1,8-Dimethylnaphthalene-bridged diphosphine ligands: synthesis and structural comparison of their palladium complexes

Ronan M. Bellabarba,*[a] Colin Hammond,†[a] Grant S. Forman,[a] Robert P. Tooze[a] and Alexandra M. Z. Slawin[b]

Received 19th January 2006, Accepted 10th March 2006
First published as an Advance Article on the web 17th March 2006
DOI: 10.1039/b600837b

The synthesis of a new series of ligands with a 1,8-dimethylnaphthalene backbone is reported, 1,8-$(R_2PCH_2)_2C_{10}H_6$, where R = ^{t}Bu **1** (dbpn), ^{i}Pr **2** (dippn), Cy **3** (dchpn) and Ph **4** (dphpn). The ligand **1** is structurally characterised by X-ray crystallography. A comparative structural study of the respective (diphosphine)Pd(dba) and (diphosphine)$PdCl_2$ complexes is carried out, comparing the X-ray crystal structures of complexes **6**, **7**, **8**, **10**, **11** and **12**. It is shown that the geometry at the metal is affected by not only ligand demands, but also by the palladium oxidation state and the electronic properties of the ligands. Two qualitative stability series are also identified: **9** < **10** < **11** ≈ **12** is observed, and $P_2Pd(dba)$ complexes are more stable than the corresponding P_2PdCl_2 complexes towards opening of the chelate ring. It is also concluded that the bite angle is heavily influenced by the electron donating properties of the ligand.

Introduction

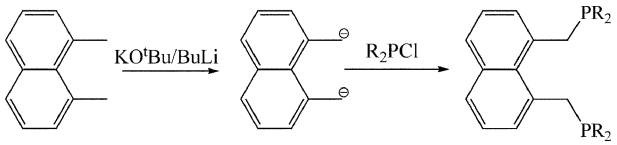
The bite angle of chelating diphosphines is an important factor in many catalytic reactions. It has been shown, for instance, that the bite angle can have a crucial influence on the stability of formal oxidation states,[1] on the rate of reductive elimination from Pd complexes,[2] on the alcoholysis of acyl–palladium bonds,[3] and on the structure of CO/ethylene polymers formed.[4] This subject has been reviewed by van Leeuwen.[5] We have found that sterically hindered wide bite angle diphosphines such as 1,2-bis(di-*tert*-butylphosphino)methyl benzene can stabilise unusual trigonal-planar palladium carbonyl complexes,[6] and others have found that it is possible to spectroscopically observe reactive palladium hydrides with the same ligand.[7] These observations may be relevant to the understanding of catalytic properties of metal complexes.

A large range of bidentate ligands has been reported in the literature and studied according to their structural parameters. As part of our ongoing investigations on this topic we wanted to carry out a comparative investigation of the structures of a series of Pd(0) and Pd(II) complexes. In this study, the ligands considered have a very rigid carbon backbone with methylene linkages to the phosphorus donor, thereby giving some scope for changes in P–P distances and ligand–metal structures. Van Leeuwen and co-workers have reported a structural study on a series of wide bite-angle ligands and their Pd(TCNE) complexes.[8] It is difficult to compare the type of structure reported below with any relevant literature studies: either the bridge is smaller (1,2-bis(di-*tert*-butylphosphino)methyl benzene),[7] contains heteroatoms present (*e.g.* Xantphos[5]), it is more flexible (*e.g.* BISBI[9]), the bridge is longer (*e.g.* transphos[5]) or it is a long aliphatic chain and thus tends to bridge two metals.[10]

We wish to report the preparation of a closely related series of 1,8-dimethylnaphthalene-bridged bidentate phosphines. We have also undertaken structural studies of some of their palladium complexes. Within this family of ligands only the ligand **4** has been previously reported,[11,12] prepared by reductive cleavage of PPh_3 and reaction with 1,8-di(bromomethyl)naphthalene, and used to prepare its palladium dichloride adduct.[12]

