DALTON COMMUNICATION

A convenient synthetic route to substituted phosphavinyl Grignard reagents: synthesis and characterisation of [{RP=C(Bu^t)-MgX(OEt$_2$)}$_2$] (R = cyclohexyl, cyclopentyl, ethyl or mesityl; X = Cl or Br)†

David E. Hibbs, Cameron Jones* and Anne F. Richards

Department of Chemistry, University of Wales, Cardiff, PO Box 912, Park Place, Cardiff, UK CF1 3TB. E-mail: jonesca6@cardiff.ac.uk

Received 23rd August 1999, Accepted 6th September 1999

The regio- and stereo-selective addition of a series of Grignard reagents across the phosphaalkyne P≡CBu^t conveniently affords high yields of the phosphavinyl Grignard reagents, [{RP=C(Bu^t)MgX(OEt$_2$)}$_2$] (R = cyclohexyl, cyclopentyl, ethyl or mesityl; X = Cl or Br), two of which have been structurally characterised.

Vinyl Gringard reagents have been widely exploited in organic and organometallic synthesis.[1] Considering the now well known analogy between low coordinate phosphorus systems and their hydrocarbon counterparts[2] it might be expected that phosphavinyl Grignard reagents would have a similar synthetic utility. Despite this, only a handful of such reagents have been reported, *e.g.* Mes*P=C(R)MgBr (Mes* = C$_6$H$_2$Bu$^t_3$-2,4,6; R = halide, SiMe$_3$);[3] all of which are substituted at the P-centre by the bulky supermesityl group. The syntheses of these complexes are generally quite cumbersome and they are normally generated *in situ* when used in organic transformations and organometallic synthesis. Their successful use in these areas prompted us to explore the development of a convenient synthetic route to a range of phosphavinyl Grignard reagents which could be isolated in the solid state and which contain a variety of P-substituents.

Recently, the insertion of phosphaalkynes into main group element–carbon bonds has been examined, though this commonly leads to phosphaalkyne coupling reactions and the formation of phosphorus-containing organometallic cage compounds.[4] Herein we report regio- and stereo-selective 1,2-additions of Grignard reagents to the phosphaalkyne, P≡CBu^t, which yield phosphavinyl Grignard reagents that are stable to further reaction with the phosphaalkyne. The first structural characterisations of such complexes are also reported.

Reaction of P≡CBu^t with one equivalent of RMgX [R = cyclohexyl (Cy), cyclopentyl (Cy^p), ethyl or mesityl (Mes); X = Cl or Br] led to the formation of the thermally stable phosphavinyl Grignard reagents **1**–**4** in high yields (>85%). All could be isolated in the solid state and **1**, **2** and **4** could be recrystallised from diethyl ether. Interestingly, treating **1**–**4** with one equivalent of P≡CBu^t did not lead to a coupling reaction to give diphosphabutadienyl systems as has been observed for a related lithium phosphaalkenyl complex.[5] Similarly, treating **1**, **2** and **4** with a further equivalent of the respective Grignard reagent did not lead to a second addition across the P=C double bond. In contrast, the less hindered system, **3**, does react with EtMgBr to give an as yet unidentified product containing a saturated phosphorus centre (^{31}P-{^{1}H} NMR δ −8).

All the reactions depicted in Scheme 1 are completely regiospecific with the magnesium halide fragment of the Grignard reagent adding to the alkynic carbon of the phosphaalkyne. This is the opposite to the addition of Grignard reagents to nitriles which generally leads to *N*-magnesioimine formation.[1] This difference, however, is not surprising considering the polarity of the phosphaalkyne employed, *viz.* $^{\delta+}$P≡C$^{\delta-}$Bu^t.[2] Moreover, all the reactions appear to be stereospecific giving one isomer as determined by NMR spectroscopy. In the cases of **1** and **2** their crystal structures (see below) show them to exist as their (*Z*)-isomers in the solid state which is most likely the isomeric form adopted by **3** and **4**.

