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Inhibited chelation in the new γ-phosphino-β-diketiminate to give phosphine → arsine coordination

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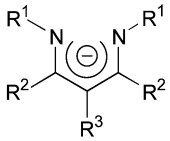
A γ-diphenylphosphino-β-diketimine has been synthesised and the ^{31}P NMR handle allows for *in situ* analysis of reaction mixtures revealing unprecedented reactivity with $AsCl_3$ to give a novel phosphinoarsine intramolecular coordination complex.

β-Diketiminate ligands **1** have been extensively used to stabilise a variety of coordination modes and oxidation states for many elements.[1] The sterically encumbered derivative **1a** (R^1 = diisopropylphenyl, R^2 = Me, R^3 = H) offers a particularly versatile chelate environment and is responsible for the isolation of complexes with the general structure **2**, as represented by the recently reported examples with E = Li,[2] MgR,[3,4] CaL,[4] SrL,[4] Ba,[4] MnR,[5] FeR,[5,6] CoR,[5] CuX,[7,8] ZnR,[3,7,9] ScR,[10] Al[11] and Ga.[12] †

Assessment of coordinate unsaturation and the influence on catalysis are paramount in these studies and apparently depend on the steric loading outside the mouth of the N,N′ chelate. Although phosphine substituents have been introduced at R^1,[13] and a metal complex of a phosphorus diketiminate heterocycle[14] has been reported, chelate complexes of electron-rich (lone pair bearing) group 15 elements with **1** are conspicuously unknown.



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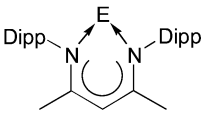
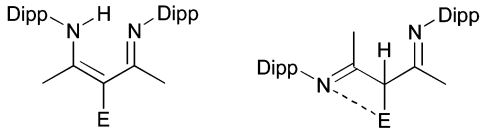


2

We now show how a phosphine and an arsine avoid chelation with **1a** with consequential activation at the γ-position of the diiminate. We have isolated **3**P, which offers a convenient NMR label, and the corresponding γ-phosphino-β-diketiminate undergoes a novel cyclisation reaction with $AsCl_3$ to give **5**, which contains P → As coordination.

Reaction of Li**1** with Ph_2PCl at −78 °C gives a yellow solution with a $^{31}P\{^1H\}$ NMR signal at δ = −11ppm (>90% relative intensity), which is assigned to the isolated compound that has been structurally characterised (Fig. 1) as **3**P, an isomer of the chelate complex **2** (E = Ph_2P). The Ph_2P fragment occupies the γ-position of the aminoimine **3**P, which exhibits a characteristic ^{1}H NMR signal at δ = 12 ppm.[2] Consequently, metathesis of LiCl is accompanied by rearrangement of the γ-proton to one of the nitrogen centers, with retention of conjugation. In this context, the N_2C_3 framework of **3**P is structurally similar to the parent aminoimine H**1**. Although γ-functionalised β-diketimines are rare,[1] the $GeCl_3$ derivative **4**Ge[15] represents a non-conjugated diimine isomer of **3**Ge, rather than a substitution product.

Reaction of **3**P with BuLi followed by $AsCl_3$ yields a single product ($^{31}P\{^1H\}$ NMR δ = 48 ppm), which has been crystallographically characterised as the cyclic compound **5** (Fig. 2). The five-membered ring is composed of a phosphonium center with distorted tetrahedral geometry adjacent to an



3P P, E = PPh_2 **4**P
3Ge Ge, E = $GeCl_3$ **4**Ge

arsenic center with disphenoidal geometry bound to one of the former (R^2) methyl carbon centers. Consequently, metathesis of LiCl in this reaction is accompanied by rearrangement of a hydrogen atom from methyl (R^2) to one of the nitrogen centers, with retention of conjugation, and coordination[16] of the former phosphine center to the arsine center **5b**.

As shown in Table 1, the N–C_β bonds in **3**P and **5** compare with those in H**1** and Li**1**, but are longer than in the terminal diimine **4**Ge.[15] The P–C bond is slightly shorter in **5** [1.764(2)Å] than in the free ligand **3**P [1.812(2)Å].