Results and discussion

The synthesis of these ligands is achieved as shown in Scheme 1 by double deprotonation[14] of 1,8-dimethylnaphthalene and reaction with the appropriate phosphorus halide to give ligands of the general formula 1,8-$(R_2PCH_2)_2C_{10}H_6$, where for R = ^{t}Bu **1**(dbpn), ^{i}Pr **2** (dippn), Cy **3** (dchpn) and Ph **4** (dphpn) (Scheme 1). The new ligands **1**, **2**, and **3** were recrystallised from alcoholic solvent and found to be pure by elemental analysis. The ligand **1** was also characterised by single-crystal X-ray diffraction (Fig. 1).

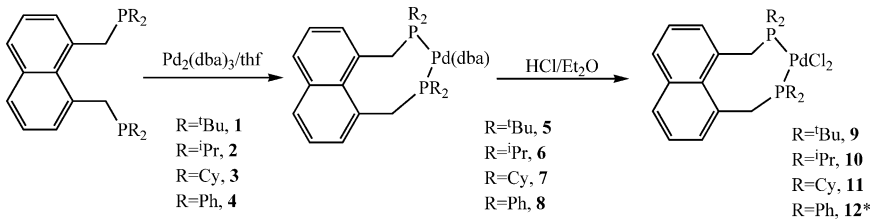


Scheme 1 Synthetic route to bidentate ligands.

Treatment of $Pd_2(dba)_3$ with two equivalents of ligands **1**, **2**, **3** and **4** gave the complexes **5** (dbpn)Pd(dba), **6** (dippn)Pd(dba), **7** (dchpn)Pd(dba) and **8** (dphpn)Pd(dba), respectively, as shown in Scheme 2. These complexes display broad ^{31}P NMR resonance data due to the fluxionality of the dba ligand at room temperature. Low-temperature NMR studies of complexes **7** and **8** showed that the complexes were still fluxional at −80 °C.

The complexes **5**, **6** and **7** can be converted to their respective dichloride complexes **9** (dbpn)$PdCl_2$, **10** (dippn)$PdCl_2$ and

[a]*Sasol Technology (UK) Ltd, Purdie Building, North Haugh, St Andrews, Fife, UK KY16 9ST. E-mail: ronan.bellabarba@uk.sasol.com; Fax: +44 (0)1334 460939; Tel: +44 (0)1334 460934*
[b]*School of Chemistry, Purdie Building, North Haugh, St Andrews, Fife, UK KY16 9ST. E-mail: amzs@st-and.ac.uk; Fax: +44 (0)1334 463384; Tel: +44 (0)1334 467280*
† Current address: School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK, BS8 1TS.



Scheme 2 Preparation of the palladium complexes. *Not synthesised by this method, see ref. 12.

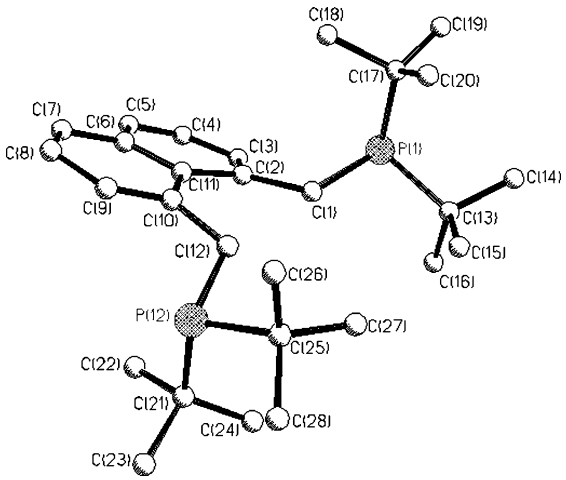


Fig. 1 X-Ray crystal structure of the ligand **1**.

