The behaviour of bis(diphenylphosphino)alkanes towards different active centres

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The reactions of bis(diphenylphosphino)alkanes with benzophenone, bis(piperidinocarbonyl)diazene, isatin, and quinoxaline1,4-di-*N*-oxide have been studied and the products characterised by elemental analysis and spectroscopic measurements.

Keywords: bis(diphenylphosphino)alkanes, benzophenone, bis(piperidinocarbonyl)diazene, isatin, quinoxaline 1,4-di-*N*-oxide, condensation, carbene

Benzophenones (diarylmethanones) are important starting materials in the synthesis and preparation of organic compounds such as heat-resistant resins, various drugs, and natural products.[1–7] 1,1′-(Azodicarbonyl)dipiperidine has different pharmacological and biological activities.[8–13] The versatility of isatin (1*H*-indole-2,3-dione) in synthetic organic chemistry is shown in its biological and pharmacological properties and its extensive use in organic synthesis.[14] Moreover, quinoxaline 1,4-di-*N*-oxide is a building block that has a broad range of biological applications.[15] Bis(diphenylphosphino)alkanes have been reported as anticancer agents.[16–20] The useful applications of these starting materials, coupled with our interest in organophosphorus chemistry,[21–25] encouraged us to synthesise new organophosphorus compounds and to identify the preferred site of attack of these compounds. We sought to obtain the target compounds by reacting bis(diphenylphosphino) alkanes **1a**–**c** with some different organic compounds; namely, benzophenone **2**, 1,1′-(azodicarbonyl)dipiperidine (ADDP, **3**), isatin **4a** and **4b**, and quinoxaline 1,4-di-*N*-oxide **5** (Scheme 1).

Results and discussion

Treatment of benzophenone **2** in dry THF at reflux temperature for 5 h with bisphosphine **1b** (molar ratio 1:1) afforded the new bis(diphenylphosphoranyl)ethane derivative **7** in good yield together with the known bisphosphine dioxide product **6b**.[26] The new products were characterised by IR, ^{1}H, ^{13}C, ^{31}P NMR, MS spectrometry and elemental analysis (*cf.* Experimental).

These molecules could have been synthesised through a mechanism involving carbene formation as suggested by Bird and Wong[27] and Markgrf *et al.*,[28] (Scheme 2). The carbene **A** could result from nucleophilic attack of the phosphorus lone pair at carbon or oxygen of the carbonyl group in the benzophenone **2**[27–29] *via* a Wittig reaction to form the final product **7**.

The reactions between bis(diphenylphosphino)alkanes **1a**,**b** and ADDP (**3**) were also investigated. Treatment of one mole of **1a** with 1 equiv. of **3** in toluene at reflux temperature for 1 h gave *N*′-[2,3-bis(diphenylphosphoryl)-1-(piperidin-1-yl)prop-1-en-1-yl]piperidine-1-carbohydrazide (**8**) as the sole, colourless product in 85% yield (Scheme 3).

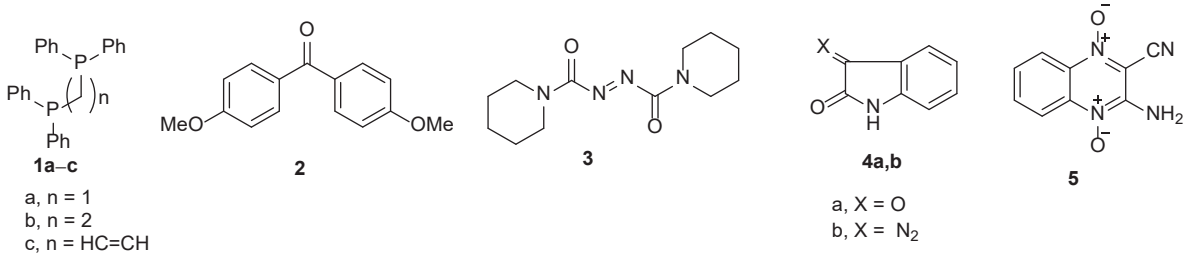
In the same manner, (3-{2-[2,3-bis(diphenylphosphoryl)-1-(piperidin-1-yl)prop-1-en-1-yl]hydrazinyl}-3-(piperidin-1-yl)prop-2-ene-1,2-diyl)bis(diphenylphosphine oxide) **9** was obtained when reaction of **1a** and **3** was carried out in a molar ratio of 2:1 in toluene at reflux temperature for 2 h (Scheme 3). The structures of the new products **8** and **9** were confirmed by IR, ^{1}H, ^{13}C, ^{31}P NMR, MS and elemental analysis (Experimental).

