

# Regiospecific synthesis of 2,3-naphthylenebis(diphenylphosphines) by double insertion of alkynylphosphines into nickel(0)–benzyne complexes

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The double insertion of diphenylprop-1-ynylphosphine into the nickel(0)–benzyne bond of the complexes  $[\text{Ni}(1,2-\eta\text{-}4,5\text{-X}_2\text{C}_6\text{H}_2)(\text{PEt}_3)_2]$  ( $\text{X} = \text{H}, \text{F}$ ) forms 2,3-naphthylenebis(diphenylphosphines) regiospecifically.

Small cycloalkynes or arynes, which are short-lived in the free state, are stabilised by coordination to  $d^{10}$  transition metal fragments such as  $\text{ML}_2$  ( $\text{M} = \text{Ni}, \text{L}_2 = \text{dcpe}, \ddagger 2\text{PEt}_3; \text{M} = \text{Pt}, \text{L}_2 = \text{dcpe}, 2\text{PPh}_3$ ).<sup>1</sup> Unsymmetrical acetylenes ( $\text{RC}\equiv\text{CR}'$ ) undergo double insertion into nickel(0)–benzyne complexes of type **1** to give a mixture of isomeric naphthalenes (**2a**, **2b**), whose ratio is determined by the stereoelectronic properties of the inserted alkyne (Scheme 1).<sup>2,3</sup>

Recently we have been interested in extending this chemistry to alkynylphosphines, which could provide a novel route to functionalised naphthylenebis(tertiary phosphines), potential ligands that are not readily accessible by conventional syntheses.<sup>4</sup> Herein, we report the regiospecific reaction of diphenylprop-1-ynylphosphine<sup>5</sup> with the  $\text{Ni}^0$ –aryne complexes  $[\text{Ni}(1,2-\eta\text{-}4,5\text{-X}_2\text{C}_6\text{H}_2)(\text{PEt}_3)_2]$  ( $\text{X} = \text{H}$  **1a**,  $\text{F}$  **1b**) (Scheme 2).

Reduction of the appropriate (2-bromoaryl)nickel(II) complexes  $[\text{NiBr}(2\text{-Br-}4,5\text{-X}_2\text{C}_6\text{H}_2)(\text{PEt}_3)_2]$  ( $\text{X} = \text{H}, \text{F}$ ) with lithium in diethyl ether at  $-40^\circ\text{C}$ , followed by evaporation of

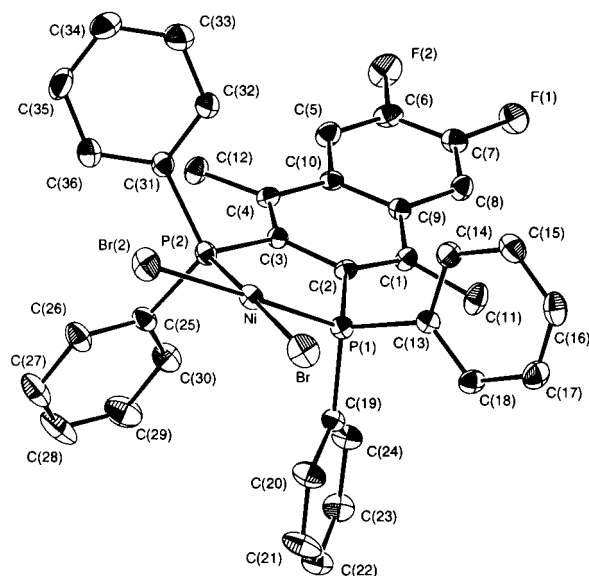
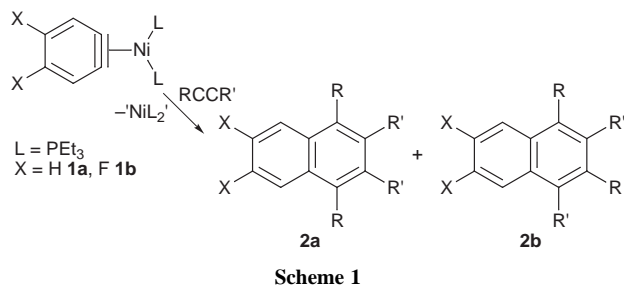
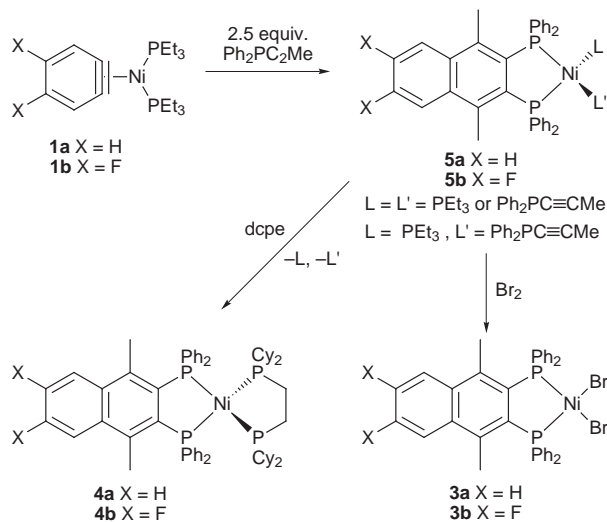