11 (dchpn)$PdCl_2$ by treatment with two equivalents of HCl (Scheme 2). The palladium dichloride complex **12**, (dphpn)$PdCl_2$, is known and has been structurally characterised by Yamamoto *et al.*[12] Although we have no doubt that the complex **12** can be obtained in the same fashion as **9–11**, we have not carried out the synthesis, but we include some structural data for comparison purposes.

The dichloride complex **9** is not stable. When synthesised as described in Scheme 2, it is isolated as a pale yellow powder which is soluble in halogenated solvents such as methylene chloride. However, upon standing in solution, it inevitably forms a gel-like substance which dries to a powder and which is then extremely insoluble in all common solvents. This deterioration seems to occur irrespective of the solvent and even at −20 °C. The ^{31}P NMR shows a single, weak peak at δ 72.1 ppm tentatively assigned to **9**. The ^{1}H NMR spectrum was difficult to interpret meaningfully due to the presence of extremely broad resonances. It seems reasonable to conclude that what is occurring is initial formation of **9**, which would be soluble, followed by ring-opening of the eight-membered chelate structure to form an insoluble polymeric material with presumably *trans*-phosphines and chlorides. Attempting the synthesis from (COD)$PdCl_2$ immediately and directly generates a similarly insoluble and intractable product.

This instability does not appear to occur in the case of the Pd(dba) complex **5** which appears to be stable in solution. The ^{1}H NMR spectrum, like all the other Pd(dba) complexes, displays very broad peaks, whilst the ^{31}P NMR shows a singlet at δ 77.5 ppm.

A similar if much less pronounced effect is observed with **10**, where a solution of this complex will very slowly generate a precipitate upon standing. However, the complex is stable enough to obtain crystals suitable for diffraction. The complex **11** appears to be stable in solution at room temperature.

The solid-state structures of complexes (dippn)Pd(dba) **6**, (dchpn)Pd(dba) **7**, (dphpn)Pd(dba) **8**, (dippn)$Pd(Cl_2)$ **10** and (dchpn)$PdCl_2$ **11** have been determined by X-ray crystallography. Unfortunately, despite several attempts, the crystallographic data for **6** was not of as high quality as could be desired, although bond distance and angle data could be determined. For comparison, we also include a structure of the free ligand **1** (Fig. 1) and some data from the previously known complex **12**.[12] The solid state structures of **6**, **7**, **8**, **10** and **11** are shown in Fig. 2–6 respectively, and selected bond distances and angles are shown in Table 1. All ^{31}P NMR and ^{1}H data are given in Table 2 and crystallographic data in Table 3.

All these structures present a near-planar naphthalene backbone; however, the bridgehead CH_2 groups appear to be slightly forced apart in the metal complexes. For instance, the difference between the C_{10}–C_2 and the C_{12}–C_1 distances in **8** (Fig. 4) is

Table 1 Selected average bond distances (Å) and angles (°)

	Pd–P	P–Pd–P	P–C–C_{Ar}
6, (dippn)Pd(dba)	2.32	104.7	117.2
7, (dchpn)Pd(dba)	2.31	103.9	117.7
8, (dphpn)Pd(dba)	2.29	98.5	111.5
10, (dippn)$PdCl_2$	2.27	100.3	119.6
11, (dchpn)$PdCl_2$	2.28	100.9	119.0
12, (dphpn)$PdCl_2$[a]	2.27	93.5	111.3

[a] Ref. 12.

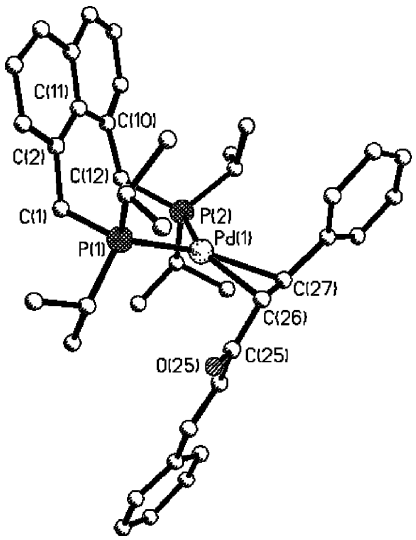


Fig. 2 X-Ray crystal structure of **6**.

