β-Diiminato ligand (L) transformations in reactions of KL with PI_3 and I_2 [L = $\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2CPh$]†

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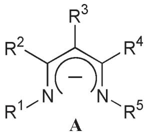
The reaction of the potassium β-diiminate KL (L = $[\{N(Ar)C(H)\}_2CPh]^-$; Ar = $C_6H_3Pr^i_2\text{-}2,6$) with PI_3 unexpectedly produced a phosphenium salt of the intermolecularly *C,C*-coupled ligand $[P(I)\{N(Ar)CH\}_2C(C_6H_4\text{-}4)C(Ph)(CH{=}NAr)_2]^+[I_3]^-$, while an intramolecularly *N,N*-coupled salt $[\overline{N(Ar)C(H)C(Ph)C(H)N}(Ar)]^+[I_5]^-$ was isolated from KL + I_2.

β-Diiminato ligands (shown in **A** in π-delocalised monoanionic form) have found extensive use in coordination chemistry and in catalysis.[1] Most are β-diketiminates (R^2 and R^4 are alkyl, aryl or silyl); only a few examples of β-dialdiminates ($R^2 = R^4 = H$) are known.[2] β-Diiminato complexes of nearly all the elements have been prepared (except those of groups 16–18). In group 15, only a few phosphorus[3–5] and antimony[6] complexes have been characterised, featuring *C*-centred[3] or *N*-centred[4] acyclic β-diketiminates. A chelating *N,N*-coordinated ligand was featured in a compound containing a P → Mo bond[5a] and in a β-diketiminato–antimony dichloride with a bulky ligand **A** ($R^1 = R^5 = C_6H_2Me_3\text{-}2,4,6$; $R^2 = R^4 = Me$).[6] Very recently it has been shown that two *C*-centred P^{III} compounds rearranged into *N,N*-chelated cationic β-diketiminates upon treatment with trimethylsilyl triflate.[5b]

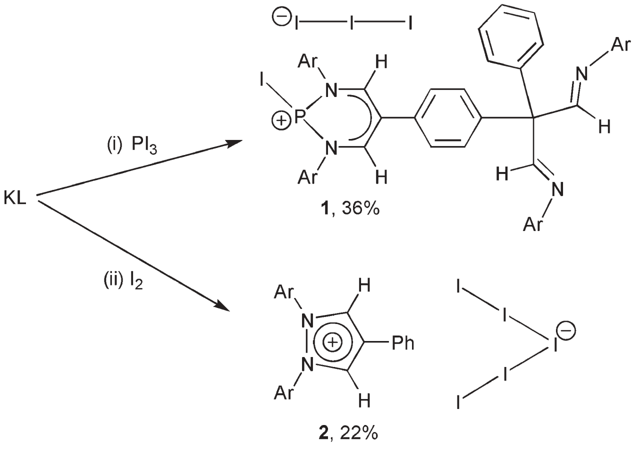


A

We now report on reactions of the β-dialdiminate KL (L = $[\{N(Ar)C(H)\}_2CPh]^-$; Ar = $C_6H_3Pr^i_2\text{-}2,6$) with PI_3 or I_2, leading to a phosphenium *N,N*-chelated β-diiminate or a pyrazolium salt, respectively, each with a polyiodide anion, Scheme 1.

Metal complexes of the widely used $Dipp_2$nacnac ligand ($R^1 = R^5 = C_6H_3Pr^i_2\text{-}2,6$; $R^2 = R^4 = Me$) can act as *C*- rather than *N*-centred nucleophiles resulting in attack on the γ-C atom of the ligand backbone, while the Me groups attached to β-C atoms can be deprotonated.[3,6,7] To avoid such reactions we employed the β-dialdiminato ligand L, in which the γ-C atom is blocked by a Ph substituent and β-C methyl groups are replaced by hydrogens.

Reaction of PCl_3 or PBr_3 with 1 equivalent of KL in thf produced a non-crystalline mixture of several *P*-containing species (shown by ^{31}P NMR spectroscopy), but PI_3 gave ((i) in Scheme 1) a modest yield of the crystalline β-dialdiminatophosphenium triiodide **1**.‡ The cation of **1** contains a modified ligand L′, which can be described as a product of oxidative coupling of two L moieties *via* the *p*-Ph position of one L and the γ-C atom of another.



