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 [Ni(1,2- η -4,5-X₂C₆H₂)(PEt₃)₂] (X = H, F) forms 2,3naphthylenebis(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 ML₂ (M = Ni, L₂ = dcpe, ‡ 2PEt₃; M = Pt, L₂ = dcpe, 2PPh₃).¹ Unsymmetrical acetylenes (RC=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).^{2,3}

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.⁴ Herein, we report the regiospecific reaction of diphenylprop-1-ynylphosphine⁵ with the Ni⁰-aryne complexes [Ni(1,2- η -4,5-X₂C₆H₂)(PEt₃)₂] (X = H **1a**, F **1b**) (Scheme 2).

Reduction of the appropriate (2-bromoaryl)nickel(II) complexes [NiBr(2-Br-4,5-X₂C₆H₂)(PEt₃)₂] (X = H, F) with lithium in diethyl ether at -40 °C, followed by evaporation of



Scheme 2



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

ether and extraction with hexane at -60 °C, yielded yellow solutions of the complexes 1a and 1b that were used in situ for all subsequent insertion reactions.^{2,3} The addition of 2.5 equiv. of diphenylprop-1-ynylphosphine at -78 °C, followed by warming to room temperature, resulted in a dark red solution containing a complex mixture as shown by ³¹P{¹H} NMR spectroscopy. However, by addition of bromine, orange nickel(II) complexes of type 3 were isolated and fully characterised.§¶ 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 $[NiBr_{2}{C_{12}H_{8}F_{2}(PPh_{2})}]$ **3b** (Fig. 1), confirmed that the reaction produced regiospecifically 2,3-naphthylenebis(diphenylphosphines) as the only observable insertion products.

Treatment of the initial dark red solutions with 1 equiv. of dcpe greatly simplified the ${}^{31}P{}^{1}H{NMR}$ spectra, which showed in each case the presence of a single Ni⁰ complex, [Ni{C₁₂H₈X₂(PPh₂)₂}dcpe)] (X = H **4a**, F **4b**), together with free PEt₃ and Ph₂PC=CMe. On the basis of these results, the ${}^{31}P{}^{1}H{NMR}$ 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 PEt₃ or Ph₂PC=CMe as ancillary ligands (Scheme 2).

Reaction of **3a** or **3b** over 24 h at 50 °C with a large excess of NaCN in Me₂SO liberated quantitatively the pure 2,3-naphthylenebis(diphenylphosphines) **6a** and **6b** as white solids {overall yields based on [Ni(cod)₂] of up to 78%}.§¶

Exposure of **5a** or **5b** to air led to nickel–phosphine bond cleavage and only partial oxidation of the naphthylenebis(diphenyl)phosphines, forming the mono(phosphine oxides) $C_{12}H_8X_2(PPh_2)\{P(O)Ph_2\}$ **7a** and **7b**,⁶ the structure of **7b** being

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confirmed by X-ray diffraction.|| The stronger oxidising agent, H_2O_2 , was necessary to accomplish complete oxidation to the bis(phosphine oxides), $C_{12}H_8X_2\{P(O)Ph_2\}_2$ **8a** and **8b**.



Theoretical calculations⁷ suggest that the PPh₂ moiety, like CO₂Me, is electron withdrawing. The regiospecificities described above are indeed similar to those observed in the insertion of methyl 2-butynoate, MeC=CCO₂Me, into complex **1b**, where the direction of insertion was believed to be electronically controlled and to require π -coordination of the alkyne.^{1–3} In agreement, preferential side bonding of the C=C bond of Ph₂PC=CMe to the Ni centre, as opposed to coordination *via* the phosphorus lone pair, has been observed. The reaction between equimolar quantities of [Ni(cod)₂], dcpe and Ph₂PC=CMe (ot per Ni⁰-η²-alkyne species, [Ni(η²-Ph₂PC=CMe)(dcpe)] **9a**, as the main product; a small amount of the P-bonded isomer **9b**, was also formed (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

