

# 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)†

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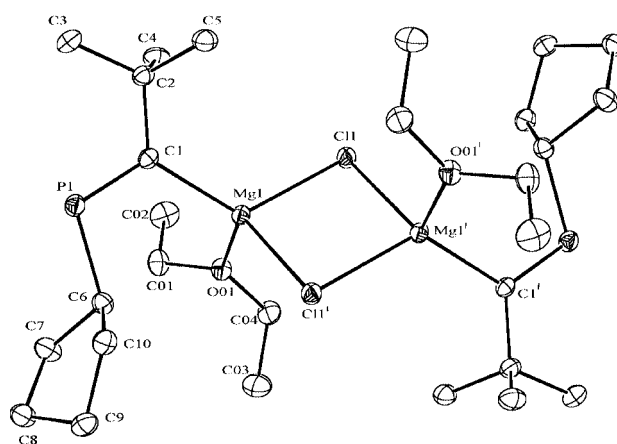
The regio- and stereo-selective addition of a series of Grignard reagents across the phosphalkyne  $P\equiv C Bu^t$  conveniently affords high yields of the phosphavinyl Grignard reagents,  $[\{RP=C(Bu^t)MgX(OEt_2)\}_2]$  (R = cyclohexyl, cyclopentyl, ethyl or mesityl; X = Cl or Br), two of which have been structurally characterised.

Vinyl Grignard reagents have been widely exploited in organic and organometallic synthesis.<sup>1</sup> Considering the now well known analogy between low coordinate phosphorus systems and their hydrocarbon counterparts<sup>2</sup> 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.  $Mes^*P=C(R)MgBr$  ( $Mes^* = C_6H_2Bu^t_{3,2,4,6}$ ; R = halide,  $SiMe_3$ );<sup>3</sup> 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.

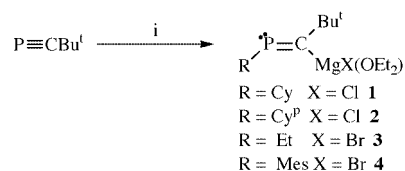
Recently, the insertion of phosphalkynes into main group element-carbon bonds has been examined, though this commonly leads to phosphalkyne coupling reactions and the formation of phosphorus-containing organometallic cage compounds.<sup>4</sup> Herein we report regio- and stereo-selective 1,2-additions of Grignard reagents to the phosphalkyne,  $P\equiv C Bu^t$ , which yield phosphavinyl Grignard reagents that are stable to further reaction with the phosphalkyne. The first structural characterisations of such complexes are also reported.

Reaction of  $P\equiv C Bu^t$  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  $P\equiv C Bu^t$  did not lead to a coupling reaction to give diphosphabutadienyl systems as has been observed for a related lithium phosphalkenyl complex.<sup>5</sup> 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 ( $^{31}P\{-^1H\}$  NMR  $\delta -8$ ).

All the reactions depicted in Scheme 1 are completely regio-specific with the magnesium halide fragment of the



**Fig. 1** Molecular structure of  $[\{Cy^pP=C(Bu^t)MgCl(OEt_2)\}_2]$  **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,  $RMgX$ ,  $Et_2O$ , 25 °C, 5 h.

Grignard reagent adding to the alkyne carbon of the phosphalkyne. This is the opposite to the addition of Grignard reagents to nitriles which generally leads to *N*-magnesiimine formation.<sup>1</sup> This difference, however, is not surprising considering the polarity of the phosphalkyne employed, *viz.*  $\delta^+P=C\delta^-Bu^t$ .<sup>2</sup> 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**.

The  $^{31}P\{-^1H\}$  NMR spectrum  $\ddagger$  of each complex displays a low field singlet resonance ( $\delta$  309–328) in the normal region for phosphalkenyl metal complexes.<sup>7</sup> In their  $^{13}C$  NMR spectra the  $^1J_{P-C}$  couplings lie in the normal region.<sup>8</sup> 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 phosphalkenes.<sup>8</sup> 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 phosphalkenes. Therefore the stereochemistry of the complexes cannot be confidently assigned from NMR data alone.

The crystal structures of **1** and **2**<sup>§</sup> 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<sup>2</sup> and is close to that seen in the only structurally characterised example of a lithium phosphalkenyl complex, [Mes\*P=C(Cl){Li(DME)<sub>2</sub>}] 1.6769(15) Å.<sup>9</sup> 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<sup>i</sup><sub>2</sub>O)Br}<sub>2</sub>]).<sup>10</sup> 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 phosphalkenyl 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

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## 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 phosphalkyne, P≡C<sup>t</sup>Bu<sup>t</sup> (0.32 ml, 0.19 g, 2 mmol) was added neat to a solution of CyMgCl (2 mmol) in Et<sub>2</sub>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.); <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 0.90–1.80 (m, 11H, C<sub>6</sub>H<sub>11</sub>), 0.82 (br s, 6H, Me), 1.36 (s, 9H, Bu<sup>t</sup>), 3.21

(br s, 4H, OCH<sub>2</sub>); <sup>13</sup>C NMR (100.6 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 14.5 (Me), 26.8 (CH<sub>2</sub>), 27.8 (CH<sub>2</sub>), 33.5 (d, <sup>2</sup>J<sub>PC</sub> 13 Hz, CH<sub>2</sub>), 34.4 (d, <sup>3</sup>J<sub>PC</sub> 18 Hz, C(CH<sub>3</sub>)<sub>3</sub>), 44.1 (d, <sup>2</sup>J<sub>PC</sub> 14 Hz, CMe<sub>3</sub>), 48.1 (d, <sup>1</sup>J<sub>PC</sub> 38 Hz, CH), 65.8 (OCH<sub>2</sub>), 260.6 (d, <sup>1</sup>J<sub>P-C</sub> 74 Hz, P=C); <sup>31</sup>P NMR (36.3 MHz, C<sub>6</sub>D<sub>6</sub>, 85% H<sub>3</sub>PO<sub>4</sub>, 298 K) δ 324; IR (ν/cm<sup>-1</sup>, Nujol) 1280 (m), 1095 (m), 1050 (m), 890 (w); MS EI *m/z* (%): 185 (CyPCMgCl<sup>+</sup>, 20), 127 (CyPC<sup>+</sup>, 61), 114 (PCy<sup>+</sup>, 100).

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

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