Table 2 ^{1}H and ^{31}P NMR data for all new compounds

	δ ^{31}P (solvent)	δ ^{1}H
1	35.9, s, C_6D_6	1.13, d ($^3J_{PH}$ = 11 Hz), 36H, ^{t}Bu; 3.97, br s, 4H, CH_2; 7.33, dt ($^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 3 Hz) 2H, ArCH; 7.59, br d ($^3J_{HH}$ = 8 Hz) ArCH; 8.37, m, 2H, ArCH.
2	8.7, s, C_6D_6	1.01, dd ($^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 11.8 Hz), 24H $(CH_3)_2CH$; 1.64, dh ($^3J_{HH}$ = 7.2 Hz, $^2J_{PH}$ = 1.8 Hz), 4H $(CH_3)_2CH$; 3.94, d ($^2J_{PH}$ = 2.6 Hz), 4H, CH_2; 7.27, dd ($^3J_{HH}$ = 7.6 Hz), 2H, ArCH; 7.35, d ($^3J_{HH}$ = 7.4 Hz), 2H, ArCH; 7.46, d ($^3J_{HH}$ = 8.2), 2H, ArCH.
3	1.0, s, C_6D_6	1.1–2.0, br m, CyH, 44H; 4.0, br s, CH_2, 4H; 7.30, t ($^3J_{HH}$ = 7.5 Hz), 2H, ArH; 7.59, d ($^3J_{HH}$ = 6.4 Hz), 2H, ArH; 7.68, d ($^3J_{HH}$ = 7.2 Hz), 2H, ArH.
4	−10.3, s, C_6D_6	4.37, d ($^2J_{PH}$ = 4.4 Hz), 4H, CH_2; 6.64, m, 2H, ArCH; 6.83–6.99, m, 18H, ArCH; 7.23, m, 4H, ArCH; 7.43, d ($^3J_{HH}$ = 7.6 Hz) 2H, ArCH.
5	77.5, s, C_6D_6	Broad/fluxional[a]
6	43.4, br, C_6D_6	Broad/fluxional[a]
7	36.0, 33.3, br, C_6D_6	Broad/fluxional[a]
8	21.9, br, C_7H_8	Broad/fluxional[a]
9	72.1, s, $CDCl_3$	Broad/fluxional[a]
10	60.9, s, CD_2Cl_2	0.49, dd ($^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 18.8 Hz), 6H $(CH_3)_2CH$; 1.33, virt. q ($^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 18.8 Hz), 12H $(CH_3)_2CH$; 1.48, dd ($^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 18.8 Hz), 6H $(CH_3)_2CH$; 2.30, dh ($^2J_{PH}$ = 4.9 Hz, $^3J_{PH}$ = 7.2 Hz), 2H $(CH_3)_2CH$; 3.35, h ($^3J_{PH}$ = 7.2 Hz), 2H $(CH_3)_2CH$; 3.50, dt ($^2J_{HH}$ = 15.2 Hz, $^2J_{PH}$ = 6.9 Hz), 2H, CH_2; 3.92, dd ($^2J_{HH}$ = 15.2 Hz, $^2J_{PH}$ = 5.4 Hz), 2H, CH_2; 7.39, m, ArCH, 4H; 7.82, m, ArCH, 2H.
11	54.26, s, $CDCl_3$	0.3, br, 2H, $CyCH_2$; 0.5, br, 2H, $CyCH_2$; 1–2.3, br m, 36H, $CyCH_2$; 2.7, br, 2H, CyCH; 3.1, br, 2H, CyCH; 3.58, dt ($^2J_{PH}$ = 6.4 Hz, $^2J_{HH}$ = 15.1 Hz), 2H, PCH_2; 3.88, dd ($^2J_{PH}$ = 5.0, $^2J_{HH}$ = 15.1 Hz), 2H, PCH_2; 7.41, m, 4H; 7.80, m, 2H.