Scheme 1 Synthesis of the salts **1** and **2** (Ar = $C_6H_3Pr^i_2\text{-}2,6$).

Because a possible oxidant in the reaction leading to **1** might have been I_2 (*via* homolysis of a P–I bond of PI_3[8]), we carried out the oxidation of KL with molecular iodine.[9] The unexpected product of this reaction ((ii) in Scheme 1) was the intramolecularly *N,N*-coupled compound **2**‡ obtained in a low yield.

Possible mechanisms leading to the salts **1** and **2** are outlined in Scheme 2. The key intermediate is the nitrenium iodide **B**, formed by two-electron oxidation of $[L]^-$ with I_2 (in (i) of Scheme 1, the source of I_2 is PI_3[8]). The nitrenium cation of **B** can be stabilised either (a in Scheme 2) by a double bond migration yielding the salt **C** or (b in Scheme 2) by a nucleophilic addition of the second N atom furnishing the pyrazolium iodide **D** which with I_2 gives **2**. The carbocation of **C**, which is conjugatively stabilised by both Ph and C=N fragments, undergoes (step (c) in Scheme 2) electrophilic attack on $[L]^-$ (only the *p*-position of the Ph substituent of L^- is available for steric reasons) to give **E**, which with PI_3 and I_2 affords **1** as the main product (P_2I_4 and KI were also identified). The low isolated yield of **2** in reaction (ii) of Scheme 1 may have been due to the presence of other unidentified products (possibly originating from pathway b of Scheme 2) in the reaction mixture, with **2** the most easily crystallisable. It may be that **B** and **C** are resonance hybrids.[10]

In the solid state complex **1** consists of separated $[PIL']^+$ cations and triiodide anions (Fig. 1).§ The phosphorus atom has a trigonal pyramidal environment with two nearly equal P–N bond lengths

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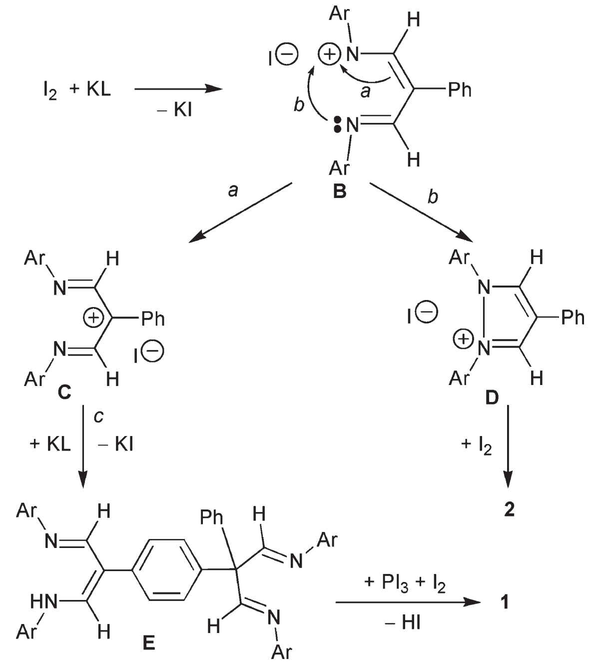
† Electronic supplementary information (ESI) available: details of experimental procedures, characterisation and crystallographic data for compounds **1** and **2**. See DOI: 10.1039/b611260a



Scheme 2 Proposed pathways to compounds **1** and **2** (Ar = $C_6H_3Pr^i_2$-2,6).

of 1.738(4) and 1.744(4) Å, which are slightly longer than the corresponding distances in the analogous β-diketiminatophosphenium triflate [PCl{N(Ar)C(Me)}$_2$C(Me)][OTf] (**F**) (1.731(2) and 1.701(2) Å).[5b] The P–I bond at 2.4928(14) Å is similar to that in PI_3 (2.463(5) Å).[11] The PN_2C_3 ring in **1** is more delocalised and closer to planarity (the phosphorus atom is out of the ligand plane by 0.359(6) Å) than that in **F**.[5b]

