A simple procedure for the separation of the catalytically important phosphabicyclononane isomers

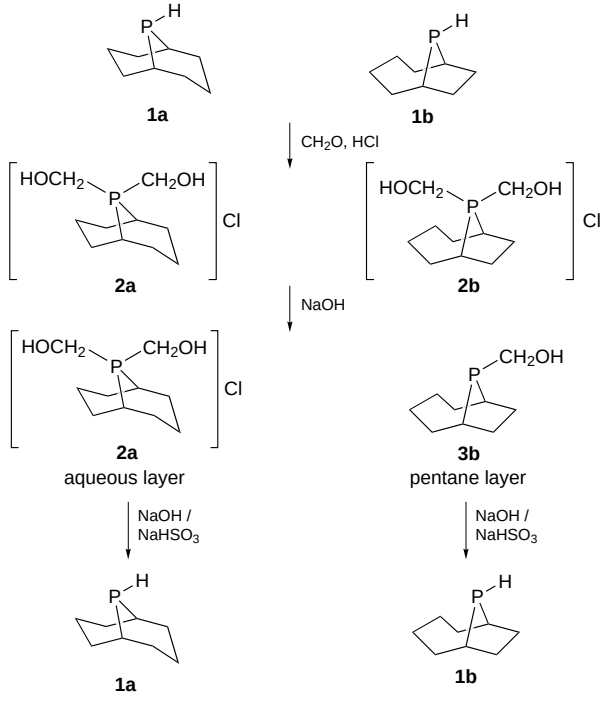
Joanne H. Downing, Victoria Gee and Paul G. Pringle*

School of Chemistry, University of Bristol, Cantocks Close, Bristol, UK BS8 1TS

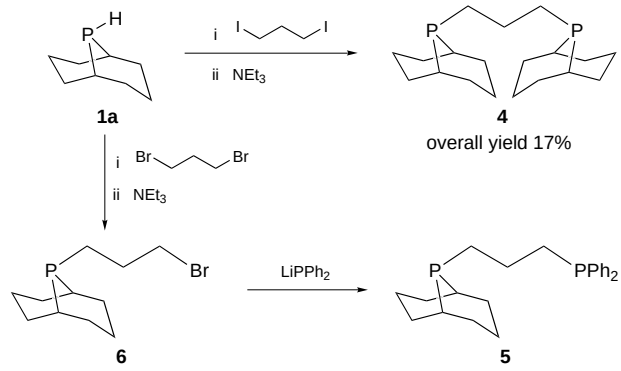
The isomeric [3.3.1]- and [4.2.1]-phosphabicyclononanes are readily separated by a sequence of hydrophosphination/dehydrophosphination steps; new diphosphine ligands derived from the [3.3.1] isomer are described.

Phosphine (PH_3) adds to cycloocta-1,5-diene to give a mixture of the bicyclic secondary phosphines **1a** and **1b**, sometimes referred to as 'phobane'.[1,2] Tertiary phosphines made from this mixture are ligands for the cobalt-catalysed hydroformylation process[3] currently carried out on a large scale industrially.[4] Recently derivatives of **1a** and **1b** have attracted attention as ligands for hydroformylation,[5] carbonylation,[6] and asymmetric catalysis.[2,7] To date there have been no reports of the separation of the isomers **1a** and **1b** although, by exploiting the difference in reactivity between the isomers, ligands derived from the symmetrical isomer **1a** have been isolated.[2,8] Here we report an easy method for separating **1a** and **1b** and the use of pure **1a** in further ligand synthesis.

The reactions which form the basis for the separation are summarised in Scheme 1. The crystalline, air-stable phosphonium salts **2a** and **2b** are readily made from the mixture of **1a** and **1b** with CH_2O in the presence of HCl. Loss of CH_2O from **2a**/**b** is promoted by NaOH but we have found that one hydroxymethyl group in **2b** is much more reactive than any of the others. Thus an aqueous solution of a **2a**/**b** mixture reacted selectively with NaOH to give neutral phosphine **3b** which was then extracted into pentane to leave pure **2a** in the aqueous layer. The crystal structure of the complex *cis*-[$PtCl_2$(**3b**)$_2$] suggests that it is the hydroxymethyl group lying over the seven-membered ring that is the reactive one.[8]



Scheme 1



Scheme 2 (Overall yield 50%)

Treatment of an aqueous solution of **2a** with NaOH and $NaHSO_3$ (to trap the generated CH_2O) gave the symmetrical secondary phosphine **1a** which was then extracted into pentane. Similarly the unsymmetrical isomer **1b** was made by treatment of a pentane solution of **3b** with aqueous NaOH and $NaHSO_3$. The separation can be carried out efficiently on a multigram scale† and both **1a** and **1b** have been isolated and fully characterised.‡

Access to **1a** has allowed us to synthesise the diphosphine derivatives **4** and **5** by the routes shown in Scheme 2; the modest overall yields reported reflect the small scale (0.1–1 g) of these preliminary reactions. Treatment of **1a** with $I(CH_2)_3I$ followed by NEt_3 gave **4**[5] exclusively in contrast to the mixture of isomers formed when $H_2P(CH_2)_3PH_2$ adds to cycloocta-1,5-diene. Treatment of **1a** with $Br(CH_2)_3Br$ gave the intermediate **6** which reacts with $LiPPh_2$ to give the unsymmetrical diphosphine **5**. The application of these new ligands in coordination chemistry and catalysis is in progress.