[a] See text.

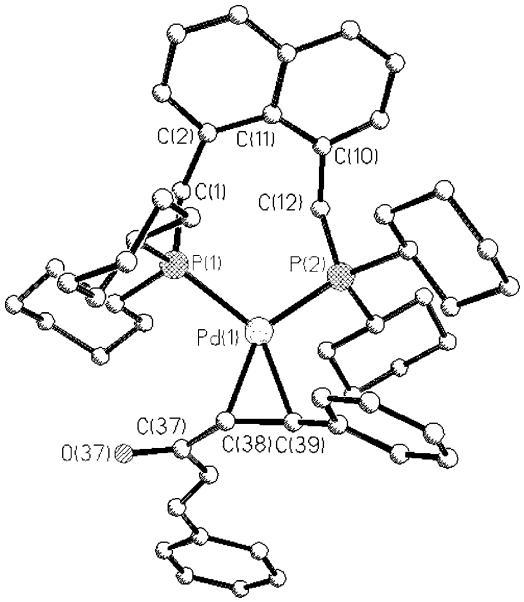


Fig. 3 X-Ray crystal structure of **7**.

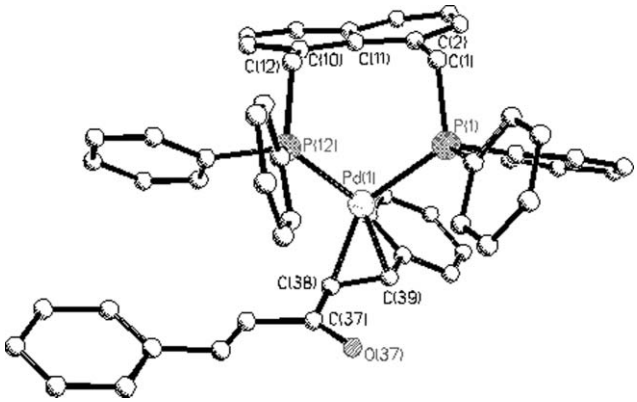


Fig. 4 X-Ray crystal structure of **8**.

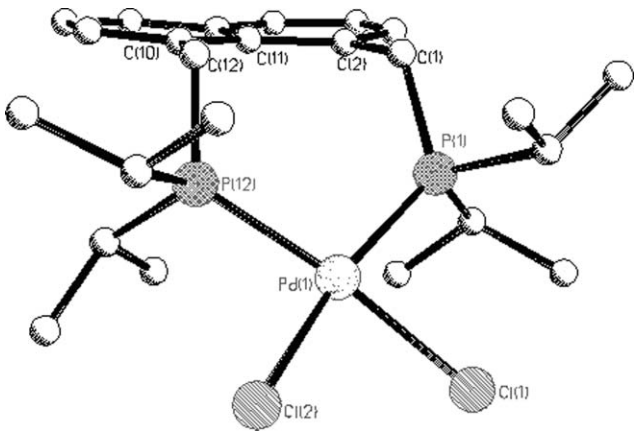


Fig. 5 X-Ray crystal structure of **10**.

approximately 0.55 Å, compared to 0.43 Å in the free ligand **1** (Fig. 1). Similar observations can be made for the other structures. All of the metal complexes have unusually short intramolecular H–H separations between H atoms at C1 and C12 in the ligand in all the complexes; the relevant separations are as short as 1.57 Å.

As is apparent from Table 1, there is only a small change in Pd–P distance with variation of the ligand or formal oxidation state of the metal. Within the limits of this study, it would appear that the metal-phosphorus bond length is not affected so much by the donor ability of the ligand but by the oxidation state of the metal. The Pd–P distance in the Pd(II) complexes is slightly shorter than in the Pd(0) complexes; but this variation is very subtle and may not be significant.