It is worth mentioning that when product **8** was refluxed in toluene for 2 h with **3** in molar ratio 1:1, **9** was formed and purified as the sole product (identified by using m.p., mixed m.p. and IR spectrum of an authentic sample) (Scheme 3).

The formation of products **8** and **9** can be explained in terms of a redox reaction between trivalent phosphorus and **3** to form ethane-1,2-diylbis(diphenylphosphine oxide) and *N*'-(piperidine-1-carbonyl)piperidine-1-carbohydrazide.[30–36] The next step is a condensation between the active methylene of pentavalent phosphorus[26] and the carbonyl group of *N*'-(piperidine-1-carbonyl)piperidine-1-carbohydrazide to give the final products (Scheme 3).

When two moles of **1a** or **1b** and one mole equivalent of **3** in THF were stirred at room temperature for 24 h, a mixture of two known products **6a** or **6b**[26] and 2,5-di(piperidin-1-yl)-1,3,4-oxadiazole **10**[28,29] were formed, isolated and purified (Scheme 4). The structure of compounds **6a**, **6b** and **10** were attested by comparison of their m.p., mixed m.p. and IR spectral data with authentic samples (*cf.* Experimental Section).The mechanism of formation of **10** is presumed to be as was first suggested by Tusondo *et al.*,[29] for reaction between *tert*-butyl phosphine and ADDP. Compound **10** was characterised *via* elemental microanalyses as well as IR, ^{1}H, ^{13}C NMR and mass spectral measurements (*cf.* Experimental).

In addition, when **4a** was refluxed with **1a** or **1b** in dry THF in a molar ratio of 1:1, (3*Z*) -3-(3-oxo-1,3-dihydro-2*H*-indol-2-ylidene) -1,3-dihydro-2*H*-indol-2-one (indirubin, **11**)[37] was separated as pink-coloured crystals in a 75% yield together with



Scheme 1

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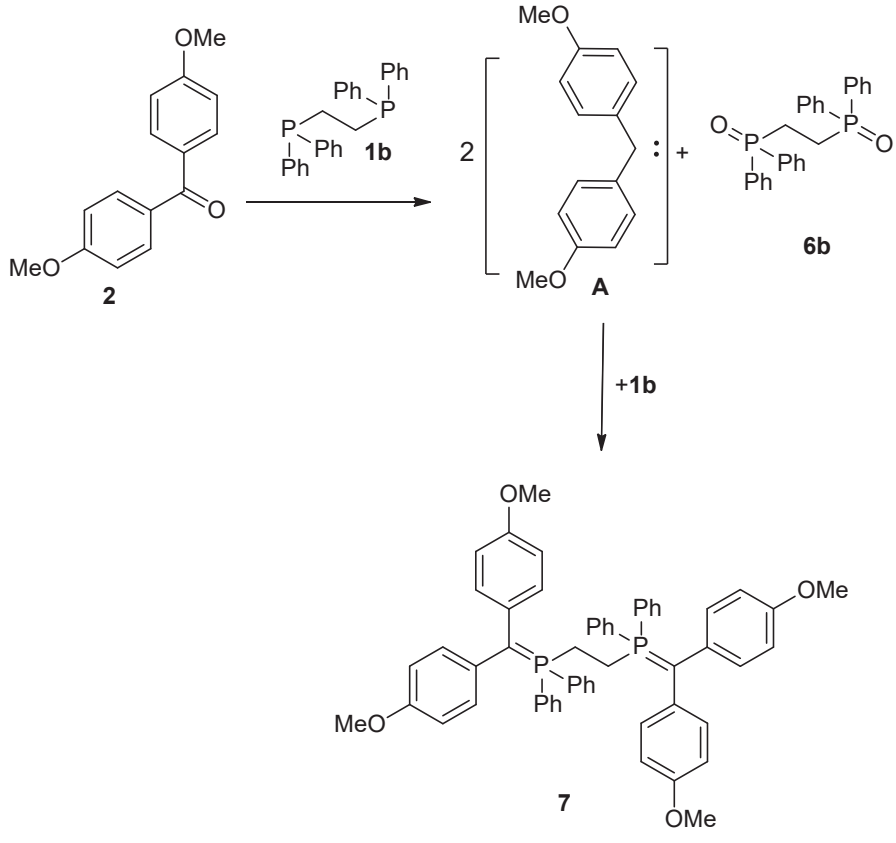
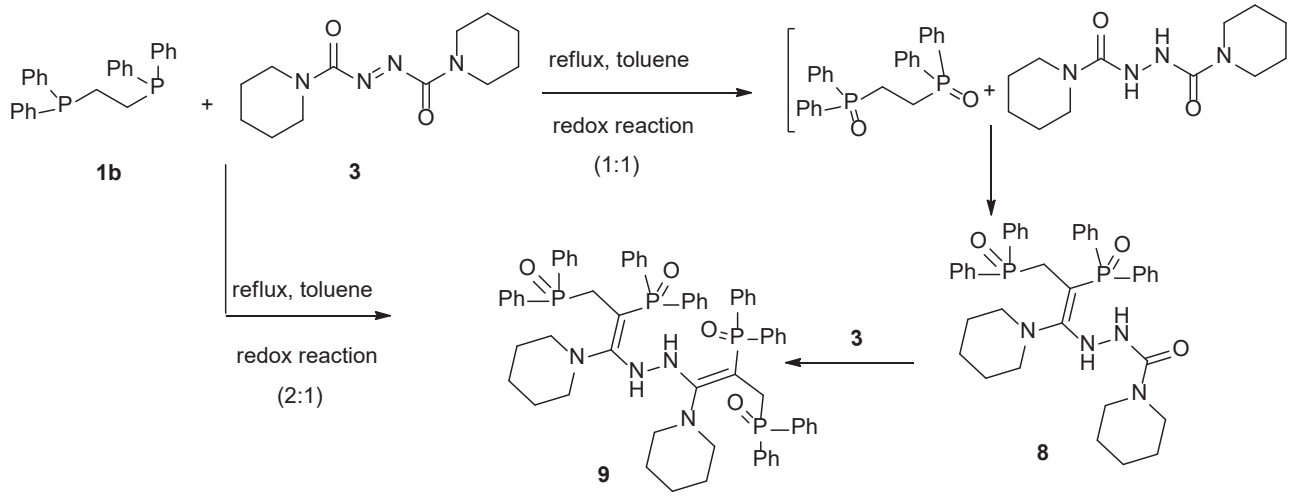
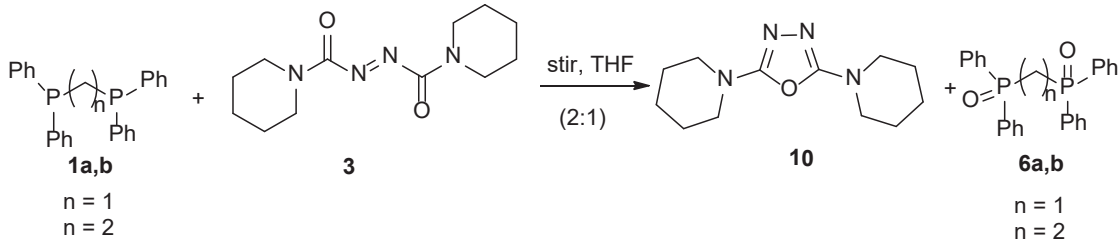


