Polyfunctional Ligands: Comparative Oxidative Coupling of $[E(PPh_2)_2]^-$ (E = CH, N) with Iodine

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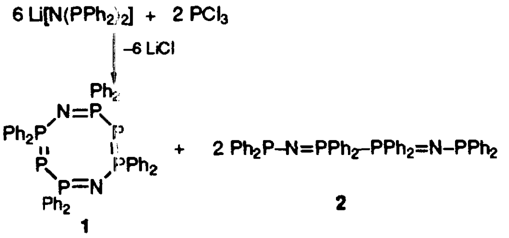
Iodine oxidation of the isoelectronic anions $[N(PPh_2)_2]^-$ and $[HC(PPh_2)_2]^-$ affords the structurally characterized P–P coupling product $Ph_2P{-}N{=}PPh_2{-}PPh_2{=}N{-}PPh_2$ and the P–C coupling product $(Ph_2P)_2C{=}PPh_2{-}CH_2{-}PPh_2$, respectively; the P–P heterocoupling product $Ph_2P{-}N{=}PPh_2{-}PPh_2{=}CH{-}PPh_2$ 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 monophosphine-derived 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_3 protection of the phosphorus lone pair, oxidation with copper(II) complexes and deprotection by a strong nitrogen base.[1] 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 $Li[N(PPh_2)_2]$ with PCl_3. 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 $Li[N(PPh_2)_2]$ with white phosphorus and must result in Scheme 1 from the reduction of PCl_3, **2** represents an oxidation product of $Li[N(PPh_2)_2]$.[2a,b] Its ^{31}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 $Li[P(PBu^t_2)_2]$ to give $(Pr^i_2)_2P{-}P(PPr^i_2)_2$.[2c] However, the most convenient access to **2** turned out to be the oxidation of $Li[N(PPh_2)_2]$ with iodine which proceeded in quantitative spectroscopic (^{31}P NMR) yields (Scheme 2).† Note that this P–P coupling reaction is particularly useful as **2** would not be accessible by the Staudinger oxidation of $Ph_2P{-}PPh_2$, since $Ph_2P{-}N_3$ as synthon is not available.[3] Only $Ph_3Si{-}N_3$ has been successfully used as an imine source,[4] whereas with $Me_3Si{-}N_3$, splitting of the P–P bond occurs under the reaction conditions required,[5a] although with $Ph_2PCH_2PPh_2$ 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 $K[PPh_2]$ to give a Cu^I complex of $Ph_2P{-}PPh_2$, and the latter ligand can be isolated after treatment with cyanide.[6] For comparison, we reacted anhydrous $CuCl_2$ with 2 equiv. of $Li[N(PPh_2)_2]$ in THF at room temperature. The ^{31}P NMR spectrum of the solution indicated the absence of **2**, even after addition of excess PPh_3 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 $Li[N(PPh_2)_2]$ in the presence of excess MCl_2 (M = Co, Ni, Pd) in refluxing toluene which led, after partial fragmentation and recombination, to spirocyclic complexes of the type $M[Ph_2PNPPh_2NPPh_2]_2$.[7] Seebach *et al.* have previously observed that the coupling of lithiated orthothioformic esters with I_2 proceeds *via* radical intermediates.[8] In phosphorus chemistry, only phospholes appear to have been P–P coupled in a manner similar to ours.[9]



Scheme 1

$$2\,Li[N(PPh_2)_2] + I_2 \xrightarrow[-2\,LiI]{} \mathbf{2}$$

Scheme 2

We then examined the comparative reactivity of $Li[HC(PPh_2)_2]$, which is isolectronic to $Li[N(PPh_2)_2]$. The reaction proceeded in THF according to Scheme 3 and afforded the air-stable ylide **3c**.† Monitoring by ^{31}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_2X spin system and are assigned to **3b**. They disappear at room

