Separation of Phobane Isomers by Selective Protonation

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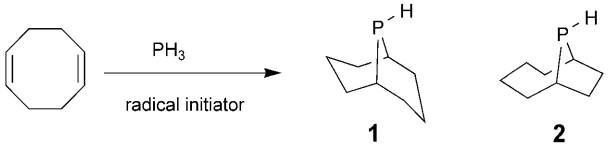
Abstract: The industrially important mixture of *sym*- and *asym*-phobanes are separated efficiently by selective protonation of the sym isomer with hydrochloric acid; carbonylation catalysts generated from diphosphanes derived from the separated isomers have quite different activities and product selectivities.

Keywords: basicity; hydrocarbonylation; palladium; phosphanes; separation

Phobane is a mixture of the *sym*- and *asym*-bicyclic secondary phosphines, 9-phosphabicyclo[3.3.1]nonane (**1**) and 9-phosphabicyclo[4.2.1]nonane (**2**), formed by the reaction of PH_3 with 1,5-cyclooctadiene [Eq. (1)].[1] The ratio of the isomers in phobane batches varies from *ca.* 2:1 to 3:2.



(1)

Derivatives of **1** and **2** have been known for almost 40 years[1] and have important applications in catalysis,[2–4] particularly in Co-based hydroformylation of long-chain alkenes.[2] It is known[5] that **1** is more nucleophilic than **2** and it would therefore be expected that phobane-derived ligands would show different coordination chemistry.[4,5] In fact, we have recently shown that the new diphosphine *o*-$C_6H_4\{CH_2P(C_8H_{14})\}_2$ derived from **1**, containing the "bisbi" backbone, forms mononuclear *trans* chelates with rhodium(I), nickel(II), palladium(II), and platinum(II).[6] Mixtures of isomeric phobanes are used because an economic separation has not been available.[7] We report here a simple, commercially viable[8,9] procedure for the separation of **1** and **2**.

Scheme 1 illustrates the method of separation. Both phosphines **1** and **2** readily dissolve in concentrated acids but we observed that **1** is significantly more basic than **2**. Thus dropwise addition of concentrated HCl to a 1 M solution of **1** and **2** in ether led to selective extraction of **1**. $^{31}P\{^1H\}$ NMR spectroscopy showed that the ethereal phase contained exclusively **2** and the aqueous phase contained a 7:1 mixture of protonated **1** and **2**. Ether extraction of the aqueous phase gave **2** in >99% purity. Addition of NaOH to the aqueous phase and extraction of the liberated **1** into ether gave **1** in 78% yield and >98% purity after sublimation. This selective protonation procedure is forgiving in the sense that too much or too little acid can easily be corrected as the separation is based on reversible equilibria. The separation is conveniently carried out on 30–40 g scales (see Experimental Section) and has been carried out on a 175 g scale.

When **1** and **2** were reacted with either $[PdCl_2(NCPh)_2]$ or $[PtCl_2(cod)]$ the mononuclear species $[MCl_2(\mathbf{1})_2]$ and $[MCl_2(\mathbf{2})_2]$ containing intact PH bonds were isolated and fully characterised by multinuclear NMR, FAB-MS and elemental analysis. This is unusual since complexes of the type $[MX_2(PHR_2)_2]$ often eliminate HX to give $[M(\mu\text{-}PR_2)(PHR_2)]_2$ (M = Pd, Pt; X = halide).[10] The ^1J(PtP) value for $[PtCl_2(\mathbf{1})_2]$ of 3300 Hz is slightly larger than the 3275 Hz for $[PtCl_2(\mathbf{2})_2]$. The ^1J(PH) and ^2J(PtH) values for $[PtCl_2(\mathbf{1})_2]$ are 377 Hz and 65 Hz, respectively, and for $[PtCl_2(\mathbf{2})_2]$ 368 Hz and 40 Hz, respectively. The ^1J(PH) value for $[PdCl_2(\mathbf{1})_2]$ is 361 Hz and for $[PdCl_2(\mathbf{2})_2]$ 353 Hz.