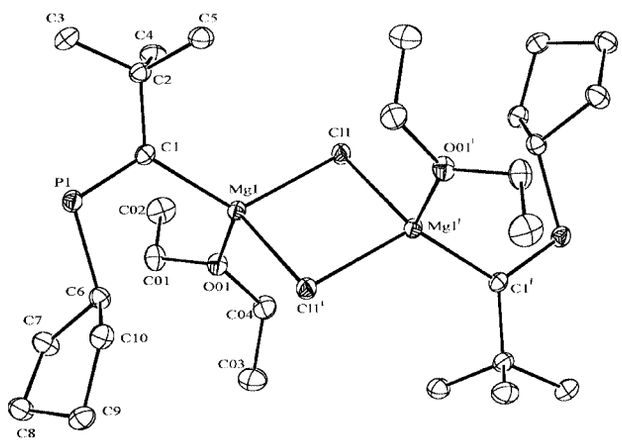
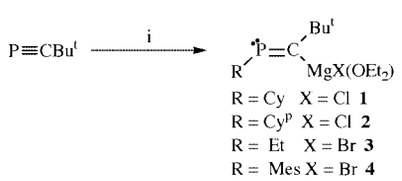


Fig. 1 Molecular structure of [{Cy^{p}P=C(Bu^t)MgCl(OEt$_2$)}$_2$] **2**. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.6725(19), P(1)–C(6) 1.861(2), C(1)–C(2) 1.534(2), C(1)–Mg(1) 2.1126(19), Mg(1)–Cl(1) 2.4177(18), Mg(1)–Cl(1)′ 2.4132(14), O(1)–Mg(1) 2.017(2), Mg(1)···Mg(1)′ 3.399(3); C(1)–P(1)–C(6) 106.49(8), P(1)–C(1)–Mg(1) 119.04(9), C(2)–C(1)–Mg(1) 122.07(11), C(2)–C(1)–P(1) 118.87(11), Mg(1)–Cl(1)–Mg(1)′ 89.44(5), Cl(1)–Mg(1)–Cl(1)′ 90.56(5), C(1)–Mg(1)–Cl(1) 123.03(6), O(1)–Mg(1)–Cl(1) 99.54(6), C(1)–Mg(1)–Cl(1)′ 121.20(7), O(1)–Mg(1)–Cl(1)′ 106.41(6), O(1)–Mg(1)–C(1) 112.30(7).



Scheme 1 Reagents and conditions: i, RMgX, Et$_2$O, 25 °C, 5 h.

The ^{31}P-{^{1}H} NMR spectrum‡[6] of each complex displays a low field singlet resonance (δ 309–328) in the normal region for phosphaalkenyl metal complexes.[7] In their ^{13}C NMR spectra the $^1J_{P=C}$ couplings lie in the normal region.[8] Surprisingly, the $^2J_{PC}$ couplings (*ca.* 14 Hz) between the phosphorus centres and the quaternary carbons of the tertiary butyl groups are at the high end of the region typically seen for tertiary butyl groups *trans* to P-lone pairs in phosphaalkenes.[8] However, in **1**–**4** the presence of the MgX substituent could significantly effect the

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3531/

Also available: spectroscopic data for compounds **2**–**4**. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3531/, otherwise available from BLDSC (No. SUP 57636, 2 pp.) or the RSC library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

electronics of these systems relative to wholly alkyl substituted phosphaalkenes. Therefore the stereochemistry of the complexes cannot be confidently assigned from NMR data alone.

The crystal structures of **1** and **2**§[6] were determined to clarify this point. The geometries of both are very similar so only the molecular structure of **2** is depicted in Fig. 1. It is dimeric through symmetrical Mg–Cl–Mg bridges and crystallises as its (*Z*)-isomer. The P(1)–C(1) bond length [1.6725(19) Å] is in the normal region for fully localised P=C double bonds[2] and is close to that seen in the only structurally characterised example of a lithium phosphaalkenyl complex, [Mes*P=C(Cl){Li(DME)$_2$}] 1.6769(15) Å.[9] Although structurally characterised halide bridged, dimeric Grignard reagents are rare, the Mg–C bond lengths in **2** [2.1126(19) Å] appear to be in the normal region for such interactions (*cf.* 2.094(11) Å in [{Mg(Et)(Pr$^i_2$O)Br}$_2$]).[10] Finally, the coordination environment about C(1) is slightly distorted trigonal planar whilst the Mg centres have heavily distorted tetrahedral geometries.

We are currently examining the use of the phosphavinyl Grignard reagents **1**–**4** in the synthesis of organophosphorus compounds and as transfer reagents in the synthesis of transition and lanthanide metal phosphaalkenyl complexes. We are also investigating the facility of isomerisations of **1**–**4**. The results of these studies will form the basis of future publications.

Acknowledgements

We gratefully acknowledge financial support from the EPSRC (studentship for A. F. R).