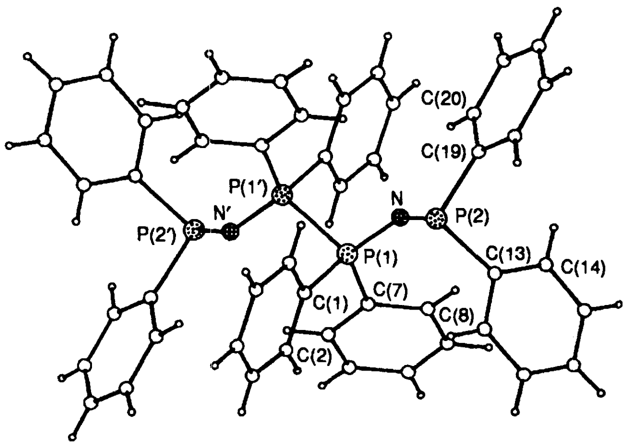
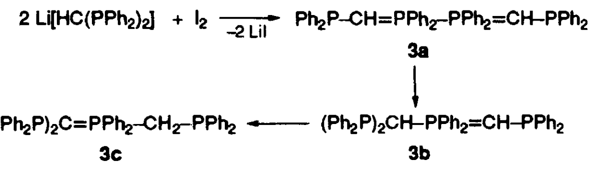
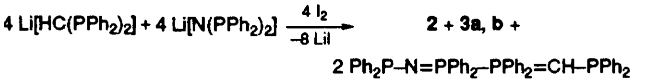


Fig 1 View of the molecular structure of **2** in the crystal. Selected distances (Å) and angles (°): P(1)–P(1′) 2.232(2), P(1)–N 1.558(3), P(2)–N 1.673(2); P(1′)–P(1)–N 108.6(1), P(1)–N–P(2) 130.7(1).



Scheme 3



$$4\ \mathrm{Li[HC(PPh_2)_2]} + 4\ \mathrm{Li[N(PPh_2)_2]} \xrightarrow[-8\ \mathrm{LiI}]{4\ \mathrm{I_2}} \mathbf{2} + \mathbf{3a,b} + 2\ \mathrm{Ph_2P{-}N{=}PPh_2{-}PPh_2{=}CH{-}PPh_2}$$

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.[10] Schmidbaur *et al.* have obtained **3c** in 30% yield in the reaction of $\mathrm{M[Ph_2P{-}CH{=}PPh_2{-}CH_2]}$ with $\mathrm{Ph_2PCl}$.[11] The analogous methyl-substituted compound could also be prepared.[12a] Compounds **3a** and **3c** were recently claimed to result from the oxidation of $\mathrm{(Me_2NCH_2CH_2NMe_2)Li[HC(PPh_2)_2]}$ with $\mathrm{(C_5Me_5)_2TiCl_2}$, although they could not be isolated as pure products.[12b,c]

In a cross-coupling experiment with $\mathrm{Li[N(PPh_2)_2]}$ and $\mathrm{Li[HC(PPh_2)_2]}$, 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 $\mathrm{[HC(PPh_2)_2]^{\cdot}}$ and $\mathrm{[N(PPh_2)_2]^{\cdot}}$, likely to be the first-formed oxidation products of $\mathrm{Li[HC(PPh_2)_2]}$ and $\mathrm{Li[N(PPh_2)_2]}$, 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)hydrazine can be found in the literature.[12c] In addition to the steric and electronic effects of the substituents, the nature of the oxidant strongly determines the structure of the coupling products.[13]

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Footnotes

† All reactions were performed under nitrogen, in carefully dried solvents. $\mathrm{Li[N(PPh_2)_2]}$ and $\mathrm{Li[HC(PPh_2)_2]}$ were generated by reaction of $\mathrm{HN(PPh_2)_2}$ or $\mathrm{CH_2(PPh_2)_2}$, respectively, with $\mathrm{Bu^nLi}$ in THF and used *in situ*.