Single crystals of $[PtCl_2(\mathbf{1})_2]$ (as its dichloromethane solvate) and $[PtCl_2(\mathbf{2})_2]$ were grown by slow diffusion of Et_2O into their CH_2Cl_2 solutions (see Figs. 1 and 2). Both complexes have approximate C_2 symmetry with the PH bonds essentially perpendicular to the coordination plane and in mutually *anti* orientations.

The structure of $[PtCl_2(\mathbf{2})_2]$ shows that the preferred phobane configuration in **2** has the hydrogen atom on P *syn* to the five-membered ring. A comparison of the

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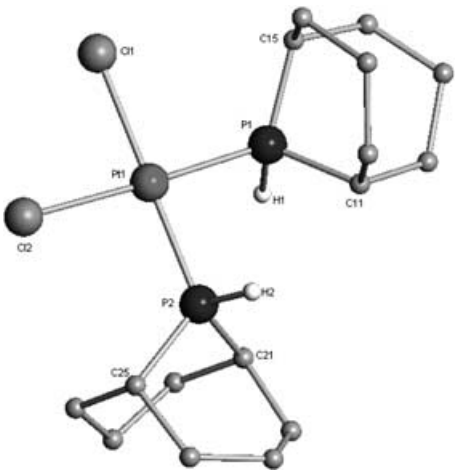


Figure 1. Molecular structure of $[PtCl_2(\mathbf{1})_2]$. Only hydrogen atoms directly bound to phosphorus are shown. Pertinent bond lengths (Å) and angles (°): Pt(1)–P(1) 2.250(3); Pt(1)–P(2) 2.235(3); Pt(1)–Cl(1) 2.377(3); Pt(1)–Cl(2) 2.368(3); P(1)–Pt(1)–P(2) 89.59(10); P(2)–Pt(1)–Cl(2) 92.75(10); P(1)–Pt(1)–Cl(1) 90.21(10); Cl(2)–Pt(1)–Cl(1) 87.46(10).

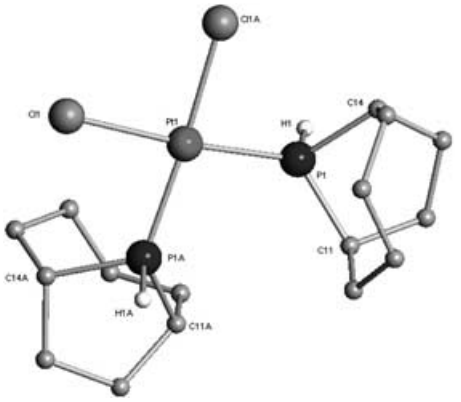
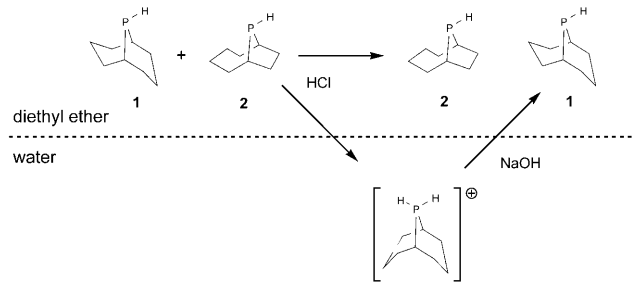


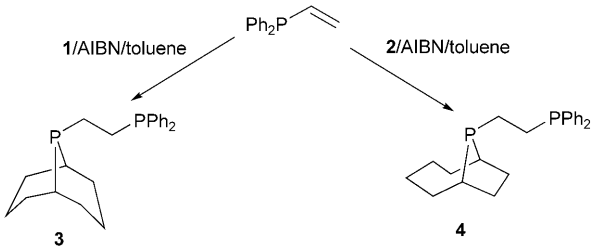
Figure 2. Molecular structure of $[PtCl_2(\mathbf{2})_2]$. Only hydrogen atoms directly bound to phosphorus are shown. Pertinent bond lengths (Å) and angles (°): Pt(1)–P(1) 2.2397(10); Pt(1)–P(1A) 2.2398(10); Pt(1)–Cl(1) 2.3611(11); Pt(1)–Cl(1A) 2.3610(11); P(1)–Pt(1)–P(1A) 97.15(5); P(1A)–Pt(1)–Cl(12) 87.46(4); P(1)–Pt(1)–Cl(1A) 87.46(4); Cl(1A)–Pt(1)–Cl(1) 88.04(6).

