# Polyfunctional Ligands: Comparative Oxidative Coupling of $[E(PPh_2)_2]^-$ (E $\square$ CH, N) with lodine

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lodine oxidation of the isoelectronic anions  $[N(PPh_2)_2]^-$  and  $[HC(PPh_2)_2]^-$  affords the structurally characterized P–P coupling product  $Ph_2P-N=PPh_2=N-PPh_2=N-PPh_2$  and the P–C coupling product  $(Ph_2P)_2C=PPh_2-CH_2-PPh_2$ , respectively; the P–P heterocoupling product  $Ph_2P-N=PPh_2=CH-PPh_2=CH-PPh_2$  is obtained in the cross-coupling experiment of  $Li[N(PPh_2)_2]$  and  $Li[HC(PPh_2)_2]$  with iodine at -40 °C.

The selective oxidative C–C coupling of two monophosphinederived carbanions is currently receiving increasing interest as it represents a useful access to chiral chelating diphosphine ligands of catalytic interest. A typical multi-step procedure involves BH<sub>3</sub> protection of the phosphorus lone pair, oxidation with copper(II) complexes and deprotection by a strong nitrogen base.<sup>1</sup> However, comparative studies with isoelectronic nitrogen-containing phosphorus systems are not available.

As part of our studies on polyfunctional phosphine ligands. we investigated the reaction of Li[N(PPh<sub>2</sub>)<sub>2</sub>] with PCl<sub>3</sub>. By using a 3:1 stoichiometry, we isolated two compounds, according to Scheme 1. Whereas 1 has been previously isolated by Schmidpeter et al. from the reaction of Li[N(PPh<sub>2</sub>)<sub>2</sub>] with white phosphorus and must result in Scheme 1 from the reduction of PCI, 2 represents an oxidation product of Li[N(PPh<sub>2</sub>)<sub>2</sub>].<sup>2a,b</sup> Its <sup>31</sup>P NMR spectrum is characterized by an AA'XX' pattern.† These products were also observed when 1,2-dibromoethane was used as an oxidant. Interestingly, this reagent also oxidizes Li[P(PBu<sup>t</sup><sub>2</sub>)<sub>2</sub>] to give  $(Pr^{i}_{2})_{2}P-P(PPr^{i}_{2})_{2}$ .<sup>2c</sup> However, the most convenient access to 2 turned out to be the oxidation of Li[N(PPh<sub>2</sub>)<sub>2</sub>] with iodine which proceeded in quantitative spectro scopic (<sup>31</sup>P NMR) yields (Scheme 2).<sup>†</sup> Note that this P-P coupling reaction is particularly useful as 2 would not be accessible by the Staudinger oxidation of Ph<sub>2</sub>P-PPh<sub>2</sub>, since Ph<sub>2</sub>P–N<sub>3</sub> as synthon is not available.<sup>3</sup> Only Ph<sub>3</sub>Si–N<sub>3</sub> has been successfully used as an imine source,4 whereas with Me<sub>3</sub>Si-N<sub>3</sub>, splitting of the P-P bond occurs under the reaction conditions required.<sup>5a</sup> although with Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> the desired phosphine-phosphinimine ligand was obtained.5b

The molecule of 2 (Fig. 1)‡ is centrosymmetric, with the inversion centre in the middle of the P(1)–P(1') bond. The atoms P(2) and P(2') are situated respectively 0.907(1) Å above and below the plane formed by N–P(1)–P(1')–N'. The P(1)–P(1') and P(2)–N distances correspond to single bonds, in contrast to that for P(1)–N which corresponds to a double bond.

It is known that  $Cu^{II}$  reacts with K[PPh<sub>2</sub>] to give a  $Cu^{I}$  complex of Ph<sub>2</sub>P–PPh<sub>2</sub>, and the latter ligand can be isolated after treatment with cyanide.<sup>6</sup> For comparison, we reacted



 $2 \text{Li}[N(PPh_2)_2] + l_2 -2 \text{Lil}$ Scheme 2 anhydrous CuCl<sub>2</sub> with 2 equiv. of Li[N(PPh<sub>2</sub>)<sub>2</sub>] in THF at room temperature. The <sup>31</sup>P NMR spectrum of the solution indicated the absence of **2**, even after addition of excess PPh<sub>3</sub> which would have displaced it from the metal. This result emphasizes the importance of the nature of the oxidant. In contrast to our *oxidative coupling* reaction, Ellermann *et al.* have recently reported an unusual *oxidative splitting* of Li[N(PPh<sub>2</sub>)<sub>2</sub>] in the presence of excess MCl<sub>2</sub> (M = Co, Ni, Pd) in refluxing toluene which led, after partial fragmentation and recombination, to spirocyclic complexes of the type M[Ph<sub>2</sub>PNPPh<sub>2</sub>NPPh<sub>2</sub>]<sub>2</sub>.<sup>7</sup> Seebach *et al.* have previously observed that the coupling of lithiated orthothioformic esters with I<sub>2</sub> proceeds *via* radical intermediates.<sup>8</sup> In phosphorus chemistry, only phospholes appear to have been P–P coupled in a manner similar to ours.<sup>9</sup>

