

Synthesis, structure and reductive dechlorination of the C-centred phosphorus(III) β -diketiminato $\text{PCl}(\text{Ph})\text{L}$ [$\text{L} = \text{C}\{\text{C}(\text{Me})\text{NC}_6\text{H}_3\text{Pr}^i_{2-2,6}\}\{\text{C}(\text{Me})\text{NHC}_6\text{H}_3\text{Pr}^i_{2-2,6}\}$]

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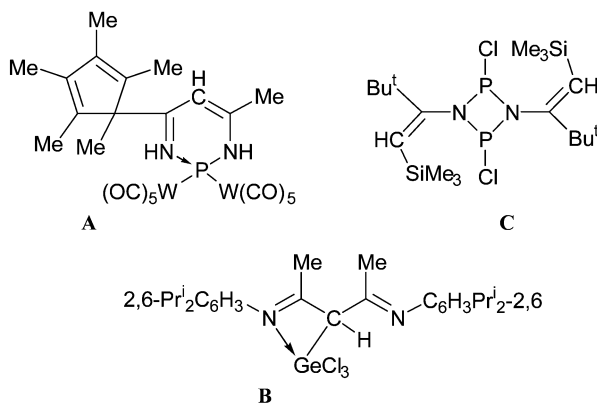
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Treatment of the β -diketimine HL with successively LiBu^n and PCl_2Ph gave the first C-centred monodentate β -diketiminato $\text{PCl}(\text{Ph})\text{L}$ **1**; with C_8K **1** underwent reductive dechlorination yielding **2**, a novel $\text{N-P}^{\text{III}}\text{-P}^{\text{III}}\text{-C}=\text{C}$ heterocycle.

The role of β -diketiminates as supporting ligands for a wide spectrum of metal complexes is rapidly growing.¹ This may be judged not only by the burgeoning literature (more than 50 papers in 2002), but also by the increasing range of their applications as catalysts (α -olefin polymerisation,² ring-opening polymerisation of lactide³ or related monomers,⁴ and copolymerisation of an epoxide and CO_2), structural models for a Type 1 Cu protein active site,⁶ and as spectator ligands for unusual metal complexes, such as $[\text{Al}(\text{L})(\text{NC}_6\text{H}_3\text{Pr}^i_{2-2,6})]$ ⁷ and $[\{\text{Fe}(\text{L})\}_2(\mu\text{-N}_2)]$ ⁸ [$\text{L} = \{\text{N}(\text{C}_6\text{H}_3\text{Pr}^i_{2-2,6})\text{C}(\text{Me})\}_2\text{CH}$].

A variety of ligand-to-metal bonding modes has been reported for metal β -diketiminates. The ligand may be terminal or bridging, almost invariably (but see ref. 9) monoanionic, often π -delocalised and for N,N' -chelated complexes the metallacycle is planar or boat-shaped. β -Diketiminates are now known of 42 elements, but there is only a single phosphorus compound **A**.¹⁰ All examples to date, bar one **B**,¹¹ have been of N -, (N,N')-, or (N,N',C)-centred ligands (but see penultimate paragraph).



Our earlier work on β -diketiminates was on N,N' -bis-(trimethylsilyl) ligands such as $[\{\text{N}(\text{SiMe}_3)\text{C}(\text{Ph})\}_2\text{CH}]^-$. We chose not to use these in the present report on P(III) chemistry, since from a 1-azaallyl precursor and a P(III) chloride there was facile loss of SiClMe_3 , as in the formation of **C** from $\text{Li}\{\text{N}(\text{SiMe}_3)\text{C}(\text{Bu}^t)\text{CHSiMe}_3\} + \text{PCl}_3$.¹²

We now report the synthesis and structure of the crystalline phosphorus(III) complex **1**, which thus far is unique in being a C-centred monodentate β -diketiminato (but see penultimate paragraph). Furthermore, we find that its reductive dechlorination affords the crystalline, X-ray-authenticated novel¹³ heterocycle **2**.

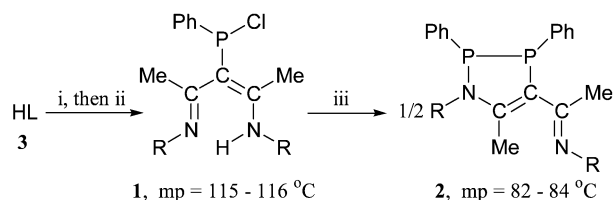
Thus, treatment of the β -diketimine **3**¹⁴ with successively LiBu^n and phenyldichlorophosphine yielded (i, then ii, in Scheme 1) **1**, while the latter with potassium graphite gave (iii

in Scheme 1) **2**, as well as **3** and the *meso*- (**4**) and *rac*- (**5**) diphosphines $\text{Ph}(\text{L})\text{P}-\text{P}(\text{L})\text{Ph}$ [$\text{L} = \{\text{N}(\text{C}_6\text{H}_3\text{Pr}^i_{2-2,6})\text{C}(\text{Me})\}_2\text{CH}$]. Colourless crystals of **1** (> 60%) and **2** (ca. 10%) and the diketimine **3** (authentic^{14b} X-ray structure) were obtained by crystallisation from hexane; the yields have not been optimised.