Significant steric crowding around the quaternary carbon atom C35 prevents free rotation around contiguous single C–C and remote C_{Ar}–N bonds, which results in non-equivalence of methyl groups and aromatic protons in this part of the molecule. This (along with its low solubility in aromatic solvents and instability in thf-d_8) precludes detailed interpretation of ^{1}H and ^{13}C NMR spectra of complex **1**. The ^{31}P NMR spectrum of **1** in C_6D_6 showed two very closely situated signals at δ 118.9 and 118.5 ppm (δ 97.23 in **F**[5b]) apparently due to the existence of two stereoisomers in solution.

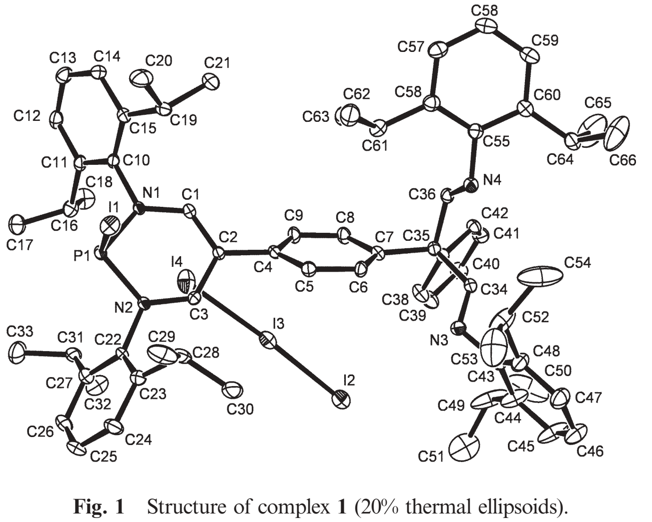


Fig. 1 Structure of complex **1** (20% thermal ellipsoids).

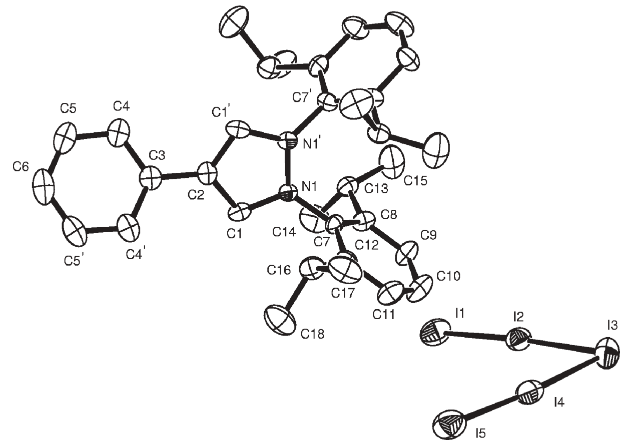


Fig. 2 Structure of complex **2** (50% thermal ellipsoids). Symmetry transformations used to generate equivalent atoms: $-x$, $-y + 1$, z.

The molecular structure of **2** is shown in Fig. 2 (only one of the two crystallographically independent cations, lying on 2-fold rotation axes, is shown; the second has very similar geometric parameters, see the electronic supplementary information (ESI†) for details). The separate pyrazolium and pentaiodide ions have no unusual features. The structure of the cation can be compared to that of the neutral pyrazolidine (−)-[{N($C_6H_4Pr^i$-2)CHMe}$_2$CMe$_2$] (**G**), which was obtained by oxidative N–N coupling of (−)-[Li_2{N($C_6H_4Pr^i$-2)CHMe}$_2$CMe$_2$](OEt$_2$) with O_2.[12] Short N–N 1.372(10), N–C 1.347(9) and C–C 1.368(9) Å bond lengths in the heterocyclic core of **2** (*cf.*,[12] analogous endocyclic bonds in **G**: N–N 1.4846(15), N–C_{av} 1.462 and C–C_{av} 1.544 Å) indicate its unsaturated character and substantial charge delocalisation.