- † E-mail: bennett@rsc.anu.edu.au
- \ddagger dcpe = bis(dicyclohexylphosphino)ethane, Cy₂PCH₂CH₂PCy₂
- § 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**: **3**a: ³¹P{¹H} NMR (CDCl₃, 80.96 MHz) δ 65.5 (s). **3b**: ³¹P{¹H} NMR (CDCl₃, 80.96 MHz) δ 65.8 (s); ¹⁹F NMR (CDCl₃, 188.1 MHz) δ –132.6 [app. t, J(HF) 9.4 Hz]. **4a**: ³¹P{¹H} NMR (C₆D₆, 80.96 MHz) δ 47.2 [t, ²/(PP) 26.6 Hz], 52.1 [t, ²/(PP) 26.6 Hz], **4b**: ³¹P{¹H} NMR (C₆D₆, 80.96 MHz) δ 47.4 [t, ²/(PP) 27.4 Hz], 52.3 [t, ²/(PP) 27.4 Hz]; ¹⁹F NMR (C₆D₆, 80.96 MHz) δ 47.4 [t, ²/(PP) 27.4 Hz], 52.3 [t, ²/(PP) 27.4 Hz]; ¹⁹F NMR (C₆D₆, 80.96 MHz) δ –139.6 [app. t, J(HF) 10.2 Hz]. **6a**: ³¹P{¹H} NMR (C₆D₆, 80.96 MHz) δ –6.2 (s). **6b**: ³¹P{¹H} NMR (C₆D₆, 80.96 MHz) δ –6.2 (s). **6b**: ³¹P{¹H} NMR (C₆D₆, 80.96 MHz] δ –6.3 [d, ³/(PP) 37.4 Hz], 31.0 [t, ³/(PP) 36.7 Hz], 31.0 [t, ³/(PP) 36.7 Hz], 31.0 [t, ³/(PP) 36.7 Hz], 19F NMR [(CD₃)₂CO, 80.96 MHz] δ –133.5 (m), –136.0 (m). **8a**: ³¹P{¹H} NMR [(CD₃)₂CO, 80.96 MHz] δ 34.3 (br s); **8b**: ³¹P{¹H} NMR [(CD₃)₂CO, 80.96 MHz] δ 34.3 (br s); **8b**: ³¹P{¹H} NMR [(CD₃)₂CO, 80.96 MHz] δ 33.4 (br s); ¹⁹F NMR [(CD₃)₂CO] 188.1 MHz] δ –133.9 (br). **9a**: ³¹P{¹H} NMR [(CD₆, 80.96 MHz] δ 34.3 (br s); **8b**: ³¹P{¹H} NMR [(CD₃)₂CO, 80.96 MHz] δ 34.3 (br s); **8b**: ³¹P{¹H} NMR [(CD₃)₂CO, 80.96 MHz] δ 34.3 (br s); **8b**: ³¹P{¹H} NMR [(CD₃)₂CO, 80.96 MHz] δ 34.3 (br s); **8b**: ³¹P{¹H} NMR [(CD₃)₂CO, 80.96 MHz] δ 34.4 (br s); ¹⁹F NMR [(CD₃)₂CO] 188.1 MHz] δ –133.9 (br). **9a**: ³¹P{¹H} NMR (C₆D₆, 80.96 MHz) δ –15.3 [dd, ³/(PP) 24.0, ³/(PP) 37.0 Hz], ⁵⁷O Hz], ⁵⁷O Hz], ^{67,7} [dd, ²/(PP) 46.4, ³/(PP) 24.0 Hz], 72.9 [dd, ²/(PP) 46.4, ³/(PP) 37.0 Hz].

|| *Crystal data and data collection parameters*: **3b**: C₃₆H₂₈Br₂F₂NiP₂, *M* = 779.07, red–brown rod, crystal size $0.42 \times 0.14 \times 0.12$ mm, monoclinic, space group *P*2₁/*c* (no. 14), *a* = 8.633(2), *b* = 22.707(3), *c* = 16.237(3) Å, β = 97.49(2)°, *U* = 3155.8(9) Å³, *Z* = 4, *D_c* = 1.640 g cm⁻³, μ (Mo-K α) = 32.94 cm⁻¹, *F*(000) = 1560, analytical absorption correction; 7474 unique data (2 θ_{max} = 55.1°), 4594 with *I* > 2 σ (*I*); *R* = 0.046, *wR* = 0.036, GOF = 1.40.

7b: $C_{36}H_{28}F_2OP_2$, 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) Å³, Z = 4, $D_c = 1.229$ g cm⁻³, μ (Mo-K α) = 1.88 cm⁻¹, *F*(000) = 1200, analytical absorption correction; 2667 unique data ($2\theta_{max} = 50.1^\circ$), 1415 with $I > 3\sigma(I)$; R = 0.043, wR = 0.035, GOF = 1.33. CCDC 182/847.

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