Scheme 2



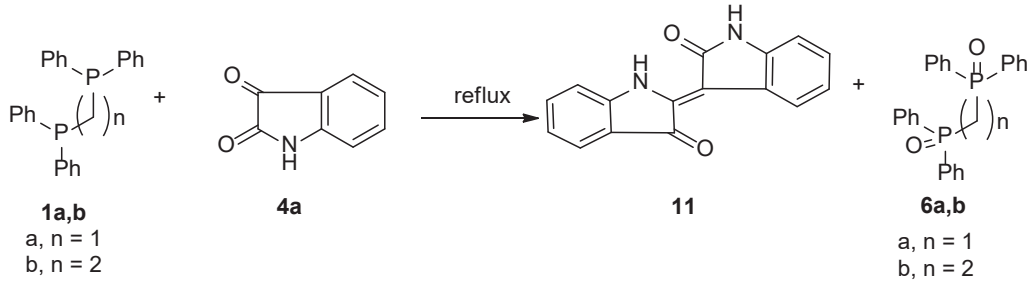
Scheme 3



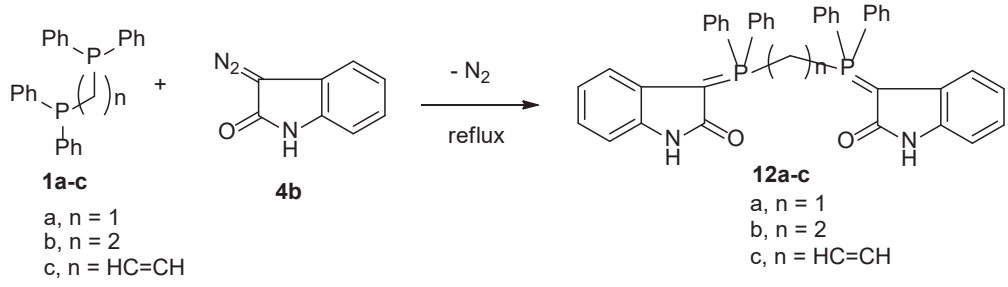
Scheme 4

the known **6a** or **6b**[26] respectively. The mechanism of formation of **11** can be interpreted in terms of formation of a carbene, followed by dimerisation of this carbene and/or a Wittig reaction (Scheme 5). This recalls the mechanism of formation of indirubin *via* reaction of isatin with triphenylphosphine.[37]