Intramolecular coordination to As and Sb has been previously reported to give a disphenoidal geometry,[17] but the *trans* configuration of the chlorine centers observed in **5** is unusual, and the As–Cl bonds [2.3785(6) and 2.5245(6)Å] are relatively long [*cf.* aminonaphthyldichloroarsine, 2.340(3), 2.207(3) Å;[17] $AsCl_4^-$ 2.15–2.49 Å].[18]

The formation of **3**P, rather than a chelate arrangement analogous to **2**, is kinetically and thermodynamically driven by the steric shield imposed by the bulky Dipp substituents as well as the incompatibility of the bite angle with the pnictogen center (Pn = P, As). Five-membered rings are typically formed by the pnictogens (rather than a six-membered ring of **2** E = ECl_2),

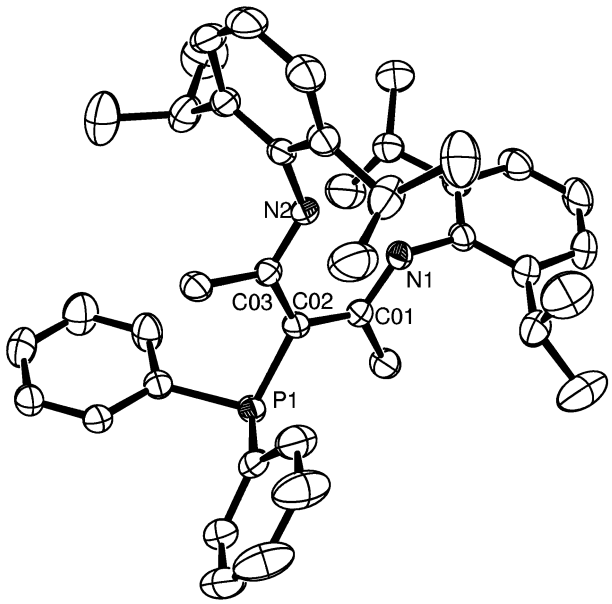


Fig. 1 Solid state structure of **3**P. Ellipsoids are 50% probability. Hydrogen atoms are not shown for clarity.

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Table 1 Comparison of selected bond lengths (Å) for H**1a**, Li**1a**, **3**P, **4**Ge and **5**

	H**1a**	Li**1a**	**3**P	**4**Ge	**5**
N–C_β	1.341(3) 1.318(3)	1.324(3) 1.325(3)	1.337(2) 1.306(2)	1.273(3) 1.268(4)	1.325(2) 1.300(2)
N–H	0.92(4)	—	0.95(3)	—	0.80(3)
P–C	—	—	1.812(2)	—	1.764(2)

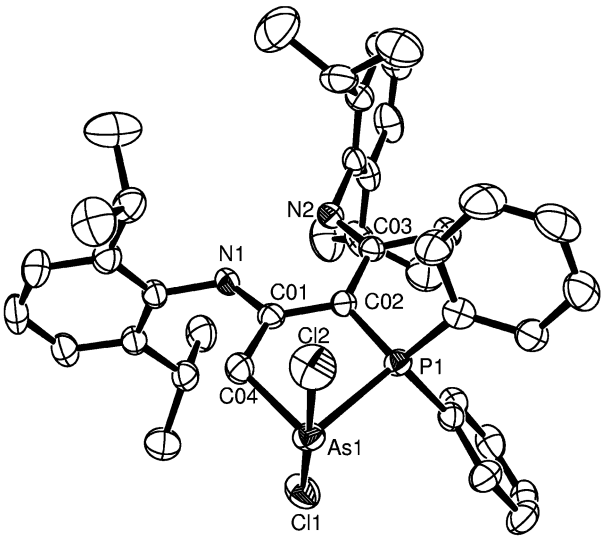
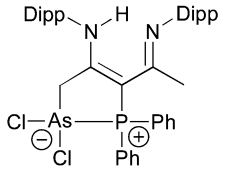
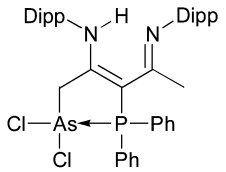


Fig. 2 Solid state structure of **5**. Ellipsoids are 50% probability, hydrogen atoms and C_6H_6 solvate are not shown for clarity. Selected bond distances (Å): P1–As1 2.3492(6), As1–Cl1 2.5245(6) As–Cl2 2.3785(6), and bond angles (°): Cl1–As–Cl2 173.85(2), P1–As1–C04 86.66(6).

also influencing the formation of **5**, which is further promoted by the supplemental P–As coordination in **5b**.