Synthesis of **2**: To a solution of 23.0 mmol $\mathrm{Li[N(PPh_2)_2]}$ in 120 ml THF was added within *ca.* 1 min 2.92 g $\mathrm{I_2}$ 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. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 25 °C, $\mathrm{SiMe_4}$): δ 7.0–7.9 (m, Ph); ^{31}P NMR (120.5 MHz, $\mathrm{C_6D_6}$, 25 °C, $\mathrm{H_3PO_4}$ ext.): δ 43.5 ($\mathrm{P^{III}}$, m, AA′), 12.0 [$\mathrm{P^{IV}}$, 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 $\mathrm{Li[HC(PPh_2)_2]}$ in 100 ml THF was added 2.65 g (20.90 mmol) $\mathrm{I_2}$ 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 × 50 ml $\mathrm{H_2O}$ allows elimination of LiI. The organic phase was dried over $\mathrm{CaCl_2}$, 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 ^{31}P NMR spectrum around δ +1.0 and −8.5)[12c] as well as dppm (5–10%). Yield **3c**: 5.0 g (62%).[12] ^{13}C NMR (75.5 MHz, $\mathrm{CDCl_3}$, 25 °C, $\mathrm{SiMe_4}$): δ 12.2 [$\mathrm{CP_3}$, ddt, ^1J(P,C) = 74, 45 Hz, ^3J(P,C) = 3 Hz], 24.4 [$\mathrm{CH_2}$, ddt, ^1J(P,C) = 53, 32 Hz, ^3J(P,C) = 6 Hz], 143–126 (Ph, m). **3a**: ^{31}P NMR (120.5 MHz, THF–$\mathrm{C_6D_6}$, 25 °C): δ 21.8 ($\mathrm{P^{IV}}$, m, AA′), −20.7 [$\mathrm{P^{III}}$, m, XX′, N = 150 Hz, J(AA′) ± 110.7, J(XX′) *ca.* 0 Hz, J(AX) ± 131.7, J(AX′) ± 21 Hz]. **3b**: ^{31}P NMR (120.5 MHz, THF/$\mathrm{C_6D_6}$, −30 °C): δ = 26.2 [$\mathrm{P^V}$, dt, ^2J(P,P) = 147, 40 Hz], −12.2 [$\mathrm{P^{III}{}_2C}$, dd, ^2J(P,P) = 40, ^4J(P,P) = 7 Hz], −17.0 [$\mathrm{P^{III}}$, dd, ^2J(P,P) = 147 Hz].

4: A solution containing an equimolar amount of $\mathrm{Li[N(PPh_2)_2]}$ and $\mathrm{Li[HC(PPh_2)_2]}$ in THF was reacted at −40 °C with the corresponding quantity of $\mathrm{I_2}$. Beside the homo-coupling products **2** and **3a,b**, **4** was identified by its ^{31}P NMR spectrum: δ 41.9 [$\mathrm{P^{III}N}$, dd, ^2J(P,P) = 87, ^3J(P,P) = 5 Hz], 20.3 [$\mathrm{P^{IV}C}$, ddd, ^1J(P,P) = 31, ^2J(P,P) = 148, ^3J(P,P) = 5 Hz], 15.1 [$\mathrm{P^{IV}N}$, dd, ^1J(P,P) = 31, ^2J(P,P) = 87 Hz], −22.5 [$\mathrm{P^{III}C}$, d, ^2J(P,P) = 148 Hz].

‡ *Crystal data* for **2** (yellow crystals from toluene): $\mathrm{C_{48}H_{40}N_2P_4}$, M = 768.75, monoclinic, space group $P2_1/c$, a = 9.634(3), b = 11.157(3), c = 19.112(5) Å, β = 93.32(2)°, V = 2051(1) Å^3, Z = 2, $D_{\text{calc.}}$ = 1.245 g cm^{-3}, Nb-filtered Cu-Kα radiation, λ = 1.54178 Å, μ = 19.71 cm^{-1}. Measurements: Siemens AED diffractometer, θ–2θ scan-type, room temp. The structure was solved using direct and Fourier methods. 3882 unique reflections measured with θ 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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