However, there is a significant difference between bite angle in the alkyl diphosphine Pd(0) complexes (**6**, **7**) and aryl diphosphine Pd(0) (**8**), and especially upon changing the formal oxidation state of the metal from Pd(0) to Pd(II) (**6** and **10**, **7** and **11**, **8** and **12**).

Table 3 Crystallographic data for **1**, **6–8**, **10** and **11**

Compound	**1**	**6**	**7**	**8**	**10**	**11**
Chemical formula	$C_{28}H_{46}P_2$	$C_{41}H_{52}OP_2Pd{\cdot}C_4H_8O$	$C_{53}H_{68}OP_2Pd$	$C_{53}H_{44}OP_2Pd{\cdot}C_4H_{10}O$	$C_{24}H_{38}Cl_2P_2Pd$	$C_{36}H_{54}Cl_2P_2Pd{\cdot}1.5CH_2Cl_2$
M	444.59	801.27	889.41	939.34	565.78	853.42
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$P2_1$	$P2_1/c$	$P2_1/n$	$Pbca$	$P\bar{1}$
a/Å	11.244(3)	14.0551(8)	11.042(2)	13.479(8)	16.743(3)	12.898(3)
b/Å	17.850(4)	19.4716(8)	18.552(4)	17.557(9)	15.594(3)	17.223(4)
c/Å	14.521(4)	15.9493(8)	22.234(4)	20.690(11)	19.512(3)	18.723(4)
α/°						83.18(2)
β/°	111.690(6)	109.305(4)	90.183(6)	109.030(8)		76.28(2)
γ/°						79.56(2)
V/Å^3	2708.1(11)	4119.5(4)	4505.9(16)	4629(4)	5094.5(16)	3960.9(14)
Z	4	4	4	4	8	4
μ(Mo-Kα)/mm^{-1}	0.173	0.563	0.521	0.513	1.073	0.913
Reflections collected, unique, observed	16668, 4776, 3964	23624, 11429, 10439	26520, 7951, 5884	31314, 8331, 7178	24175, 4467, 3846	24442, 13631, 7840
R_{int}	0.0475	0.1456	0.0515	0.0443	0.0629	0.0749
R_1, wR_2 [$I > 2\sigma(I)$]	0.0513, 0.1175	0.1309, 0.3007	0.0564, 0.1087	0.0592, 0.1372	0.0751, 0.1440	0.1059, 0.2094

Fig. 6 X-Ray crystal structure of **11**.

Similar observations have been previously made on palladium complexes of xylene-bridged diphosphine ligands.[13]

This series of structures can be considered in the light of what Van Leeuwen and Dierkes assert[5] on the subject of a "metal preferred" bite angle and a "ligand preferred" bite angle.

The metal preferred bite angle is influenced by the formal oxidation state. In this case, the same bidentate ligand leads to a structure which is closer to the ideal square-planar conformation (*i.e.* P–Pd–P closer to 90°) when bound to Pd(II). We feel that, sterically, the halide ligands in these cases have but a small part to play, as the same diphosphine ligand-metal fragment in the complex $[(dphpn)Pd(CNAr)_2]^{2+}$ prepared by Yamamoto and co-workers[12] exhibits a P–Pd–P angle of 93.1°, very close to the 93.5° in **12**.

The ligand preferred bite angle is determined by the constraints imposed by the backbone and by steric interactions.[5] In this study we have tried to limit to the utmost the influence of any other parameters that could affect the solid state structure of the complexes, such as bite angle, nature of the metal, and ancillary ligands. The only parameters that we tried to vary in complexes **6–11** were the nature of the phosphine, and the oxidation state of the metal. Despite the attempted simplification, it is apparent that there are significant effects on the bite angle. Thus, the P–Pd–P angle for the Pd(0) complexes **6** and **7** is very similar (103.7, 103.9°), whilst the phenyl analogue **8** has a much more acute angle (98.5°). The same trend is observed in the Pd(II) complexes **10**, **11** and **12**. It is also conceivable that these trends are due to crystal packing interactions, and not ligand properties, but we feel that solid-state interactions cannot account for these significant differences.