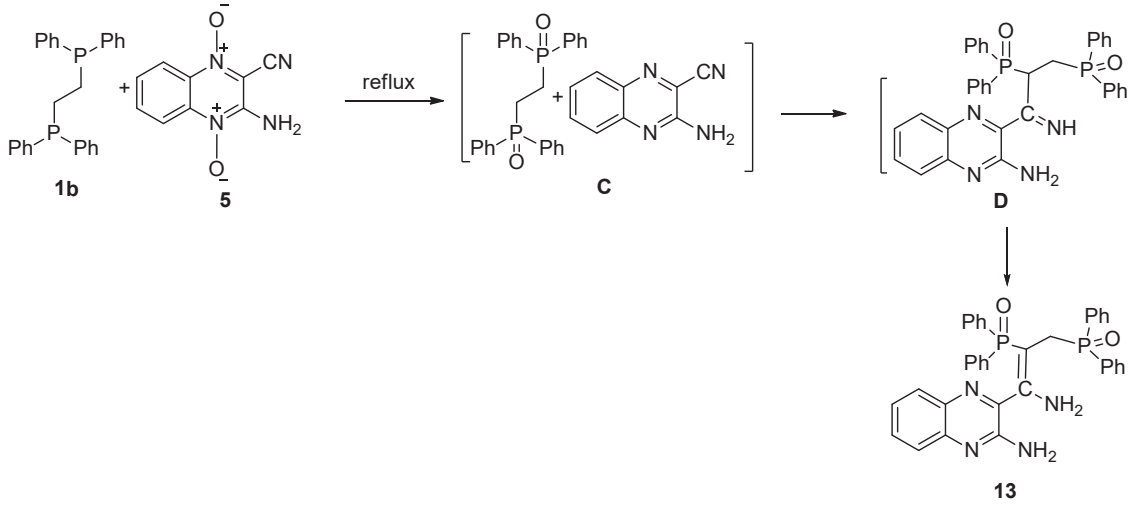
The reaction of **4b** with bisphosphines **1a** and **1b** was investigated to study in comparison the results that we obtained with isatin. When **4b** was refluxed with **1a** or **1b** in molar ratio 2:1; the 3,3'-[methylenebis(diphenylphosphoranylylidene)] bis(indolin-2-one) (**12a**); 3,3'-[ethylenebis(diphenylphospho



Scheme 5



Scheme 6



Scheme 7

ranylylidene)]bis(indolin-2-one) (**12b**); and/or 3,3'-[ethene-1,2-diylbis(diphenylphosphoranylylidene)]bis(indolin-2-one) (**12c**) were obtained (Scheme 6). The structures of the phosphoranylidene derivatives **12a**–**c** were confirmed on the basis of IR, ^{1}H, ^{13}C, ^{31}P NMR, MS and elemental analysis (*cf.* Experimental).

The mechanism of formation of **12a**–**c** can be summarised in terms of initial evolution of dinitrogen from **4b** at reflux temperature, followed by formation of a carbene intermediate and nucleophilic attack of trivalent phosphorus *via* a Wittig reaction mechanism to form the final products **12a**–**c**[27–29,37](Scheme 6).

Finally, this study was extended to investigate the behaviour of 1,2-bis(diphenylphosphino)ethane **1b** towards quinoxaline 1,4-di-*N*-oxide (**5**) (Scheme 7). When **5** reacted with **1b** in dry THF at reflux temperature for 2 h in a molar ratio of 1:1, the deep red crystalline [3-amino-3-(3-aminoquinoxalin-2-yl)prop-2-ene-1,2-diyl]bis(diphenylphosphine oxide) (**13**) was isolated in 85% yield. The structure of the new compound **13** was confirmed by IR, NMR, MS and elemental analysis. (Scheme 7; *cf.* Experimental).

A mechanism for the formation of **13** can be proposed in terms of deoxygenation of **5** through reduction by the trivalent phosphorus compound[38,39] to obtain 3-aminoquinoxaline-2-carbonitrile and **6b**. The active methylene of **6b** could then react with 3-aminoquinoxaline-2-carbonitrile (**C**) to give the final product **13** as shown in Scheme 7 *via* nucleophilic attack of an active methylene group of **6** on the carbonitrile group and the intermediate **D**.

