporation of acetonitrile followed by dissolution of the residue in dichloromethane allows recovery of **5a**.

In order to check which is the most reactive centre towards methyltrifluoromethane sulfonate (phosphorus or zirconium), we added this reagent to phosphine **3**. Reaction of **3** with 1 equiv. of methyltrifluoromethane sulfonate in tetrahydrofuran (THF) results in its clear conversion to the phosphonium salt **8**, while stabilisation of the Zr centre occurs by complexation with THF. [**8** ¹H NMR (CD₂Cl₂) δ 2.30 (d, ²J_{HP} 12.6 Hz, PMe)]. Treatment of **8** with *tert*-butyl isocyanide then methyltrifluoromethane sulfonate (1 equiv.) provides an alternative route to **5a** (Scheme 2).

In summary, a series of phosphorus–zirconium salts, which are stable either in solid state (**5a**) or in solution (**6a**, **8**, **9**), have been synthesised in high yield. This combination of accessibility, stability and reactivity on phosphorus and/or zirconium makes these new derivatives potentially valuable, synthetic reagents.

This work was supported by the CNRS (France) and the Committee for Scientific Research (Poland) Grant No. 2.1307.91.01.

Received, 29th July 1993; Com. 3/04545E

References

- See for example: *Organophosphorus Reagents in Organic Synthesis*, ed. J. I. G. Cadogan, Academic, New York, London, 1979; K. Jöde, *Houben Weyl*, Thieme, Stuttgart, 1982, vol. E1, p. 491; H. J. Bestman and R. Zimmermann, *Houben Weyl*, Thieme, Stuttgart, 1982, vol. E1, 1982, p. 616; H. J. Cristau, K. El Hamad and E. Torreilles, *Phosphorus, Sulfur and Silicon and the Related Elements*, 1992, **66**, 47.
- F. S. Dyachkovskii, A. K. Shilova and A. E. Shilov, *J. Polym. Sci. Part C*, 1967, **16**, 2333; J. J. Eisch, A. M. Piotrowski, S. K. Brownstein, E. J. Gabe and F. L. Lee, *J. Am. Chem. Soc.*, 1985, **107**, 7219; P. G. Gassman and M. R. Callstrom, *J. Am. Chem. Soc.*, 1987, **109**, 7875; E. Gianetti, G. M. Nicoletti and R. Mazzocchi, *J. Polym. Sci., Polym. Chem. Ed.*, 1985, **23**, 2117; J. A. Ewen, *J. Am. Chem. Soc.*, 1984, **106**, 6355; P. J. Toscano and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 653; D. Hedden and T. J. Marks, *J. Am. Chem. Soc.*, 1988, **110**, 1647; K.-H. Dahmen, D. Hedden, R. L. Burwell, Jr and T. J. Marks, *Langmuir*, 1988, **4**, 1212; A. Zambelli, P. Longo and A. Grassi, *Macromolecules*, 1989, **22**, 2186; P. Pino, P. Cioni and J. Wei, *J. Am. Chem. Soc.*, 1987, **109**, 6189; J. A. Ewen, R. L. Jones, A. Razavi and J. D. Ferrara, *J. Am. Chem. Soc.*, 1988, **110**, 6255.
- For example, the sequential one-pot addition of alkylpyrazines, alkynes and a proton source to a solution of [(C₅H₅)₂Zr(Me)(thf)]⁺ affords (*E*)-alkenyl substituted alkylpyrazines. See A. S. Guran and R. F. Jordan, *J. Org. Chem.*, 1992, **57**, 5994.
- W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
- G. M. Sheldrick, in *Crystallographic Computing 3*, ed. C. Kruger and R. Goddard, OUP, 1975, 175.
- D. J. Watkins, J. R. Carruthers and P. W. Betteridge, *CRYSTAL User Guide*, Chemical Crystallography Laboratory, University of Oxford, 1990.
- C. K. Johnson, ORTEP2 Report ORNL 5138, Oak Ridge National Laboratory, Oak Ridge TN, 1976.

¶ *Crystal data for 5a*: C₃₂H₅₄F₆N₃O₆PS₂Zr, *M* = 877, monoclinic, space group P2₁/c, *a* = 14.026(9), *b* = 18.175(4), *c* = 16.774(8) Å, β = 94.2(1)°, *V* = 4265(6) Å³, *Z* = 4, *D*_c = 1.37 g cm⁻³, λ(Mo-Kα) = 0.71073 Å, μ = 4.48 cm⁻¹. The data 7785 reflections, 4442 unique and no weak [*I* > 3σ(*I*)] were collected at 20 °C on an Enraf-Nonius CAD-4 diffractometer using the ω-2θ mode (θ_{max} = 25°) and an empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares analysis using 4227 reflections with *I* > 3σ(*I*) to *R* = 0.065, *R*_w = 0.077. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in the calculation, but not refined. The CF₃SO₃ moiety not bonded to the cation showed marked thermal motion. For this reason an *R* value of only 0.065 was attained. All calculations were performed on an ALLIANT VFX 80 mini super calculator using SHELX,⁵ CRYSTALS⁶ and ORTEP⁷ programs.

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.

|| *Selected spectroscopic data for 6a*: ³¹P NMR (CD₃CN) δ 59.3; ¹H NMR (CD₃CN) δ 1.40 [s, 9 H, (CH₃)₃C], 1.42 (d, *J*_{HP} 6.8 Hz, 12 H, CH₃CH), 1.45 (d, *J*_{HP} 6.8 Hz, 12 H, CH₃CH), 2.29 (d, *J*_{HP} 12.6 Hz, 3 H, CH₃P), 2.85 (m, 2 H, CH₂–C=N), 3.20 (m, 2 H, CH₂–P), 3.92 (m, 4 H, CH₃CH), 6.04 (s, 10 H, C₅H₅); ¹³C NMR (CD₃CN) same values as for **5a** [except δ 230.50 (d, *J*_{CP} 30.5 Hz, C=N)].