Each of **1** and **2** gave satisfactory microanalyses, multi-nuclear NMR spectral solution and mass spectral data,[†] which were consistent with the X-ray crystal structures,[‡] illustrated in Figs. 1 (**1**) and 2 (**2**); evidence for compounds **4** and **5** at present rests solely on their NMR spectra: $\delta\{^31\text{P}\{^1\text{H}\}\}$ 9.49 (**4**) and -23.44 (**5**) in C_6D_6 at 293 K. We suggest that reduction of **1** proceeds sequentially by dechlorination to afford the radical $\cdot\text{P}(\text{L})\text{Ph}$, its coupling to yield **4/5** and elimination of LH, as shown in **6**.

The NCCC N bond lengths in crystalline **1** are closely similar to those of **3**,^{14b} with the exception of the significantly longer C2–C3 bond in **1**. The parameters around the pyramidal phosphorus atom are unexceptional.¹⁵

The heterocyclic ring of crystalline **2** is non-planar (unlike that of the almost planar cation of the phosphonium salt **D**¹²) with the atom P 2 0.36(1) Å out-of-the almost planar



Scheme 1 Reagents and conditions: i, LiBu^n in C_6H_{14} , Et_2O , -78°C ; ii, PCl_2Ph , -78°C ; iii C_8K , Et_2O , 20°C ($\text{R} = \text{C}_6\text{H}_3\text{Pr}^i_{2-2,6}$).

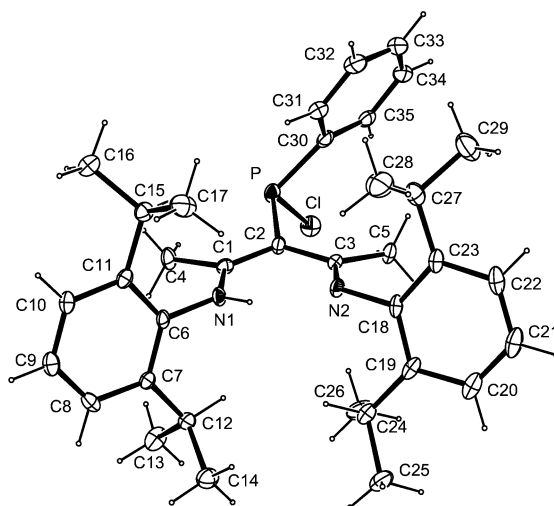


Fig. 1 Molecular structure of crystalline **1**. Selected bond lengths (Å) and angles ($^\circ$): P–Cl 2.129(2), P–C2 1.773(5), P–C30 1.828(6), C1–C2 1.398(7), C2–C3 1.488(7), C1–N1 1.329(7), C3–N2 1.302(6); C2–P–Cl 107.90(19), C2–P–C30 102.8(2), Cl–P–C30 100.2(2), C1–C2–C3 120.7(5), C1–C2–P 114.6(4), C3–C2–P 124.3(4).

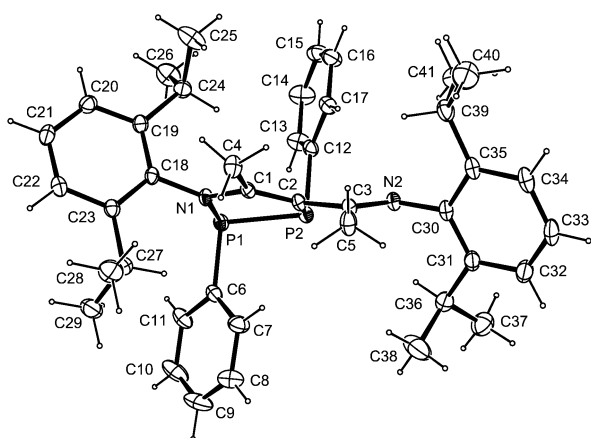
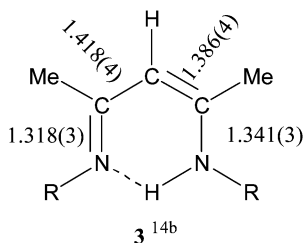


Fig. 2 Molecular structure of crystalline **2**. Selected bond lengths (Å) and angles (°): P1–P2 2.2036(8), P1–N1 1.756(2), P2–C2 1.828(2), N1–C1 1.384(2), C1–C2 1.366(3), C2–C3 1.463(3), C3–N2 1.290(3), C18–N1 1.449(3); N1–P1–P2 93.43(6), P1–P2–C2 90.66(7), P1–N1–C1 117.97(13), N1–C1–C2 118.42(18), C1–C2–P2 117.09(15), P2–P1–C6 99.76(4), N1–P1–C6 102.27(9), P1–P2–C2 90.66(7), P1–P2–C12 96.92(7), C2–P2–C12 102.02(9).