Conclusion

This study reports simple routes for the synthesis of some organophosphorus derivatives using bis(diphenylphosphino) alkanes as a starting organophosphorus materials. Whereas bisphosphine **1b** reacted with benzophenone **2** to give the new bis(diphenylphosphoranyl)ethane derivative **7** and bisphosphine dioxide **6b**, **8** and **9** were obtained from the reaction of **1b** with **3** in molar ratio 1:1 and 2:1, respectively, in refluxing toluene. When two moles of **1a** or **1b** and 1 equiv. of **3** in THF were stirred at room temperature for 24 h, products **6a** and **6b** respectively and **10** resulted. The reaction of bisphosphines **1a** and **1b** with

isatin yields **6a** or **6b** respectively, together with indirubin (**11**). Moreover, **4b** reacts with bisphosphines **1a–c** in refluxing toluene in molar ratio 2:1 to give **12a–c** respectively. On the other hand, when **5** was refluxed with **1b** in molar ratio of 1:1, **13** was produced.

Experimental

All chemicals were supplied by either Fluka or Aldrich chemical companies and were used without further purification. Melting points were determined in open glass capillaries using an Electrothermal IA 9000 series digital melting point apparatus (Electrothermal, Essex, UK) and are uncorrected. The IR spectra were measured in KBr pellets with a Perkin-Elmer Infracord Spectrophotometer model 157(Grating). ^{1}H NMR (500 MHz), ^{13}C{1H} NMR (125 MHz) and ^{31}P{1H} NMR (202.48 MHz) spectra were recorded at room temperature on a JEOL-500 MHz spectrometer as solutions in deuterated chloroform ($CDCl_3$)/ or dimethyl sulfoxide (DMSO). All chemical shifts are quoted in δ relative to the trace resonance of protonated chloroform (δ 7.25 ppm), $CDCl_3$ (δ 77.0 ppm), protonated dimethyl sulfoxide (δ 2.50 ppm), DMSO-d_6 (δ 39.51 ppm) and external 85% aqueous H_3PO_4 (δ 0.0 ppm). Mass spectra (EI) were measured at 70 eV on a Shimada GCS-OP 1000 Ex spectrometer provided with a data system. Elemental analyses were performed using an Elmenter Varu EL Germany instrument. The reported yields are based upon pure materials isolated by column chromatography. Solvents were dried/purified according to conventional procedures.

Synthesis of 1,2-Bis{[bis(4-methoxyphenyl)methylene]diphenylphosphoranyl}ethane (**7**)

Compounds **2** (0.24 g, 1 mmol) and **1b** (0.39 g, 1 mmol) were refluxed in dry THF (30 mL) at ambient temperature for 5 h. The course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on silica gel column to give two products; **7** and the known **6b**.[26]

Ethane-1,2-diylbis(diphenylphosphene)dioxide (**6b**): Eluent: petroleum ether/acetone (50/50, v/v); colourless crystals; yield 25%; m.p. 276–277 °C.[26]

1,2-Bis{[bis(4-methoxyphenyl)methylene]diphenylphosphoranyl}ethane (**7**): Eluent: petroleum ether/acetone (90/10, v/v); colourless crystals; yield 45%, m.p. 185–187 °C; IR ν_{max}/cm^{-1} (KBr): 1630 (P=C), 1437 (P–Ph); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.92–2.99 (ddd, J_{HH} = 6.8 Hz, $^{2}J_{PH}$ = 25.3 Hz, $^{3}J_{PH}$ = 11.0 Hz, 4H, CH_2–CH_2), 3.38 (s, 12H, OCH_3), 7.26–7.74 (m, 36H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.1 (d, J_{PC} = 130.0 Hz, CH_2–CH_2), 50.6 (4 × OCH_3), 67.0 (d, J_{PC} = 130.0 Hz, $^{2}J_{PC}$ = 40.1 Hz, C=P), 128.6 (ArCH), 128.9 (ArC), 130.7 (ArC), 130.8 (ArC), 132.0 (ArC), 134.4 (ArC), 135.8 (ArC), 136.8 (ArC), 159.5 (C–O); ^{31}P NMR ($CDCl_3$): δ 33.24 ppm; MS (FAB+): *m/z* (%) = 850 ([M]$^+$, 10); Anal. calcd for $C_{56}H_{52}O_4P_2$ (850.96): C, 79.04; H, 6.16; P, 7.28; found: C, 79.21; H, 6.20; P, 7.15%.