Another measurable parameter of this is the 'fold angle', *i.e.* the angle between the P-donor, the CH_2 carbon and the aryl carbon. These angles follow similar trends and appear to correlate with the bite angle at the metal, as shown in Table 1.

Conclusions

We found that in the series of complexes **5–12**, the structure is obviously influenced by the ligand's requirements, but also affected by the metal oxidation state and the donating ability of the P-fragments. In the case of ligand **1**, the balance between steric demands of the ligand and the requirements of the metal leads to complexes which are unstable when the metal fragment is Pd(II): in qualitative terms, the favourable chelation is offset by the demands of binding a very bulky ligand and of forming an eight-membered

ring. Thus the qualitative stability series **9** < **10** < **11** ≈ **12** is observed, but also that $P_2Pd(dba)$ complexes are more stable than the corresponding P_2PdCl_2 complexes towards ring-opening of the chelate ring in this series. Similar behaviour has been previously observed by Milstein.[1a] It is difficult to distinguish between steric and electronic effects on the bite angle and more work would be required to do so. However, we anticipate that this study should provide useful extra data for any ongoing investigations.

Experimental

All syntheses involving air-sensitive materials were carried out using dried and degassed solvents under dinitrogen. 1,8-Dimethylnaphthalene, $^tBu_2PCl$, $^iPr_2PCl$, Cy_2PCl, Ph_2PCl and KO^tBu (Aldrich or Strem) were used as supplied (unless clearly degraded, in which case they were vacuum distilled trap-to-trap) and stored in Young's tap ampoules. BuLi was received from suppliers, transferred to and stored in Young's tap ampoules at 4 °C. With the exception of $CDCl_3$, NMR solvents were degassed and stored in Young's tap ampoules under dinitrogen. ^1H and ^{31}P NMR spectra were recorded using a Bruker AV300 spectrometer, and referenced either internally (^1H, 300.06 MHz, residual protio solvent resonance relative to $SiMe_4$ at δ 0) or externally (^{31}P, 121.47 MHz, externally to 85% H_3PO_4 at δ 0). All chemical shifts are quoted in δ (ppm), using the high frequency positive convention, and coupling constants in Hz. Elemental analyses were carried out by Stephen Boyer at London Metropolitan University.

Synthesis of diphosphine ligands: typical procedure

BuLi (2.5 M solution in hexanes, 1.6 mL, 4 mmol) and KO^tBu (450 mg, MW 112.2, 4 mmol)[14] were suspended in petroleum ether (bp 40–60 °C, 50 ml) and 1,8-dimethylnaphthalene (312 mg, MW 156.2, 2 mmol) was added. The mixture was stirred for at least 2 h, during which time the suspension changed colour to brown and then to brick red. The liquid was filtered off, the red solid was washed twice with petroleum ether (bp 40–60 °C, 20 ml) and dried under vacuum.‡

The red solid was cooled to −78 °C, and cold diethyl ether (50 ml) was added to it to yield a red suspension. The desired halophosphine (4 mmol, 2 equivalents) was added slowly *via* syringe at −78 °C, then the mixture was allowed to warm to room temperature and stirred for at least 1 h, until all red coloration was discharged to yield a white or pale yellow suspension. The suspension was filtered and the residue extracted with diethyl ether (3 × 50 mL), and the combined extracts dried under vacuum to yield the crude product which could be recrystallised from refluxing methanol (**1**,**2**), ethanol (**3**) or pentane (**4**) if required. Unoptimised yields and elemental analysis: **1**, 50%. Anal. (%). Found (required): C, 75.57 (75.64); H, 10.59 (10.43); HRMS, *m*/*z* found: 445.3141, required: 445.3153; **2**, 40%. Anal. (%). Found (required): C, 74.09 (74.20); H, 9.92 (9.86); **3**, 56%. Anal. (%). Found (required): C, 78.78 (78.79); H, 9.99 (9.92); **4**,[11,12] 15%.

