

β -Diiminato ligand (L) transformations in reactions of KL with PI₃ and I₂ [L = {N(C₆H₃Prⁱ₂-2,6)C(H)}₂CPh]

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Experimental details

General Methods: All manipulations were carried out in an atmosphere of dry argon using standard Schlenk tube techniques. Solvents were dried from the appropriate drying agent, distilled, degassed and stored over a potassium mirror. The NMR spectra were recorded on a DPX 300 spectrometer with solvent signals as internal reference (¹H and ¹³C{¹H}) or with an external reference (85% H₃PO₄ for ³¹P{¹H}). Elemental analyses (C, H, N) were carried out at the University of North London. Phosphorus content was determined using Perkin Elmer Plasma 400 ICP-AES instrument. KL was prepared by refluxing a thf solution of LH with excess KH; the latter was removed by filtration and the concentration of KL in the solution was determined by titration of an aliquot with 0.1 M HCl.

Synthesis of [P(I){N(Ar)C(H)}₂C(C₆H₄-4)C(Ph)(CH=NAr)₂]⁺[I₃]⁻ (I). KL (3.73 mmol, 26.3 mL of a 0.142 M solution in thf) was added dropwise to a solution of PI₃ (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 Et₂O producing a dark red solution and a red-orange precipitate (0.88 g). The precipitate was filtered off and dried; the featureless ¹H NMR spectrum and the phosphorus content of 8.65% indicated that it consisted of P₂I₄ and KI (for the 1 : 1 mixture, the calculated P content is 8.42%); thus, the total amount of phosphorus in the precipitate was 0.076 g (2.45 mmol, 65.5% based on PI₃). The dark-red filtrate was concentrated and layered with hexane. Storing at room temperature for 5 days gave compound **1** (1.0 g, 0.68 mmol, 36.4% based on L or 18.2% based on PI₃) as red needle crystals decomposing without melting above 130 °C. Anal. Calc. for C₆₆H₈₁I₄N₄P: C, 53.9; H, 5.51; N, 3.81. Found: C, 53.8, H, 5.41, N, 3.83%. ³¹P{¹H} NMR (C₆D₆): δ

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118.9 and 118.5. ^1H NMR (thf- d_8): δ 9.01 (br s, 1 H), 8.96 (d, 1 H, $J = 1.5$ Hz), 8.51 (br s, 1 H), 7.84-6.95 (m, 22 H), 3.33 (two septets, 4 H, CHMe_2), 3.12 (septet, 1 H, $J = 6.6$ Hz, CHMe_2), 2.96 (septet, 3 H, $J = 6.6$ Hz, CHMe_2), 1.51 (d, 12 H, $J = 6.6$ Hz, CHMe_2), 1.39 (d, 12 H, $J = 6.6$ Hz, CHMe_2), 1.26 (two d, 6 H, $J = 6.6$ Hz, CHMe_2), 1.06 (m, 18 H, CHMe_2).

*Synthesis of $[\overline{\text{N}(\text{Ar})\text{C}(\text{H})\text{C}(\text{Ph})\text{C}(\text{H})\text{N}(\text{Ar})}]^+ [\text{I}_5]^-$ (**2**).* A solution of I_2 (0.5 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 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 days 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 $\text{C}_{33}\text{H}_{41}\text{I}_5\text{N}_2$: C, 36.0; H, 3.73; N, 2.55. Found: C, 36.0, H, 3.93, N, 2.63%. ^1H NMR (thf- d_8): δ 9.64 (s, 1 H, NCHCPh), 7.84 (d, 2 H, $J = 7.3$ Hz, $o\text{-H}^{\text{Ph}}$), 7.69 (t, 2 H, $J = 8.0$ Hz, $p\text{-H}^{\text{Ar}}$), 7.62 (t, 2 H, $J = 7.7$ Hz, $m\text{-H}^{\text{Ph}}$), 7.54 (t, 1 H, $J = 7.3$ Hz, $p\text{-H}^{\text{Ph}}$), 7.49 (d, 4 H, $J = 8.0$ Hz, $m\text{-H}^{\text{Ar}}$), 2.22 (septet, 4 H, $J = 6.6$ Hz, CHMe_2), 1.27 (d, 12 H, $J = 6.6$ Hz, CHMe_2), 0.90 (d, 12 H, $J = 6.6$ Hz, CHMe_2). ^{13}C NMR (thf- d_8): δ 158.6, 148.4, 144.8, 134.7, 130.7, 128.0, 127.2, 127.0, 126.0, 30.7, 26.1, 22.2.

Crystallography: Data for the crystal structure determination of **1** and **2** were collected on a Nonius Kappa CCD diffractometer at 173(2) K with Mo- $\text{K}\alpha$ X-rays ($\lambda = 0.71073$ Å). Crystal data and refinement details are listed in Table 1S. The structures were solved by direct method and refined using SHELXL-97. In crystals of complex **2** there is one I_5 anion in a general position and two cations lying on 2-fold rotation axes.

Table 1S Crystal data and structure refinement for **1** and **2**

Compound	1	2
Empirical formula	C ₆₆ H ₈₁ I ₄ N ₄ P	C ₃₃ H ₄₁ I ₅ N ₂
Formula weight	1468.92	1100.18
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>Pnc</i> 2 (No. 30)
<i>a</i> /Å	10.4165(2)	21.8936(5)
<i>b</i> /Å	17.3501(5)	13.9582(3)
<i>c</i> /Å	19.9124(6)	12.3029(3)
α /°	67.651(1)	90
β /°	88.601(2)	90
γ /°	79.776(2)	90
<i>V</i> /Å ³	3271.88(15)	3759.71(15)
<i>Z</i>	2	4
<i>D</i> _c /Mg m ⁻³	1.49	1.94
μ (Mo-K α)/mm ⁻¹	1.97	4.16
<i>F</i> (000)	1464	2072
Reflections collected	48640	23950
Independent reflections	12860 [R(int) = 0.057]	7201 [R(int) = 0.048]
Reflections with <i>I</i> > 2 σ (<i>I</i>)	8372	5894
Data/restraints/parameters	12860/0/676	7201/1/365
Goodness-of-fit on <i>F</i> ²	1.020	1.020
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.055, <i>wR</i> 2 = 0.096	<i>R</i> 1 = 0.039, <i>wR</i> 2 = 0.080
R indices (all data)	<i>R</i> 1 = 0.101, <i>wR</i> 2 = 0.111	<i>R</i> 1 = 0.055, <i>wR</i> 2 = 0.085
Largest diff. peak and hole/ e Å ⁻³	1.39 and -1.13 (near I)	0.73 and -0.73