Reactions of 1,2-Bis(diphenylphosphino)alkanes (**1a** *and* **1b**) *with 1,1'(azodicarbonyl)dipiperidine (ADDP,* **3**)*; general procedure*

- After **1b** (0.39 g, 1 mmol) and **3** (0.25 g, 1 mmol) were refluxed in dry toluene (30 mL) for 1 h the sole product, N'-*(2,3-bis(diphenylphosphoryl)-1-(piperidin-1-yl)prop-1-en-1-yl)piperidine-1-carbohydrazide* (**8**), was separated.
- After **1b** (0.78 g, 2 mmol) and **3** (0.25 g, 1 mmol) were refluxed in dry toluene (30 mL) for 2 h, *(3-{2-[2,3-Bis(diphenyl-phosphoryl)-1-(piperidin-1-yl)prop-1-en-1-yl]hydrazinyl}3-(piperidin-1-yl)-prop-2-ene-1,2-diyl)bis(diphenylphosphine oxide)* (**9**) was separated.
- After **8** (0.66 g, 1 mmol) and **3** (0.25 g, 1 mmol) were refluxed in dry toluene (30 mL) for 2 h, compound **9** was separated.
- After **1a** or **1b** (2 mmol) and **3** (0.25 g, 1 mmol) were stirred in dry THF (30 mL) for 24 h, compounds **10**, **6a** and **6b** were separated respectively.

The course of each reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residues were chromatographed on a silica gel column to give the product.

N'-[2,3-bis(diphenylphosphoryl)-1-(piperidin-1-yl)prop-1-en-1-yl]piperidine-1-carbohydrazide (**8**): Eluent: petroleum ether/ethyl acetate (90/10, v/v); colourless crystals; yield 85%; m.p. 171–172 °C; IR ν_{max}/cm^{-1} (KBr): 3320 (NH), 1640 (C=O), 1635 (P=C), 1437 (P–Ph), 1225 (P=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.57, 1.58, 1.59, 1.70, 2.16, 2.27 (m, 12H, 6 × CH_2 pip.), 2.51, 2.52 (dd, J_{HH} = 6.8 Hz, $^{2}J_{PH}$ = 25.3 Hz, $^{3}J_{PH}$ = 11.0 Hz, 2H, CH_2–P), 3.38 (m, 8H, 4 × CH_2, pip.), 6.51 (d, 2H, 2NH), 7.26–7.70 (m, 20H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.4 (s, 4 × CH_2, Pip.), 25.4 (s, 4 × CH_2, Pip.), 26.1 (d, J_{PC} = 130.0 Hz, CH_2), 44.9 (s, 2 × CH_2, Pip.), 67.1 (d, J_{PC} = 130.0 Hz, $^{2}J_{PC}$ = 40.1 Hz, =C–P), 128.8 (ArC), 128.9 (ArC), 130.7 (ArC), 130.8 (ArC), 132.0 (ArC), 134.4 (ArC), 135.8 (ArC), 136.8 (ArC), 158.1 (C=O), 161.5 (N=C); ^{31}P NMR ($CDCl_3$): δ 33.26, 33.48; MS (EI): *m/z* (%) = 666 ([M]$^+$, 5). Anal. calcd for $C_{38}H_{44}N_4O_3P_2$ (666.73): C, 68.45; H, 6.65; N, 8.40; P, 9.29; found: C, 68.56; H, 6.42; N, 8.55; P, 9.02%.

(3-{2-[2,3-Bis(diphenylphosphoryl)-1-(piperidin-1-yl)prop-1-en-1-yl]hydrazinyl}-3-(piperidin-1-yl)prop-2-ene-1,2-diyl) bis(diphenylphosphine oxide) (**9**): Eluent: petroleum ether/ethyl acetate (80/20, v/v); colourless crystals; yield 35%; m.p. 227–230 °C; IR ν_{max}/cm^{-1} (KBr): 3324 (NH), 1630 (P=C), 1432 (P–Ph), 1223 (P=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88, 0.91, 0.93, 1.25 (m, 12H, 6 × CH_2 pip.), 1.29, 1.34 (dd, J_{HH} = 6.8 Hz, $^{2}J_{PH}$ = 25.3 Hz, $^{3}J_{PH}$ = 11.0 Hz, 4H, 2 × CH_2–P), 2.23, 2.52 (m, 8H, 4 × CH_2, pip.), 4.38 (d, 2H, 2 × NH), 7.25–7.69 (m, 40H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.3 (s, 4 × CH_2, Pip.), 25.2 (s, 4 × CH_2, Pip.), 26.2, 26.4 (d, J_{PC} = 130.0 Hz, 2 × CH_2), 45.5 (s, 2 × CH_2, Pip.), 80.0 (d, J_{PC} = 130.0 Hz, $^{2}J_{PC}$ = 40.1 Hz, =C–P), 126.8 (ArC), 126.9 (ArC), 128.7 (ArC), 130.8 (ArC), 132.0 (ArC), 134.4 (ArC), 135.8 (ArC), 136.8 (ArC), 171.5 (N=C); ^{31}P NMR ($CDCl_3$): δ 33.13; MS (FAB$^+$): *m/z* (%) = 1078 ([M]$^+$, 5). Anal. calcd for $C_{64}H_{66}N_4O_4P_4$ (1079.13): C, 71.23; H, 6.16; N, 5.19; P, 11.48; found: C, 71.42; H, 6.20; N, 5.32; P, 11.23%.