5a



5b

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Notes and references

† **3**P: Li*1*(Et_2O) (3.24 g, 6.50 mmol) was dissolved in toluene (50 ml) in a Schlenk vessel, and added to a −78 °C solution of $ClPPh_2$ (1.43 g, 6.50 mmol) in toluene (15 ml) *via* cannula. The reaction mixture was stirred for 12 h and warmed to rt. LiCl was filtered and the solvent was slowly removed giving yellow crystals 3.22 g, 82.0%; Anal. Calcd. (found) C 81.68 (82.38), H 8.19 (8.20), N 4.65 (4.22)%; mp 144–147 °C. FT-IR cm^{-1} (Ranked intensity); 1526(1), 1322(8), 1191(10), 1028(4), 795(9), 769(5), 742(3), 696(2), 555(6), 427(7); $^{31}P\{^1H\}$ NMR −11 ppm. Crystal data: $C_{41}H_{49}N_2P_1$; M = 602.83 g mol^{-1}, Monoclinic, $P2_1/n$, a = 10.6899(6), b = 36.444(2), c = 10.8213(6) Å, β = 118.846(1)°, V = 3692.7(4) Å^3, T = 193(2) K, Z = 4, D_c = 1.084, measured reflections 20603, unique 7571, refined parameters 403, $R[I > 2\sigma I]$ = 0.0515, $wR_2(F^2)$ = 0.1264

5: 1.6 M ^{n}BuLi in hexanes (1.16 ml) was added to a solution of **3**P (0.10 g, 0.17 mmol) in toluene (3 ml) at rt. The mixture was stirred for 2 h at rt, cooled to −30 °C, and added to a solution of $AsCl_3$ (0.003 g, 0.17 mmol) in toluene (3 ml) at −30 °C. After 12 h at −30 °C, the mixture was warmed to rt, filtered and crystallized by vapour diffusion with pentane; 0.06 g, 44%; Anal. Calcd. (found) C, 65.95 (66.10); H, 6.62 (6.76); N, 3.75 (3.80)%; dp 177 °C; FT-IR cm^{-1}(Ranked Intensity); 1537(1), 1190(9), 1101(5), 801(10), 778(3), 746(8), 688(6), 523(4), 477(2), 436(7); $^{31}P\{^1H\}$ NMR 48 ppm. Crystal data: $C_{50}H_{59}N_2PAs_1Cl_2$; M = 864.78 g mol^{-1}, Triclinic, $P1$, a = 11.4457(9), b = 12.462(1), c = 16.902(1) Å, α = 94.920(2), β = 107.742(1), γ = 90.251(2)°, V = 2322.0(3) Å^3, T = 193(2) K, Z = 2, D_c = 1.237, measured reflections 13450, unique 9346, refined parameters 509, $R[I > 2\sigma I]$ = 0.0374, $wR_2(F^2)$ = 0.0949.

X-Ray crystallography. Crystals of **3**P and **5** were placed in a −80 °C stream of dry nitrogen and data were collected on a Bruker P4/RA SMART 1000 CCD diffractometer using a graphite monochrometer with Mo K_α radiation (λ = 0.71073 Å). The structure of **3**P was solved using direct methods SHELXS-97 and refined with full-matrix least squares on F^2 using SHELX-97. HN1 was located in the Fourier map and refined isotropically. The structure of **5** was solved using Patterson methods SHELXS-97 and refined with full-matrix least squares on F^2 SHELX-97. HN1 was located in the Fourier map and refined isotropically. All other hydrogen atoms were placed in geometrically calculated positions and were refined using a riding model. CCDC 203503 and 203504. See http://www.rsc.org/suppdata/cc/b3/b301333b/ for crystallographic data in .cif or other electronic format.

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