PIN1C1C2 array. The geometrical parameters are appropriate for the illustrated structure **2**; for example, the P–P bond length is in the normal range for a diphosphine.¹⁶

Compound **1** may well be the first of a family of C-centred β -diketimines. The fact that mononuclear P(III) compounds are rarely four-coordinate (but see **A**¹⁰) is a pointer to new experiments; those related to i and ii of Scheme 1 involving in place of $PClPh_2$ a non-metal chloride such as pivaloyl and trimethylsilyl are in hand.

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Note added to proof. In the proof stage, we became aware of a paper (also received on 4th February 2003) reporting an analogue of **2** in which the Cl atom of **2** was replaced by Ph.¹⁷

Notes and references

† *Selected spectroscopic data:* **1** ¹H NMR (293 K, C_6D_6): δ 1.04–1.22 (4d, 24 H, $CHCH_3$), 2.12 (s, 6 H, CCH_3), 3.07 (sept, 2 H, $CHCH_3$), 3.18 (sept, 2 H, $CHCH_3$), 6.99–7.15 (m, 9 H, aromatic), 7.75–7.80 (m, 2 H, aromatic), 15.53 (s, 1 H, NH); ¹³C{¹H} NMR (C_6D_6): δ 20.99 (s, CCH_3), 21.30 (s, CCH_3), 23.37 (s, $CHCH_3$), 23.46 (s, $CHCH_3$), 24.25 (s, $CHCH_3$),

24.48 (s, $CHCH_3$), 28.58 (s, $CHCH_3$), 28.99 (s, $CHCH_3$), 99.01 [d, ¹ $J(^{13}C-^{31}P)$ 41.5, CP], 123.86, 123.89, 126.43, 127.73, 127.79, 127.84, 128.84, 128.95, 129.05, 129.30, 139.73, 141.88 (aromatic), 143.78 [d, ¹ $J(^{13}C-^{31}P)$ 33.2, *ipso-C*], 172.01 [d, ² $J(^{13}C-^{31}P)$ 28.2 Hz, CCH_3]; ³¹P{¹H} NMR (C_6D_6): δ 94.12; MS (*m/z* (%), assignment): 561 (4, [**1**]⁺).

²H NMR (293 K, C_6D_6): δ 0.39–1.15 (5d, 15 H, $CHCH_3$), 1.21–1.25 (m, 9 H, $CHCH_3$), 2.10 [d, ⁴ $J(^1H-^{31}P)$ 1.7, 3 H, CCH_3], 2.33 (s, 3 H, CCH_3), 3.09 (sept, 2 H, $CHCH_3$), 3.24 (sept, 2 H, $CHCH_3$), 7.06–7.22 (m, 12 H, aromatic), 7.72–7.77 (m, 2 H, aromatic), 7.84–7.87 (m, 2 H, aromatic); ¹³C{¹H} NMR (C_6D_6): δ 19.24 [d, ¹ $J(^{13}C-^{31}P)$ 2.2, $CHCH_3$], 22.60 [d, ¹ $J(^{13}C-^{31}P)$ 7.7, $CHCH_3$], 23.01 [d, ³ $J(^{13}C-^{31}P)$ 10.8, CCH_3], 23.63 [d, ¹ $J(^{13}C-^{31}P)$ 3.4, $CHCH_3$], 23.97 [d, ³ $J(^{13}C-^{31}P)$ 5.7, CCH_3], 28.23 [d, ¹ $J(^{13}C-^{31}P)$ 3.6, $CHCH_3$], 23.41, 23.53, 24.25, 28.75, 28.89 (5s), 108.89–147.83 (aromatic), 162.32 [s, $C(CH_3)N$], 166.44 [d, ² $J(^{13}C-^{31}P)$ 20.1 Hz, $C(CH_3)N$]; ³¹P{¹H} NMR (C_6D_6): δ 58.89 [d, ¹ $J(^{31}P-^{31}P)$ 229.5], –11.88 [d, ¹ $J(^{31}P-^{31}P)$ 229.5 Hz]; MS (*m/z* (%), assignment): 633 (24, [**2**]⁺).

‡ *Crystal data:* **1**: $C_{35}H_{46}ClN_2P$, $M = 561.16$, orthorhombic, space group $Pna2_1$ (No.33), $a = 14.5108(8)$, $b = 25.9696(13)$, $c = 8.4582(4)$ Å, $U = 3187.4(3)$ Å³, $Z = 4$, $\mu(Mo-K\alpha) 0.20$ mm⁻¹. Final residual was $R_I = 0.056$ for the 2746 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.136$ for all the 3317 reflections collected. CCDC 203507.

2: $C_{41}H_{50}N_2P_2C_6H_6$, $M = 710.88$, monoclinic, space group $P2_1/n$ (No.14), $a = 14.5205(3)$, $b = 19.8810(5)$, $c = 15.4891(4)$ Å, $\beta = 110.874(1)^\circ$, $U = 4178.0(2)$ Å³, $Z = 4$, $\mu(Mo-K\alpha) = 0.14$ mm⁻¹. Final residual was $R_I = 0.048$ for 5536 reflections with $I > 2\sigma(I)$ and $wR_2 = 0.109$ for all the 6913 reflections collected. CCDC 203508. See <http://www.rsc.org/suppdata/cc/b3/b301294h/> for crystallographic files in .cif or other electronic format.

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