2,5-Di(piperidin-1-yl)-1,3,4-oxadiazole (**10**): Eluent: petroleum ether/ethyl acetate (80/20, v/v); colourless crystals; yield 65%; m.p. 75–76 °C (lit. 75 °C).[28,29] ^{1}H NMR (500 MHz, δ ppm, CDCl3): 1.62 (m, 12H, CH_2-pip.), 3.30 (m, 8H, CH_2-pip.), MS (EI): *m/z* (%) = 236 ([M]$^+$, 80).

Reaction of 1,2-Bis(diphenylphosphino)alkane (**1a** *or* **1b**) *with Isatin* (**4a**)

Isatin (**4a**) (0.29 g, 2 mmol) and (**1a** or **1b**) were refluxed in dry THF (30 mL) for 2 h. The course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on a silica gel column to give the products Indirubin, **11**[37] and **6a** or **6b**[26] respectively.

*(3Z)-3-(3-oxo-1,3-dihydro-2*H*-indol-2-ylidene)-1,3-dihydro-2*H*-indol-2-one* (*Indirubin*, **11**): Eluent: petroleum ether/ethyl acetate (80/20, v/v); pink crystals; yield 75%.[37] M.p. 350 °C (lit.[28,29] m.p 350 °C). ^{1}H NMR (500 MHz, DMSO): δ = 6.87–7.01 (m, 8H, H arom.), 9.01, 10.08 (2s, 2 NH exchangeable with D_2O) ppm. MS (EI): *m/z* (%) = 262 (75) [M]$^+$.

Reaction of 1,2-Bis(diphenylphosphino)alkane (**1a–c**) *with Diazoisatin* (**4b**)*; general procedure*

Diazoisatin (**4b**) (0.31 g, 2 mmol) and **1a–c** (1 mmol) were refluxed in dry THF (30 mL) for 1–4 h. The course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on a silica gel column to give the products **12a–c** respectively.

3,3'-[Methylenebis(diphenylphosphoranylylidene)]bis(indolin-2-one) (**12a**): Eluent: petroleum ether/ethyl acetate (80/20, v/v); yellow crystals; yield 65%; m.p. 185–187 °C; IR ν_{max}/cm^{-1} (KBr): 1655 (amide C=O), 1632 (P=C), 1437 (P–Ph); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.16 (t, J_{HH} = 11.9 Hz, $^{2}J_{PH}$ = 24.9 Hz, $^{3}J_{PH}$ = 11.0 Hz, 2H, CH_2), 6.78–7.24 (m, 28H, ArH), 8.56 (s, 2H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 29.5 (t, J_{PC} = 135.6 Hz, CH_2), 67.5 (d, J_{PC} = 130.0 Hz, $^{2}J_{PC}$ = 40.1 Hz, C=P), 95.2 (d, J_{PC} = 130.0 Hz, P–C), 113.1 (ArCH), 121.9 (ArC), 125.7 (ArC), 127.8 (ArC), 128.0 (ArC), 131.4 (ArC), 132.8 (ArC), 140.8 (ArC), 171.5 (C=O); ^{31}P NMR ($CDCl_3$): δ 31.14; MS (EI): *m/z* (%) = 646 ([M]$^+$, 25); Anal. calcd for $C_{41}H_{32}N_2O_2P_2$ (646.65): C, 76.15; H, 4.99; N, 4.33; P, 9.58; found: C, 76.02; H, 5.05; N, 4.22; P, 9.75%.