It is noteworthy that no cyclic product was observed when the β-diket- or dialdimine H[{N($C_6H_3Pr^i_2$-2,6)C(R^2)}$_2C_\gamma R^3$] was oxidised by $AgPF_6$; intermolecular C_γ–C_γ coupling was the main reaction pathway.[13]

In conclusion, we report on the crystalline β-dialdiminatophosphenium triiodide **1** and the pyrazolium pentaiodide **2**. Each was obtained from the potassium β-dialdiminate K[{N($C_6H_3Pr^i_2$-2,6)C(H)}$_2$CPh] and PI_3 (**1**) or I_2 (**2**). Intermolecular $C_{p\text{-Ph}}$–C_γ (**1**) or intramolecular N–N (**2**) oxidative coupling of the ligand is implicated in the formation of the cations of **1** and **2**. The nitrenium iodide [N(Ar)=C(H)–C(Ph)=C(H)–N(Ar)]I is suggested as a common intermediate.

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Notes and references

‡ *Synthesis of [P(I){N(Ar)C(H)}$_2$C(C_6H_4-4)C(Ph)(CH=NAr)$_2$][I_3] (1).* KL (3.73 mmol, 26.3 mL of a 0.142 M solution in thf) was added dropwise to a solution of PI_3 (1.54 g, 3.74 mmol) in thf (20 ml) under stirring at −35 °C. The mixture was warmed up to room temperature and stirred for 24 h. The volatiles were removed in *vacuo*, and the residue was treated with Et_2O producing a dark red solution and a red-orange precipitate. The precipitate was filtered off, the filtrate was concentrated and layered with hexane. Storing at room temperature overnight gave compound **1** (yield 1.0 g, 0.68 mmol, 36% based on L) as red needle crystals decomposing without melting above 130 °C. Anal. Calc. for $C_{66}H_{81}I_4N_4P$: C, 53.9; H, 5.51; N, 3.81. Found: C, 53.8; H, 5.41; N, 3.83%. ^{31}P NMR (C_6D_6): δ 118.9 and 118.5.

Synthesis of $[\overline{\mathrm{N(Ar)C(H)C(Ph)C(H)N}}\mathrm{(Ar)}][\mathrm{I_5}]$ *(**2**)*. A solution of I_2 (0.50 g, 1.97 mmol) in Et_2O (20 mL) was added to a stirred suspension of KL (1.97 mmol, obtained by removing thf from 20 mL of a 0.098 M solution) in Et_2O (20 mL) at room temperature. After stirring overnight the mixture was filtered, the filtrate was concentrated and stored at −27 °C for 3 d yielding dark red crystals of compound **2** (0.16 g, 0.15 mmol, 22% based on I_2), mp 175 °C (decomp.). Anal. Calc. for $C_{33}H_{41}I_5N_2$: C, 36.0; H, 3.73; N, 2.55. Found: C, 36.0; H, 3.93; N, 2.63%.

§ *Crystal data*. For **1**: [$C_{66}H_{81}I_4N_4P$], M = 1468.92, triclinic, space group $P\bar{1}$, a = 10.4165(2), b = 17.3501(5), c = 19.9214(6) Å, α = 67.651(1), β = 88.601(2), γ = 79.776(2)°, V = 3271.88(15) $Å^3$, Z = 2, T = 173(2) K, μ = 1.97 mm^{-1}, 12860 independent reflections [R_{int} = 0.057], final $R1$ = 0.055 [for 8372 reflections with $I > 2\sigma(I)$], $wR2$ = 0.111 (all data). For **2**: [$C_{33}H_{41}I_5N_2$], M = 1100.18, orthorhombic, space group $Pnc2$, a = 21.8936(5), b = 13.9582(3), c = 12.3029(3) Å, V = 3759.71(15) $Å^3$, Z = 4, T = 173(2) K, μ = 4.16 mm^{-1}, 7201 independent reflections [R_{int} = 0.048], final $R1$ = 0.039 [for 5894 reflections with $I > 2\sigma(I)$], $wR2$ = 0.085 (all data). CCDC 616856 and 616857. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611260a

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