Notes and references

‡ Synthesis and spectroscopic data for **1**. The following typical synthetic method can be easily adapted for the syntheses of **2**–**4**. The phosphaalkyne, P≡CBu^t (0.32 ml, 0.19 g, 2 mmol) was added neat to a solution of CyMgCl (2 mmol) in Et$_2$O (10 ml) at −60 °C. The resulting solution was warmed to room temperature without stirring and left to stand for 5 hours during which time crystals of **1** deposited (0.56 g, 89%), mp 109–115 °C (decomp.); ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K) δ 0.90–1.80 (m, 11H, C$_6$H$_{11}$), 0.82 (br s, 6H, Me), 1.36 (s, 9H, Bu^t), 3.21 (br s, 4H, OCH$_2$); ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 298 K) δ 14.5 (Me), 26.8 (CH$_2$), 27.8 (CH$_2$), 33.5 (d, $^2J_{PC}$ 13 Hz, CH$_2$), 34.4 (d, $^3J_{PC}$ 18 Hz, C(*C*H$_3$)$_3$), 44.1 (d, $^2J_{PC}$ 14 Hz, *C*Me$_3$), 48.1 (d, $^1J_{PC}$ 38 Hz, CH), 65.8 (OCH$_2$), 260.6 (d, $^1J_{P-C}$ 74 Hz, P=C); ^{31}P NMR (36.3 MHz, C$_6$D$_6$, 85% H$_3$PO$_4$, 298 K) δ 324; IR (ν/cm^{-1}, Nujol) 1280 (m), 1095 (m), 1050 (m), 890 (w); MS EI *m*/*z* (%): 185 (CyPCMgCl$^+$, 20), 127 (CyPC$^+$, 61), 114 (PCy$^+$, 100).

§ Crystal data for **1**: C$_{15}$H$_{24}$ClMgOP, M = 317.12 triclinic, space group $P\bar{1}$, a = 11.6149(5), b = 12.4410(7), c = 15.8853(4) Å, α = 72.073(3), β = 70.757(3), γ = 65.849(3)°, V = 1937.24(15) Å^3, Z = 4, D_c = 1.087 g cm^{-3}, F(000) = 688, μ (Mo-Kα) = 3.05 cm^{-1}, reflections 7849 (collected), 7849 (unique), 150(2) K; **2**: C$_{14}$H$_{28}$ClMgOP, M = 303.10 triclinic, space group $P\bar{1}$, a = 8.162(9), b = 9.682(7), c = 12.341(10) Å, α = 70.69(2), β = 75.440(18), γ = 78.995(16)°, V = 884.6(14) Å^3, Z = 2, D_c = 1.138 g cm^{-3}, F(000) = 656, μ (Mo-Kα) = 3.31 cm^{-1}, reflections 3583 (collected), 3583 (unique), 150(2) K. Final R (on F) and wR (on F^2) were 0.0545 and 0.1299 for **1**, and 0.0346 and 0.0951 for **2** [$I > 2\sigma(I)$]. CCDC reference number 186/1641. See http://www.rsc.org/suppdata/dt/1999/3531/ for crystallographic files in .cif format.

1 J. M. Brown and S. K. Armstrong, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. Stone and G. Wilkinson, Elsevier, Oxford, 1995, vol. 11.

2 (*a*) K. B. Dillon, F. Mathey and J. F. Nixon, in *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998; (*b*) *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, ed. M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart, 1990 and refs. therein.

3 (*a*) M. van der Sluis, V. Beverwijk, A. Termaten, E. Gavrilova, F. Bickelhaupt, H. Kooijman, N. Veldman and A. L. Spek, *Organometallics*, 1997, **16**, 1144; (*b*) M. van der Sluis, J. B. M. Wit and F. Bickelhaupt, *Organometallics*, 1996, **15**, 174.

4 A. Hoffman, B. Breit and M. Regitz, *Chem. Ber.*, 1997, **539**, 61.

5 A. M. Arif, A. R. Barron, A. H. Cowley and S. W. Hall, *J. Chem. Soc., Chem. Commun.*, 1988, 171.

6 Spectroscopic data for **2**–**4** have been submitted as supplementary material.

7 L. Weber, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 271 and refs. therein.

8 See ref. 2(*b*) pp. 463–471.

9 E. Niecke, M. Nieger, O. Schmidt, D. Gudat and W. W. Schoeller, *J. Am. Chem. Soc.*, 1999, **121**, 519.

10 C. E. Holloway and M. Melnik, *Coord. Chem. Rev.*, 1994, **135**, 287.

Communication 9/06839B