Structural authentication of an N-functionalised disecondary diphosphane

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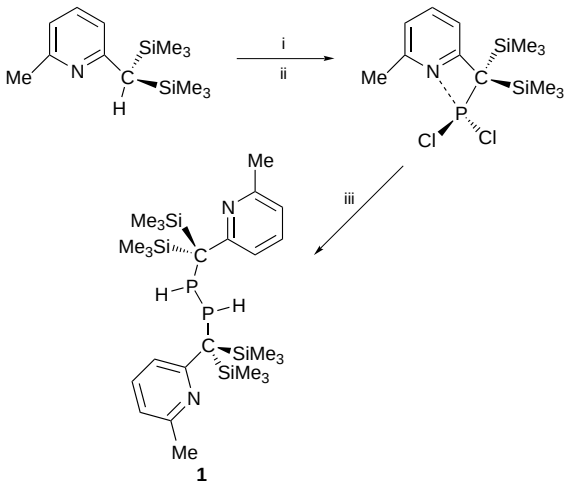
The reaction of $RPCl_2$ [R = (6-Me-2-pyridyl)$(SiMe_3)_2C^-$] with $LiAlH_4$ in Et_2O gives the novel N-functionalised disecondary diphosphane compound [R(H)P–P(H)R] rather than the expected phosphorus dihydride complex RPH_2; the *meso* and *rac* isomers of the diphosphane crystallise separately with the *meso* isomer being structurally authenticated.

Disecondary diphosphanes,† $(R'PH)_2$ (R′ = alkyl or aryl) normally formed in the equilibration reaction of organophosphide oligomers, $(R'P)_n$, with organophosphorus hydrides, $n\,R'PH_2$, have been studied extensively in solution by NMR spectroscopy.[1] However in the solid state examples are limited to those where they have been synthesised *in situ* and isolated as Lewis base donors, bonding through phosphorus, and bridging two metal centres; namely Cr in {[$Cr(CO)_5$][MesP(H)P(H)Mes][$Cr(CO)_5$]}[2] (Mes = 2,4,6-$Me_3C_6H_2$), Mn in {[$MnCp(CO)_2$][PhP(H)P(H)Ph][$MnCp(CO)_2$]}[3] and Ag in $[PhPH_2Ag\{\mu\text{-}(PhPH)_2\}]_2[AsF_6]_2$.[4] The mechanism of formation of the diphosphanes is in each case unknown but has been attributed to the dimerisation of the reactive radical [R′(H)P]· species which is also accessible from the deprotonation of protic and/or polar solvents by a reactive phosphinidene intermediate [R′P:].[5]

Herein we report the synthesis and characterisation of the first non-complexed N-functionalised disecondary diphosphane, **1**. In attempting to synthesise the simple phosphorus dihydride derivative of the bulky alkyl ligand (6-Me-2-pyridyl)-$(SiMe_3)_2C^-$, R, *via* the reduction of $RPCl_2$ with $LiAlH_4$ we observed that on each occasion the product obtained by crystallisation was not the dihydride but the diphosphane, [(6-Me-2-pyridyl)$(SiMe_3)_2$CPH]$_2$ **1**. This was totally unexpected given that $LiAlH_4$ is an almost ubiquitous reagent used in the formation of $R'PH_2$ species from various phosphine, phosphinous and phosphonic sources.[6]

In a typical reaction (Scheme 1) an Et_2O solution of a slight stoichiometric excess of $LiAlH_4$ was added to a pale orange Et_2O solution of the crystals of the dichloride complex $RPCl_2$, formed from the metathetical reaction of $RLi\cdot Et_2O$ and PCl_3, at −78 °C and the reaction mixture allowed to warm slowly to ambient temperature over 4 h. Filtration followed by *in vacuo* concentration of the solution and cooling to −30 °C allowed for the growth of a moderate yield of **1** as colourless needles.‡



Scheme 1 *Reagents and conditions*: i, Bu^nLi, Et_2O, −78 °C; ii, PCl_3, Et_2O, −78 °C, 2 h; iii, $LiAlH_4$, Et_2O, −78 °C, 4 h

The structure (Fig. 1) of the single crystal analysed by X-ray techniques proved to be the *meso* isomer: crystallising in the triclinic space group $P\bar{1}$ (no. 2) with two molecules in the unit cell, each molecule possessing a centre of inversion.§ The P–P bond distance of 2.222(3) Å is comparable with that of 2.258(3) Å in the Mn complex, 2.253(2) Å in the Cr complex and 2.202(4) Å in the Ag complex. The pyridyl nitrogens are located away from the P centre indicating there are no N···P interactions.