Fig. 1 ORTEP (25% probability) representation of **3b**. Hydrogen atoms have been omitted for clarity.



Scheme 1



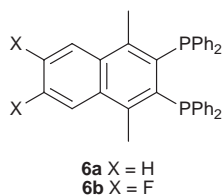
Scheme 2

ether and extraction with hexane at  $-60^\circ\text{C}$ , yielded yellow solutions of the complexes **1a** and **1b** that were used *in situ* for all subsequent insertion reactions.<sup>2,3</sup> The addition of 2.5 equiv. of diphenylprop-1-ynylphosphine at  $-78^\circ\text{C}$ , followed by warming to room temperature, resulted in a dark red solution containing a complex mixture as shown by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. However, by addition of bromine, orange nickel(II) complexes of type **3** were isolated and fully characterised.<sup>§¶</sup> The high overall yields of **3a** and **3b** (up to 97%), together with the molecular structure determination of the chelate, planar-coordinated dibromonickel(II) complex  $[\text{NiBr}_2\{\text{C}_{12}\text{H}_8\text{F}_2(\text{PPh}_2)\}]$  **3b** (Fig. 1), confirmed that the reaction produced regiospecifically 2,3-naphthylenebis(diphenylphosphines) as the only observable insertion products.<sup>||</sup>

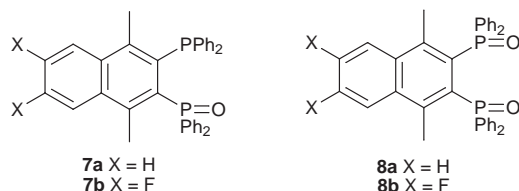
Treatment of the initial dark red solutions with 1 equiv. of dcpe greatly simplified the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, which showed in each case the presence of a single  $\text{Ni}^0$  complex,  $[\text{Ni}\{\text{C}_{12}\text{H}_8\text{X}_2(\text{PPh}_2)_2\}\text{dcpe}]$  ( $\text{X} = \text{H}$  **4a**,  $\text{F}$  **4b**), together with free  $\text{PEt}_3$  and  $\text{Ph}_2\text{PC}\equiv\text{CMe}$ . On the basis of these results, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (202.4 MHz) of the dark red solution could be assigned to a mixture of unsymmetrical nickel(0)–tertiary phosphine complexes of type **5**, all containing the newly formed naphthylenebis(diphenylphosphine) with a combination of  $\text{PEt}_3$  or  $\text{Ph}_2\text{PC}\equiv\text{CMe}$  as ancillary ligands (Scheme 2).

