Synthesis of a Metal-free Three-co-ordinate Phosphorus(v) Hydride and its Conversion into a Phospha-alkene *via* Reductive Hydride Shift

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The reaction of $ClP[=C(SiMe_3)_2]_2$ with Pr^iMgCl affords the phospha-allene $HP[=C(SiMe_3)_2]_2$, which isomerises to the phospha-alkene, $(Me_3Si)_2CHP=C(SiMe_3)_2$, *via* a reductive hydride shift.

A $NiCl_2$ complex of the ligand $HP(=NAr)_2$ (Ar = 2,4,6-$Bu^t_3C_6H_2$) has recently been described;[1] however, metal-free three-co-ordinate phosphorus(v) hydrides have not been reported. We describe (i) the preparation of (1), the first example of this class of compound, and (ii) isomerisation of (1) to the corresponding phospha-alkene $(Me_3Si)_2CHP=C-(SiMe_3)_2$ (2), *via* a novel reductive hydride transfer.

Treatment of $ClP[=C(SiMe_3)_2]_2$[2] (3) with an equimolar quantity of Pr^iMgCl in Et_2O at 25 °C resulted in gas evolution.† Filtration of the yellow reaction mixture, followed

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† Presumably the reaction proceeds *via* a β-hydride abstraction from an isopropyl methyl group of $Pr^iP[=C(SiMe_3)_2]_2$.

$(Me_3Si)_2CHP=C(SiMe_3)_2$

(2)

$ClP[=C(SiMe_3)_2]_2$

(3)
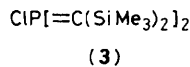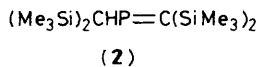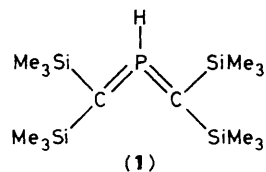
by solvent evacuation, afforded yellow, solid **(1)** in *ca.* 60% yield (m.p. 44—46 °C). The compound is thermally sensitive (*vide infra*). The composition $C_{14}H_{37}P$ was established by high-resolution mass spectroscopy (M^+, calc. 348.1710; found 348.1720). The presence of the P^V–H moiety was evident from ^{31}P n.m.r. data for **(1)** (δ_P +33.1, $^1J_{PH}$ 405.8 Hz) which are comparable to literature values {*e.g.* δ_P +13.5, $^1J_{PH}$ 446 Hz for $P(Bu^t)(=NR)(NR_2)H$ (R = Me_3Si)[3] and δ_P 11.2, $^1J_{PH}$ 603 Hz for $[NiCl_2(ArN)_2PH]$ (Ar = $2,4,6\text{-}Bu^t_3C_6H_2)^1$}. $^{13}C\{^1H\}$ and ^1H N.m.r. data are also in accord with the proposed structure.‡

Interestingly, it is not possible to prepare **(1)** from **(3)** using conventional reduction methodology. For example, the reaction of **(3)** with $LiAlH_4$ produces the secondary phosphine $[(Me_3Si)_2CH]_2PH$,[4] whilst the reaction of **(3)** with Bu^nSnH affords the phospha-alkene **(2)**.[5]

Studies by Appel *et al.*[2,6] have established that chloroalkyl-substituted phospha-alkenes **(4)** undergo oxidative chloride transfer to afford the corresponding chlorophospha-allenes.[6] Consideration of the P–X and C–X bond enthalpies suggests
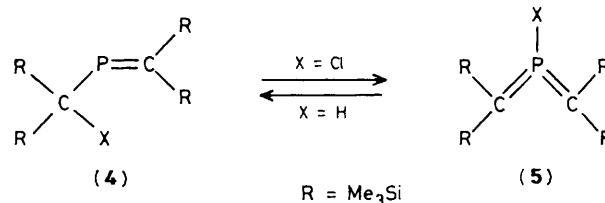
that this reaction might be reversed when X = H since, whilst the P–Cl and C–Cl bond enthalpies are comparable, a P–H bond is *ca.* 100 kJ mol⁻¹ weaker than a C–H bond.§ Such a reductive hydride transfer does indeed take place. Thus, heating **(1)** slightly above the m.p. (44—46 °C) causes quantitative conversion into **(2)**. The same conversion can be effected in toluene solution; however, the reaction temperature is higher (reflux).

References

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‡ Compound **(1)** $^{13}C\{^1H\}$ n.m.r. (C_6D_6, 75.4 MHz, ambient temperature) δ 4.8 (m, Si–CH₃), 93.3 (d, $^1J_{PC}$ 30.9 Hz, P=C); ^1H n.m.r. (C_6D_6, 360 MHz, ambient temperature) δ 0.29 (36H, d, $^4J_{PH}$ 3.0 Hz, Si–CH₃), 7.61 (1H, d, $^1J_{PH}$ 405.8 Hz, P–H).

§ *Ab initio* M.O. calculations on model systems in which R = H indicate that the energy difference between **(4)** and **(5)** is 66.3 kJ mol⁻¹ lower when X = H than when X = Cl. K. Dobbs, personal communication.