P–Pt–P bond angles shows that while the structure of $[PtCl_2(\mathbf{1})_2]$ is very close to square planar, that for $[PtCl_2(\mathbf{2})_2]$ is considerably distorted from square planar. This might be a result of the greater bulk of the ligand **2**. The C(15)–P(1)–C(11) angle of 97.1(5)° for $[PtCl_2(\mathbf{1})_2]$ is 4° larger than C(14)–P(1)–C(11) in $[PtCl_2(\mathbf{2})_2]$ at 93.1(2)°.

One explanation of why **1** is more basic, more nucleophilic and perhaps a better σ-donor than **2** lies in the electronic effects on the P lone pair of the constraints of the bicyclic structures. In **1**, the P is part of two six-membered rings while in **2**, the P is part of a five-membered ring and a seven-membered ring. The intracyclic C–P–C bond angles in derivatives of **1** are *ca.* 4° larger than in derivatives of **2** (see structures $[PtCl_2(\mathbf{1})_2]$ and $[PtCl_2(\mathbf{2})_2]$ above and others[9]). The greater C–P–C angle in **1** is accommodated by a decreased *p*-character in the P hybrid orbitals involved in the P–C bonding; the consequent increase in *p*-character in the P lone pair orbital (i.e., the HOMO) in **1** makes it higher in energy and therefore the lone pair more accessible.[11]

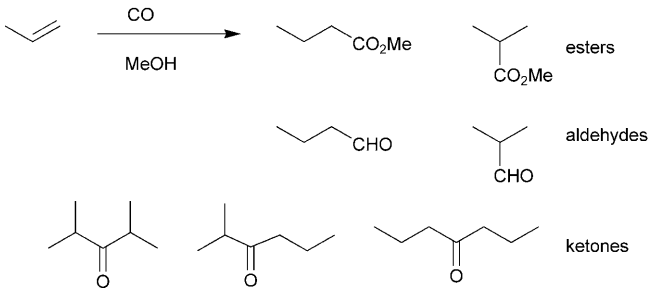


Scheme 1. Separation of **1** and **2** with HCl in an H_2O/Et_2O biphasic system.



Scheme 2. Bidentate ligands derived from **1** and **2**.

Palladium-catalysed hydrocarbonylation of propene can give esters (methoxycarbonylation), aldehydes (hydroformylation) or ketones (hydroacylation), see Scheme 3.[12]



Scheme 3.

The availability of pure **1** and **2** opens up the possibility of systematic comparisons of individual *sym*- and *asym*-phobane derivatives. For example, the diphosphines **3** and **4** were made by the radical initiated addition reactions shown in Scheme 2.

The results with **3** and **4** are given in Table 1 along with the results for dppe. It can be seen that the activity of the

Table 1. Hydrocarbonylation of propene in methanol.[a]

Entry	Ligand	Rate[b]	Aldehydes [%]	Ketones [%]	Esters [%]
1	dppe	3	20	71	9
2	**3**	225	23	70	7
3	**4**	475	36	27	37

[a] Batch experiments 250 ml Hastelloy C autoclave, 50 mL solvent, $pCO = 20$ bar, $pH_2 = 40$ bar (at room temperature); 10 mL propene, 0.1 mmol $Pd(OAc)_2$, 0.12 mmol ligand, 0.2 mmol methanesulfonic acid; 105 °C.
[b] Initial rates, averaged over a period corresponding to $< 30\%$ conversion.

catalyst derived from **3** is less than half that with its isomer **4** and both catalysts show much greater activity than the dppe system under these conditions. Moreover the chemoselectivities of **3** and **4** are quite different.

In conclusion we have demonstrated that the 9-phosphabicyclononane isomers can conveniently be separated by selective protonation with HCl, a procedure that has commercial potential.[7] Ligands derived from the pure isomers show significant differences in their catalytic properties.