We then examined the comparative reactivity of  $\text{Li}[\text{HC}(\text{PPh}_2)_2]$ , which is isolectronic to  $\text{Li}[\text{N}(\text{PPh}_2)_2]$ . The reaction proceeded in THF according to Scheme 3 and afforded the air-stable ylide 3c.<sup>†</sup> Monitoring by <sup>31</sup>P NMR indicated that at room temperature **3a** (AA'XX' spin system) is converted within *ca*. 3 h to **3c** (AMM'X spin system). When the reaction was carried out at -40 °C, new signals were observed, in addition to those of **3a**, which correspond to an AM<sub>2</sub>X spin system and are assigned to **3b**. They disappear at room



Fig 1 View of the molecular structure of 2 in the crystal. Selected distances (Å) and angles (°): P(1)-P(1') 2.232(2), P(1)-N 1.558(3), P(2)-N 1.673(2); P(1')-P(1)-N 108.6(1), P(1)-N-P(2) 130.7(1).



### Scheme 4

temperature with the appearance of those of **3c**; the corresponding migration of the hydrogen atom leads to the more substituted and therefore more stable ylide.<sup>10</sup> Schmidbaur *et al.* have obtained **3c** in 30% yield in the reaction of M[Ph<sub>2</sub>P– CH=PPh<sub>2</sub>–CH<sub>2</sub>] with Ph<sub>2</sub>PCl.<sup>11</sup> The analogous methyl-substituted compound could also be prepared.<sup>12*a*</sup> Compounds **3a** and **3c** were recently claimed to result from the oxidation of (Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)Li[HC(PPh<sub>2</sub>)<sub>2</sub>] with (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub>, although they could not be isolated as pure products.<sup>12*b*,*c*</sup>

In a cross-coupling experiment with  $\text{Li}[N(\text{PPh}_2)_2]$  and  $\text{Li}[\text{HC}(\text{PPh}_2)_2]$ , we found at -40 °C a P-P-heterocoupling product **4** in a ratio of *ca*. 2:1:1 hetero **4**:homo **2**: homo **3a,b**, corresponding to a statistical distribution (Scheme 4).† Compound **4** is unstable at room temperature. These results indicate that the radicals [HC(PPh\_2)\_2] and [N(PPh\_2)\_2], likely to be the first-formed oxidation products of Li[HC(PPh\_2)\_2] and Li[N(PPh\_2)\_2], respectively, have a stronger tendency to form P-P or P-C coupled dimers rather than C-C dimers. Note that neither 1,1,2,2-tetrakis(diphenylphosphino)ethane nor 1,1,2,2-tetrakis(diphenylphosphino)ethane nor the literature.<sup>12c</sup> In addition to the steric and electronic effects of the substituents, the nature of the oxidant strongly determines the structure of the coupling products.<sup>13</sup>

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## Footnotes

<sup>†</sup> All reactions were performed under nitrogen, in carefully dried solvents. Li[N(PPh<sub>2</sub>)<sub>2</sub>] and Li[HC(PPh<sub>2</sub>)<sub>2</sub>] were generated by reaction of HN(PPh<sub>2</sub>)<sub>2</sub> or CH<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>, respectively, with Bu<sup>n</sup>Li in THF and used *in situ*.

Synthesis of **2**: To a solution of 23.0 mmol Li[N(PPh<sub>2</sub>)<sub>2</sub>] in 120 ml THF was added within *ca*. 1 min 2.92 g I<sub>2</sub> in small portions. After the yellow solution was stirred for 2 h at room temp., 100 ml toluene was added and the volume reduced to 80 ml. A light yellow precipitate formed, which was filtered, washed with 5 ml toluene and dried. Single crystals were obtained from the filtrate. Yield: 6.45 g (73%). mp 174 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, SiMe<sub>4</sub>):  $\delta$  7.0–7.9 (m, Ph); <sup>3</sup>P NMR (120.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, H<sub>3</sub>PO<sub>4</sub> ext.):  $\delta$  43.5 (P<sup>III</sup>, m, AA'), 12.0 [P<sup>IV</sup>, m, XX', N = 85 Hz, J(AA') ca. 0, J(AX) ± 89.1, J(AX') ± 4.7, J(XX') ± 85.6 Hz].