Two significantly different melting points, 122–123 and 177–178 °C with decomposition to dark red products, were obtained for different crystals taken from the same sample. This coupled with the fact that NMR data obtained on several different samples was consistent and reproducible is indicative that both the *meso* and the *rac* (DL) isomers co-crystallise from solution. The NMR data also revealed that the *meso* and *rac* isomers were always present in solution in 1 : 0.6 ratio, respectively; a ratio which did not change in the temperature range −90 to 80 °C. There was no spectroscopic evidence that the target dihydride complex was formed either directly as originally proposed or by the disproportionation of the diphosphane into higher phosphide oligomers and the accompanying hydride species. This implies that the diphosphane is

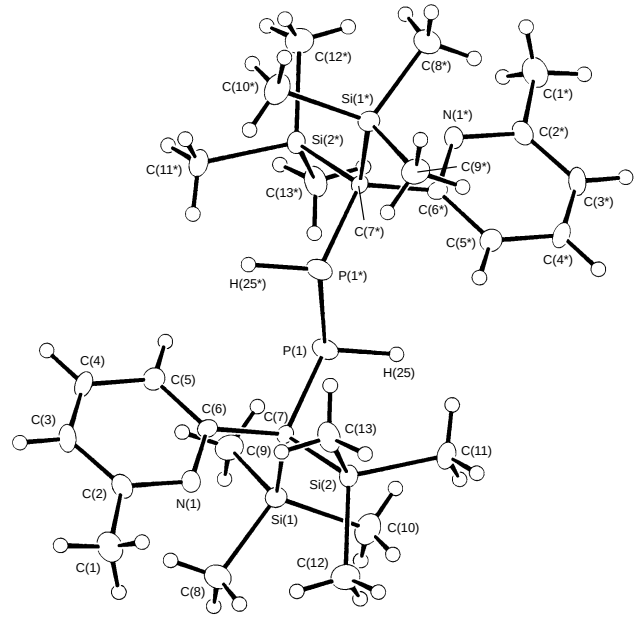


Fig. 1 Crystal structure of **1**. Selected distances (Å) and angles (°): P(1)–P(1*) 2.222(3), P(1)–C(7) 1.872(4), C(7)–C(6) 1.528(6), C(7)–Si(1) 1.931(4), C(7)–Si(2) 1.934(5), P(1*)–P(1)–C(7) 104.5(2), P(1)–C(7)–Si(1) 103.8(2), P(1)–C(7)–Si(2) 111.1(2), P(1)–C(7)–C(6) 116.4(2).

thermally robust and requires greater temperatures to force the creation of the equilibrium observed for other diphosphanes.

The NMR data on **1** can be compared with those obtained and compiled by Albrand and Taïeb[1] on a series of disecondary diphosphanes, R′ = Ph, Me, Et, cyclohexyl, CF_3, all relating to an AA′XX′ spin system. The $^{31}P\{^1H\}$ spectrum has two peaks at δ −99.5 (*rac*) and −91.5 (*meso*). The undecoupled ^{31}P spectrum has the two peaks split into two symmetrical sets of doublets of doublets, the coupling constants for the peaks centred at δ −99.5 being $^1J_{PH}$ 128 and $^2J_{PH}$ 74 Hz and for the peaks centred at δ −91.5 being $^1J_{PH}$ 152 and $^2J_{PH}$ 61 Hz. While the ^{31}P chemical shifts correlate most closely with those for R′ = Et (δ −99.6 and −93.8) the $^1J_{PH}$ and $^2J_{PH}$ values of 192.9, 192.9 and 11.2, 6.5 Hz, respectively, are clearly very different, as they are for all of the diphosphanes investigated, and must relate to the increased polarisation of the C–P bonds induced by the proximity of the two $SiMe_3$ groups.

The ^1H NMR spectrum also shows the high degree of P–H coupling. Two sets of doublets of doublets are present, one centred on δ 3.82 with coupling constants corresponding to those of the *meso* isomer at δ 91.5 in the ^{31}P spectrum and the other at δ 4.48 with coupling constants relating to the *rac* isomer at δ 99.5 in the ^{31}P spectrum. The two inner peaks of the doublet of doublets at δ 3.82 also show $^3J_{HH}$ splitting with a coupling constant of 4.89 Hz while those centred on δ 4.48 are smaller at 1.6 Hz. The differing electronic environments of the isomers are highlighted by the four signals present for the four $SiMe_3$ groups in both the ^1H and the ^{13}C spectra with the largest chemical shift separation (*cf.* δ 0.51 and δ 0.24 with δ 0.42 and δ 0.34) occurring for those relating to the *rac* isomer.