Experimental Section

All solvents were N_2-saturated and the phobane mixture was supplied by Shell Chemicals.

Separation of the Phobane Isomers 1 and 2

A 3:2 mixture of *sym*-phobane (**1**) and *asym*-phobanes (**2**) (31.7 g, 223.4 mmol) was dissolved in diethyl ether (225 cm^3) and water (400 cm^3) was added. The biphasic mixture was stirred vigorously while 10 M HCl (225 cm^3) was added dropwise over 105 min. $^{31}P\{^1H\}$ NMR spectroscopy showed the ether layer **A** contained a *ca.* 7:1 mixture of **2** and **1** and the aqueous layer **B** contained a *ca.* 7:1 mixture of **1** ($\delta = -16.6$ ppm) and **2** ($\delta = -1.3$ ppm). The two phases were then separated and the aqueous layer **B** was extracted with diethyl ether (3×220 cm^3). The organic extracts were combined and then the solvent was removed under reduced pressure. To the resulting crude **2** (which contained 10–15% of **1**), diethyl ether (250 cm^3) and water (420 cm^3) were added. The biphasic mixture was stirred vigorously while N_2-saturated 10 M HCl (150 cm^3) was added dropwise over 90 min. $^{31}P\{^1H\}$ NMR spectroscopy of the ether phase showed there to be only **2** present. The two phases were separated and the aqueous layer was extracted with diethyl ether (3×150 cm^3). The organic extracts were combined, washed with saturated $NaHCO_3$ solution (30 cm^3) and then dried over $MgSO_4$. The solvent was removed under reduced pressure to give **2** as a colourless solid of analytical purity; yield: 6.0 g (42.3 mmol, 47%).

To the vigorously stirred aqueous layer **A**, fresh diethyl ether was added (225 cm^3) and the mixture was cooled with ice while a 14.4 M NaOH solution (200 cm^3) was added over 45 min. The phases were then separated and the aqueous phase was extracted with diethyl ether (3×100 cm^3). The organic extracts were combined and dried over $MgSO_4$. The solvent was then removed under reduced pressure to give 90% pure **1** as a white solid; yield: 14 g (99 mmol, 78%). Sublimation (60 °C at 2mmHg) of this product gave (according to NMR) 98% pure **1**.

X-Ray Crystallographic Study

Crystal structures were determined from data collected on a Siemens SMART diffractometer for $2.0 < \theta < 27.5^0$ ($\lambda = 0.71073$ Å) at 173 K. The structures were solved by direct and Fourier methods and refined by least-squares against all unique F^2 data corrected for absorption (although in the case of $[PtCl_2(\mathbf{1})_2] \cdot CH_2Cl_2$ there are apparently unresolved inaccuracies with this correction leading to large residuals close to the metal atom).

Crystal data for $[PtCl_2(\mathbf{1})_2] \cdot CH_2Cl_2$: $M = 635.26$, triclinic, space group $P\bar{1}$, $a = 10.259(3)$, $b = 10.299(2)$, $c = 11.516(4)$ Å, $\alpha = 72.29(2)^\circ$, $\beta = 75.02(2)^\circ$, $\gamma = 75.07(2)^\circ$, $V = 1098.4(5)$ $Å^3$, $Z = 2$, $\mu = 7.019$ mm^{-1}, 3854 unique data, $R_1 = 0.0603$.

Crystal data for $[PtCl_2(\mathbf{2})_2]$: $M = 550.33$, monoclinic, space group C2/c, $a = 11.179(2)$, $b = 8.566(2)$, $c = 19.996(7)$ Å, $\beta = 95.96(2)^0$, $V = 1904.4(11)$ $Å^3$, $Z = 4$, $\mu = 7.809$ mm^{-1}, 1683 unique data, $R_1 = 0.0218$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 258822 and 258823. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information Available

Text giving preparative procedures and spectroscopic and elemental analysis data for compounds **1**–**4**, $[MCl_2(\mathbf{1})_2]$ and $[MCl_2(\mathbf{2})_2]$ (M = Pd, Pt).

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