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Footnotes and References

* E-mail: paul.pringle@bristol.ac.uk

† The separation of **1a** and **1b** was carried out as follows (under nitrogen except where specified). To a stirred solution of a crude mixture of **1a** and **1b** supplied by Albright and Wilson Ltd (77 g, *ca*. 60% **1a**/**b** by ^{31}P NMR with the ratio of **1a** to **1b** of *ca*. 1.1 : 1) in aqueous CH_2O (95 cm^3, 35% m/m, 1.20 mol) was added aqueous HCl (120 cm^3, 5 M, 0.60 mol) dropwise over 30 min. After 1 h, the volatiles were removed on a rotary evaporator in air to give a viscous white oil. In air, trituration with propan-2-ol (400 cm^3) gave a white solid which was filtered off, washed with cold propan-2-ol (50 cm^3) and diethyl ether (50 cm^3); the yield of salts **2a** and **2b** was 56 g which represents *ca*. 72% yield. The solid was dissolved in hot (*ca*. 60 °C) water (*ca*. 20 cm^3) and then when the solution had cooled to *ca*. 40 °C, acetone was added until the solution turned cloudy (*ca*. 50 cm^3). Then the mixture was refrigerated (0 °C) for 16 h to give crystalline **2a**/**b** in > 80% recovery. To a rapidly stirred solution of **2a**/**b** (8.5 g, 36 mmol) in water (20 cm^3) with a layer of pentane (35 cm^3), was added aqueous NaOH (16 cm^3, 1 M, 16 mmol) dropwise by syringe over 5 min. After a further 10 min, the pentane layer was separated and the aqueous layer washed with pentane (2 × 10

cm^3). To the aqueous layer, more aqueous NaOH (1 M, 1 cm^3) was added (to remove the final traces of **2b**) and then in a separating funnel (in air), the aqueous layer was washed with pentane (2 × 30 cm^3) and then separated. The aqueous layer was then deaerated, pentane (50 cm^3) was added, then aqueous NaOH (37.6 cm^3, 1 M, 37.6 mmol) added dropwise over 5 min and finally solid $NaHSO_3$ (7.8 g, 75 mmol) was added and the mixture stirred for 1 h. Then the pentane layer was separated and the aqueous layer washed with pentane (2 × 20 cm^3). The pentane extracts were combined, dried over $MgSO_4$, filtered and then evaporated to dryness to give a white solid **1a** (2.32 g, 87%) which was 99.5% pure **1a** (by ^{31}P NMR).

In a separate experiment a pentane solution (*ca.* 30 cm^3) of **3b** (obtained as described above but from 1.78 g of **2a**/**b**, 7.5 mmol) was treated with water (20 cm^3) and NaOH (3.25 cm^3, 1 M, 3.25 mmol) followed by solid $NaHSO_3$ (3.44 g, 33 mmol) and the mixture rapidly stirred for 44 h. Then the pentane layer was separated and the aqueous layer washed with pentane (3 × 10 cm^3). The pentane extracts were combined, dried over $MgSO_4$, filtered and then evaporated to dryness to give a white solid **1b** (0.26 g, 55%) which was 99% pure **1b** (by ^{31}P NMR).

‡ *Selected spectroscopic data*. **1a**: ^{31}P NMR ($CDCl_3$, 162 MHz) δ −54.1 [^1J(PH) 192.1 Hz]; ^{1}H ($CDCl_3$, 400 MHz) δ 3.20 [d, 1 H, ^1J(PH) 192.1 Hz], 1.55–2.55 (br m, 14 H); ^{13}C ($CDCl_3$, 100 MHz) δ 33.9 [d, J(PC) 6.1 Hz], 30.0 [d, J(PC) 9.2 Hz], 22.6 (s), 22.4 [d, J(PC) 42.7 Hz], 22.1 (s); mass spectrum (EI) m/z 142 (M^+). **1b**: ^{31}P NMR ($CDCl_3$, 162 MHz) δ −48.4 [^1J(PH) 188.1 Hz]; ^{1}H ($CDCl_3$, 400 MHz) δ 2.70 [d, 1H, ^1J(PH) 188.0 Hz], 2.59 (br s, 2 H), 2.06 (m, 2 H), 1.35–1.82 (m, 10 H). ^{13}C ($CDCl_3$, 100 MHz) δ 37.1 [d, J(PC) 7.6 Hz], 35.5 [d, J(PC) 7.6 Hz], 35.3 [d, J(PC) 15.3 Hz], 25.8 [d, J(PC) 7.6 Hz]; mass spectrum (EI) m/z 142 (M^+). ^{31}P NMR data (162 MHz): **2a** (D_2O) δ +23.1; **2b** (D_2O) δ 55.4; **3a** ($CDCl_3$) δ −31.7; **3b** ($CDCl_3$) δ 4.3; **4** (C_6D_6) δ −37.6; **5** (C_6D_6) δ −38.1 (s, PC_8H_{14}), −17.2 (s, PPh_2); **6** (C_6D_6) δ −37.8.

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