The mechanism of formation of the diphosphane can as yet only be speculated upon but two possibilities exist; dimerisation of a monohydride species, [R(H)P], radical or otherwise, occurring more rapidly than replacement of a remaining chloride by a hydride or formation of the diphosphene [RP=PR] which is subsequently hydrogenated by the $LiAlH_4$. Why this should occur for (6-Me-2-pyridyl)$(SiMe_3)_2CPCl_2$ and not, for example, 2,4,6-$Bu^t_3C_6H_2PCl_2$,[7] is puzzling though in several EPR studies we have shown that it is possible for the pyridyl system to stabilise a radical species for a significant amount of time. Thus [(2-pyridyl)$(SiMe_3)_2CHg]^{\cdot}$,[8] generated from {(2-pyridyl)$(SiMe_3)_2C_2$}M on exposure to unfiltered UV light at 100 K, gave a decaying EPR signal with $t_{0.5}$ = 300 s while $t_{0.5}$ for the radicals [{(2-pyridyl)$(SiMe_3)_2C$}$_2$M]$^{\cdot}$ (M = Al, Ga)[9] generated by the Na/K reduction of the {(2-pyridyl)(Si-$Me_3)_2C$}$_2$MCl complexes were of the order of 3600 s, though coupling in this case occurred, not unexpectedly, through the γ position of the pyridyl ring. Clearly in the absence of metallic centres and the absence of unfavourable M–M bond formation the possibility of [R(H)P]$^{\cdot}$ coupling exists as a viable mechanism. The attempt to form the As analogue by the same route resulted in crystallisation of only the thermally unstable $RAsH_2$ complex.

Compound **1** should prove to be a valuable, flexible and interesting new ligand having, with the added functionality of the two pyridyl nitrogens, four possible donating sites. We are currently investigating the potential of forming novel metal complexes of **1**.

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Notes and References

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† Also referred to in the literature as diphosphines.

‡ *Analytical data* for **1**: colourless needle crystals. typical yield, after three crystallisations, 63%. Two isomers in 1 : 0.6 ratio (*rac* : *meso*). Mp 122–123 °C (decomp.) and 177–178 °C (decomp.). ^1H NMR (400 MHz, C_6D_6, 25 °C) δ 7.40 (d, 1 H, α), 7.33 (d, 0.6 H, α), 7.23 (m, 1.6 H, β), 6.51 (m, 1.6 H, γ), 4.48 (dd, 0.6 H, $^1J_{PH}$ 128, $^2J_{PH}$ 75 Hz), 3.82 (dd, 1 H, $^1J_{PH}$ 149, $^2J_{PH}$ 63 Hz) 2.36 (s, 3 H, Me), 2.33 (s, 1.8 H, Me) 0.51 (s, 0.6 × 9 H, $SiMe_3$), 0.42 (s, 9 H, $SiMe_3$), 0.34 (s, 9 H, $SiMe_3$) 0.27 (s, 0.6 × 9 H, $SiMe_3$). ^{13}C NMR (50.3 MHz, C_6D_6, 25 °C) δ 162.8, 156.4, 135.7, 120.1, 118.5, 28.9, 23.9, 2.42, 1.83, 1.80, 1.32. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, 25 °C) δ −99.5, −91.5. ^{31}P NMR (81 MHz, C_6D_6, 25 °C) δ −99.5 (dd $^1J_{PH}$ 128, $^2J_{PH}$ 74 Hz), −91.5 (dd, $^1J_{PH}$ 152, $^2J_{PH}$ 61 Hz). Elemental analysis (%); required (found) C, 55.32 (55.30); H, 8.86 (9.05); N, 4.96 (4.97).

§ *Crystallographic data* for **1**: Nicolet R3m diffractometer, crystals mounted in oil under N_2, $[RP(H)]_2$, $C_{26}H_{50}N_2P_2Si_4$, M = 564.98, triclinic, space group $P\bar{1}$, a = 8.790(5), b = 9.184(6), c = 11.735(6) Å, α = 93.99(5), β = 101.16(4), γ = 112.86(4)°, U = 845.3(10) Å^3, D_c = 1.110 g cm^{-3}, T = 173 K, Z = 2, F(000) = 306.00. μ_{Mo} = 2.87 cm^{-1}, $A^*_{min,max}$ = 0.79, 1.00. $2\theta_{max}$ = 45°, final R,R_w = 0.052, 0.038 (statistical weights), GOF 2.08, N_o = 1552 'observed' [$I > 2\sigma(I)$] reflections out of N = 2203 unique. The positions of all H atoms were calculated and included as invariants; fixed temperature and constrained in x, y, z, U_{iso}. CCDC 182/740.

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