Reaction of **3a** or **3b** over 24 h at  $50^\circ\text{C}$  with a large excess of  $\text{NaCN}$  in  $\text{Me}_2\text{SO}$  liberated quantitatively the pure 2,3-naphthylenebis(diphenylphosphines) **6a** and **6b** as white solids {overall yields based on  $[\text{Ni}(\text{cod})_2]$  of up to 78%}.<sup>§¶</sup>

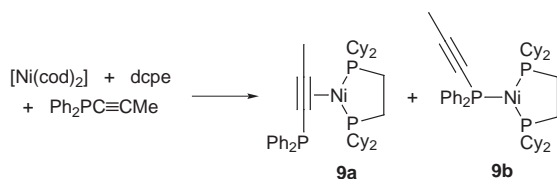
Exposure of **5a** or **5b** to air led to nickel–phosphine bond cleavage and only partial oxidation of the naphthylenebis(diphenylphosphines), forming the mono(phosphine oxides)  $\text{C}_{12}\text{H}_8\text{X}_2(\text{PPh}_2)\{\text{P}(\text{O})\text{Ph}_2\}$  **7a** and **7b**,<sup>6</sup> the structure of **7b** being



confirmed by X-ray diffraction. The stronger oxidising agent,  $\text{H}_2\text{O}_2$ , was necessary to accomplish complete oxidation to the bis(phosphine oxides),  $\text{C}_{12}\text{H}_8\text{X}_2\{\text{P}(\text{O})\text{Ph}_2\}_2$  **8a** and **8b**.



Theoretical calculations<sup>7</sup> suggest that the  $\text{PPh}_2$  moiety, like  $\text{CO}_2\text{Me}$ , is electron withdrawing. The regioselectivities described above are indeed similar to those observed in the insertion of methyl 2-butynoate,  $\text{MeC}\equiv\text{CCO}_2\text{Me}$ , into complex **1b**, where the direction of insertion was believed to be electronically controlled and to require  $\pi$ -coordination of the alkyne.<sup>1–3</sup> In agreement, preferential side bonding of the  $\text{C}\equiv\text{C}$  bond of  $\text{Ph}_2\text{PC}\equiv\text{CMe}$  to the Ni centre, as opposed to coordination *via* the phosphorus lone pair, has been observed. The reaction between equimolar quantities of  $[\text{Ni}(\text{cod})_2]$ , dcpe and  $\text{Ph}_2\text{PC}\equiv\text{CMe}$  gave the  $\text{Ni}^0$ - $\eta^2$ -alkyne species,  $[\text{Ni}(\eta^2\text{-Ph}_2\text{PC}\equiv\text{CMe})(\text{dcpe})]$  **9a**, as the main product; a small amount of the P-bonded isomer **9b**, was also formed (Scheme 3).



Scheme 3

This chemistry is currently being investigated as a potential method for the synthesis of water-soluble diphosphines. We thank the Royal Society for the award of a Fellowship to C. J. C.

## Notes and References

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‡ dcpe = bis(dicyclohexylphosphino)ethane,  $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2$

§ Supplementary data describing full experimental details are available. (See <http://www.rsc.org/suppdata/cc/1998/1307>)