**3c**: To a solution of 20.90 mmol Li[HC(PPh<sub>2</sub>)<sub>2</sub>] in 100 ml THF was added 2.65 g (20.90 mmol) I<sub>2</sub> in small portions. The colour changed from yellow–green to yellow–orange. Stirring was maintained at room temp. for a few hours, until complete isomerisation of **3a** to **3c** had occurred. Addition of *ca*. 50 ml toluene and  $2 \times 50$  ml H<sub>2</sub>O allows elimination of LiI. The organic phase was dried over CaCl<sub>2</sub>, its volume reduced to *ca*. 20 ml and 50 ml hexane was added. The colourless precipitate was washed with ether. This removes a secondary product (10–15% yields), which is under investigation (signals in the <sup>31</sup>P NMR spectrum around  $\delta$  +1.0 and -8.5)<sup>12c</sup> as well as dppm (5–10%). Yield **3c**: 5.0 g (62%).<sup>12</sup> <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>, 25 °C, SiMe<sub>4</sub>):  $\delta$  12.2 [CP<sub>3</sub>, ddt, <sup>1</sup>*J*(P,C) = 74, 45 Hz, <sup>3</sup>*J*(P,C) = 3 Hz], 24.4 [CH<sub>2</sub>, ddt, <sup>1</sup>*J*(P,C)

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= 53, 32 Hz,  ${}^{3}J(P,C) = 6$  Hz], 143–126 (Ph, m). **3a**:  ${}^{31}P$  NMR (120.5 MHz, THF–C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  21.8 (PIV, m, AA'), -20.7 [PIII, m, XX', N = 150 Hz, J(AA') \pm 110.7, J(XX') ca. 0 Hz,  $J(AX) \pm 131.7$ ,  $J(AX') \pm 21$  Hz]. **3b**:  ${}^{31}P$  NMR (120.5 MHz, THF/C<sub>6</sub>D<sub>6</sub>, -30 °C):  $\delta$  = 26.2 [PV, dt,  ${}^{2}J(P,P) = 147$ , 40 Hz], -12.2 [PIII<sub>2</sub>C, dd,  ${}^{2}J(P,P) = 40$ ,  ${}^{4}J(P,P) = 7$  Hz], -17.0 [PIII, dd,  ${}^{2}J(P,P) = 147$  Hz].

**4**: A solution containing an equimolar amount of Li[N(PPh<sub>2</sub>)<sub>2</sub>] and Li[HC(PPh<sub>2</sub>)<sub>2</sub>] in THF was reacted at -40 °C with the corresponding quantity of I<sub>2</sub>. Beside the homo-coupling products **2** and **3a,b**, **4** was identified by its <sup>31</sup>P NMR spectrum:  $\delta$  41.9 [P<sup>III</sup>N, dd, <sup>2</sup>*J*(P,P) = 87, *3J*(P,P) = 5 Hz], 20.3 [P<sup>IV</sup>C, ddd, <sup>1</sup>*J*(P,P) = 31, <sup>2</sup>*J*(P,P) = 148, <sup>3</sup>*J*(P,P) = 5 Hz], 15.1 [P<sup>IV</sup>N, dd, <sup>1</sup>*J*(P,P) = 31, <sup>2</sup>*J*(P,P) = 87 Hz], -22.5 [P<sup>III</sup>C, d, <sup>2</sup>*J*(P,P) = 148 Hz].

‡ *Crystal data* for **2** (yellow crystals from toluene): C<sub>48</sub>H<sub>40</sub>N<sub>2</sub>P<sub>4</sub>, M = 768.75, monoclinic, space group  $P2_1/c$ , a = 9.634(3), b = 11.157(3), c = 19.112(5) Å,  $\beta = 93.32(2)^\circ$ , V = 2051(1) Å<sup>3</sup>, Z = 2,  $D_{calc.} = 1.245$  g cm<sup>-3</sup>, Nb-filtered Cu-Kα radiation,  $\lambda = 1.54178$  Å,  $\mu = 19.71$  cm<sup>-1</sup>. Measurements: Siemens AED diffractometer,  $\theta$ -20 scan-type, room temp. The structure was solved using direct and Fourier methods. 3882 unique reflections measured with  $\theta$  in the range 3–70°; 2560 with  $I > 2\sigma(I)$ ; no absorption correction was made; refinement by full-matrix least-squares methods; anisotropic thermal parameters for all non-H atoms in the final cycle; isotropic refinement of the H atoms, which were all located in the final difference Fourier-synthesis; R = 0.0338,  $R_w = 0.0392$ . SHELX-76 and SHELXS-86 computer programs were used. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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