3,3'-[Ethane-1,2-diylbis(diphenylphosphoranylylidene)] bis(indolin-2-one) (**12b**): Eluent: petroleum ether/ethyl acetate (85/15, v/v); brown crystals; yield 75%; m.p. 127–128 °C; IR ν_{max}/cm^{-1} (KBr): 1654 (amide C=O), 1640 (P=C), 1432 (P–Ph); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.71–1.81 (m, J_{HH} = 11.9 Hz, $^2J_{PH}$ = 25.2 Hz, $^3J_{PH}$ = 11.0 Hz, 4H, CH_2–CH_2), 6.73–7.24 (m, 28H, ArH), 8.76 (s, 2H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 53.3 (d, J_{PC} = 135.6 Hz, CH_2–CH_2), 77.5 (d, J_{PC} = 130.0 Hz, $^2J_{PC}$ = 40.1 Hz, C=P), 101.2 (d, J_{PC} = 130.0 Hz, P–C), 112.1 (ArCH), 122.9 (ArC), 126.7 (ArC), 128.8 (ArC), 129.0 (ArC), 132.4 (ArC), 133.8 (ArC), 141.8 (ArC), 172.5 (C=O); ^{31}P NMR ($CDCl_3$): δ 19.72; MS (EI): *m/z* (%) = 660 ([M]$^+$, 5); Anal. calcd for $C_{42}H_{34}N_2O_2P_2$ (660.68): C, 76.35; H, 5.19; N, 4.24; P, 9.38; found: C, 76.05; H, 5.42; N, 4.34; P, 9.53%.

3,3'-[Ethene-1,2-diylbis(diphenylphosphoranylylidene)] bis(indolin-2-one) (**12c**): Eluent: petroleum ether/ethyl acetate (85/15, v/v); yellow crystals; yield 75%; m.p. 159–161 °C; IR ν_{max}/cm^{-1} (KBr): 1654 (amide C=O), 1645 (P=C), 1435 (P–Ph); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.90 (s, 2H, NH), 6.68–7.67 (m, 28H, ArH), 6.91 (2 × dt, J_{HH} = 10.8, 6.5 Hz, $^2J_{PH}$ = 25.2 Hz, $^3J_{PH}$ = 11.0 Hz, 2H, CH=CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 87.5 (d, J_{PC} = 130.0 Hz, $^2J_{PC}$ = 40.1 Hz, C=P), 103.2 (d, J_{PC} = 130.0 Hz, P–C), 111.1 (ArCH), 121.2 (ArC), 122.5 (ArC), 125.2 (ArC), 128.5 (ArC), 131.6 (ArC), 133.8 (ArC), 140.5 (ArC), 153.3 (d, J_{PC} = 135.6 Hz, CH=CH), 170.5 (C=O); ^{31}P NMR ($CDCl_3$): δ 22.82; MS (EI): *m/z* (%) = 658 ([M]$^+$, 15); Anal. calcd for $C_{42}H_{32}N_2O_2P_2$ (658.66): C, 76.59; H, 4.90; N, 4.25; P, 9.41; found: C, 76.60; H, 4.95; N, 4.03; P, 9.35%.

Reaction of 1,2-Bis(diphenylphosphino)alkanes (**1a** *and* **1b**) *with quinoxaline 1,4-di-N-oxide* (**5**)

Compound **5** (0.29 g, 1 mmol) and **1b** (0.39 g, 1 mmol) were refluxed in dry THF (30 mL) for 2 h. The course of the reaction was monitored by TLC. The volatile materials were evaporated under reduced pressure. The residue was chromatographed on a silica gel column to afford **13**.

[3-Amino-3-(3-aminoquinoxalin-2-yl)prop-2-ene-1,2-diyl] bis(diphenylphosphine oxide) (**13**): Eluent: petroleum ether/ethyl acetate (85/15, v/v); deep red crystals; yield 85%; m.p. 206–208 °C; IR ν_{max}/cm^{-1} (KBr): 3420 (NH_2), 1615 (C=C), 1549 (C=N), 1435 (P–Ph), 1230 (P=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.75 (s, 2H, NH_2), 2.26 (d, J_{HH} = 11.9 Hz, $^2J_{PH}$ = 25.1 Hz, $^3J_{PH}$ = 11.0 Hz, 2H, CH_2), 7.01–7.68 (m, *J* = 7.4, 1.7 Hz, 24H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.5 (d, J_{PC} = 130.0 Hz, $^2J_{PC}$ = 40.1 Hz, CH_2), 105.5, 159.2 (C=C), 134.1, 15.1 (cyclic C=N), 126.1 (ArCH), 127.2 (ArC), 128.5 (ArC), 128.2 (ArC), 129.5 (ArC), 131.6 (ArC), 132.8 (ArC), 141.5 (ArC); ^{31}P NMR($CDCl_3$): δ 32.82, 31.11; MS (EI): *m/z* (%) = 600 ([M]$^+$, 15). Anal. calcd for $C_{35}H_{30}N_4O_2P_2$ (600.59): C, 69.99; H, 5.03; N, 9.33; P, 10.31; found: C, 70.10; H, 5.15; N, 9.20; P, 10.25%.

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