¶ Selected NMR data for compounds **3**, **4**, **6–9**: **3a**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 80.96 MHz)  $\delta$  65.5 (s). **3b**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 80.96 MHz)  $\delta$  65.8 (s);  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 188.1 MHz)  $\delta$  -132.6 [app. t,  $J(\text{HF})$  9.4 Hz]. **4a**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 80.96 MHz)  $\delta$  47.2 [t,  $^2J(\text{PP})$  26.6 Hz], 52.1 [t,  $^2J(\text{PP})$  26.6 Hz]; **4b**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 80.96 MHz)  $\delta$  47.4 [t,  $^2J(\text{PP})$  27.4 Hz], 52.3 [t,  $^2J(\text{PP})$  27.4 Hz];  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ , 188.1 MHz)  $\delta$  -139.6 [app. t,  $J(\text{HF})$  10.2 Hz]. **6a**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 80.96 MHz)  $\delta$  -6.2 (s). **6b**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 80.96 MHz)  $\delta$  -5.6 (s);  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ , 188.1 MHz)  $\delta$  -138.5 [app. t,  $J(\text{HF})$  10.3 Hz]. **7a**:  $^{31}\text{P}\{^1\text{H}\}$  NMR [ $(\text{CD}_3)_2\text{CO}$ , 80.96 MHz]  $\delta$  -6.6 [d,  $^3J(\text{PP})$  37.4 Hz], 31.0 [t,  $^3J(\text{PP})$  37.4 Hz]. **7b**:  $^{31}\text{P}\{^1\text{H}\}$  NMR [ $(\text{CD}_3)_2\text{CO}$ , 80.96 MHz]  $\delta$  -6.3 [d,  $^3J(\text{PP})$  36.7 Hz], 31.0 [t,  $^3J(\text{PP})$  36.7 Hz];  $^{19}\text{F}$  NMR [ $(\text{CD}_3)_2\text{CO}$ , 188.1 MHz]  $\delta$  -135.3 (m), -136.0 (m). **8a**:  $^{31}\text{P}\{^1\text{H}\}$  NMR [ $(\text{CD}_3)_2\text{CO}$ , 80.96 MHz]  $\delta$  34.3 (br s); **8b**:  $^{31}\text{P}\{^1\text{H}\}$  NMR [ $(\text{CD}_3)_2\text{CO}$ , 80.96 MHz]  $\delta$  33.4 (br s);  $^{19}\text{F}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ] 188.1 MHz]  $\delta$  -133.9 (br). **9a**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 80.96 MHz)  $\delta$  -15.3 [dd,  $^3J(\text{PP})$  24.0,  $^3J(\text{PP})$  37.0 Hz], 67.7 [dd,  $^2J(\text{PP})$  46.4,  $^3J(\text{PP})$  24.0 Hz], 72.9 [dd,  $^2J(\text{PP})$  46.4,  $^3J(\text{PP})$  37.0 Hz].

|| Crystal data and data collection parameters: **3b**:  $\text{C}_{36}\text{H}_{28}\text{Br}_2\text{F}_2\text{NiP}_2$ ,  $M = 779.07$ , red-brown rod, crystal size  $0.42 \times 0.14 \times 0.12$  mm, monoclinic, space group  $P2_1/c$  (no. 14),  $a = 8.633(2)$ ,  $b = 22.707(3)$ ,  $c = 16.237(3)$  Å,  $\beta = 97.49(2)^\circ$ ,  $U = 3155.8(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.640$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 32.94$  cm<sup>-1</sup>,  $F(000) = 1560$ , analytical absorption correction; 7474 unique data ( $2\theta_{\text{max}} = 55.1^\circ$ ), 4594 with  $I > 2\sigma(I)$ ;  $R = 0.046$ ,  $wR = 0.036$ , GOF = 1.40.

**7b**:  $\text{C}_{36}\text{H}_{28}\text{F}_2\text{OP}_2$ ,  $M = 576.56$ , colourless plates, crystal size  $0.44 \times 0.19 \times 0.06$  mm, monoclinic, space group  $Cc$  (no. 9),  $a = 9.541(3)$ ,  $b = 28.86(1)$ ,  $c = 11.187(4)$  Å,  $\beta = 106.87(3)^\circ$ ,  $U = 2948(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.229$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 1.88$  cm<sup>-1</sup>,  $F(000) = 1200$ , analytical absorption correction; 2667 unique data ( $2\theta_{\text{max}} = 50.1^\circ$ ), 1415 with  $I > 3\sigma(I)$ ;  $R = 0.043$ ,  $wR = 0.035$ , GOF = 1.33. CCDC 182/847.

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Received in Cambridge, UK, 24th March 1998; 8/02291G