‡ This red material is the dipotassium salt of 1,8-dimethylnaphthalene (**CAUTION**: extremely pyrophoric) and best used as soon as possible, although it can be stored under inert atmosphere for a few weeks.

Synthesis of Pd(dba) complexes: typical procedure

$Pd_2(dba)_3$ (100 mg, 0.11 mmol) and the ligand (2 equivalents) were suspended in thf (25 ml), and the mixture was stirred at room temperature for 1 h. The mixture was filtered to give a clear orange solution which reduced to a solid foam under vacuum. This material is a mixture of product and dba; washing with cold diethyl ether to remove as much dba as possible was, in our hands, the most successful method of purification but accompanied by unacceptable losses of product. Attempts at crystallisation invariably resulted in co-precipitation or co-crystallisation of yellow dba and orange–red product. For this reason, the product was often contaminated with dba, but pure enough for our purposes. Yields are typically 70–90%. Single crystals could be obtained from evaporation of a diethyl ether solution or from pentane at −20 °C.

Synthesis of $PdCl_2$ complexes: typical procedure

The material obtained in the previous step was dissolved in diethyl ether and treated with 2.1 equivalents of a solution of HCl in diethyl ether with stirring. A yellow precipitate forms rapidly, which can be isolated by filtration and exhaustively washed with diethyl ether to yield the product in quantitative yield. X-Ray diffraction quality crystals of the stable complexes **10** and **11** could be obtained by layering a dichloromethane solution with diethyl ether.

Crystallography

Crystal data and refinement details are shown in Table 3. Data (Mo radiation) were collected at −180 °C using a Rigaku MM007 high brilliance rotating anode/confocal optics with for **1**, **6**, **7**, **10** and **11** a Mercury ccd detector and for **8** a Saturn ccd detector. In all cases a full hemisphere was collected. Intensities were corrected for Lorentz-polarisation and for absorption. The structures were solved by direct methods. For **6** we collected full data sets on five different crystals but always experienced difficulty with crystal quality and solvent, only the Pd, P and O atoms are refined anisotropically in this structure. For all of the other structures all non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealised and refined with riding thermal parameters. Refinements were by full-matrix least squares based on F^2 using SHELXTL.[15]

CCDC reference numbers 295570–295575.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600837b

Acknowledgements

We would like to thank Dr Tomas Lebl for VT NMR experiments and Ms Caroline Horsburgh for high-resolution MS.

References

1 (*a*) M. Portnoy and D. Milstein, *Organometallics*, 1993, **12**, 1655–1664; (*b*) M. Portnoy and D. Milstein, *Organometallics*, 1993, **12**, 1665–1673.
2 J. M. Brown and P. J. Guiry, *Inorg. Chim. Acta*, 1994, **220**, 249–259.
3 P. W. N. M. van Leeuwen, M. A. Zuideveld, B. H. G. Swennenhuis, Z. Freixa, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz and A. L. Spek, *J. Am. Chem. Soc.*, 2003, **125**, 5523–5539.

4 E. Drent, J. A. M. Broeckhoven and M. J. Doyle, *J. Organomet. Chem.*, 1991, **417**, 235.
5 P. Dierkes and P. W. N. M. van Leeuwen, *J. Chem. Soc., Dalton Trans.*, 1999, 1519–1529.
6 R. M. Bellabarba, R. P. Tooze and A. M. Z. Slawin, *Chem. Commun.*, 2003, 1916–1917.
7 W. Clegg, G. R. Eastham, M. R. J. Elsegood, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman and S. Zacchini, *J. Chem. Soc., Dalton Trans.*, 2002, 3300–3308.
8 M. K. Kranenburg, J. G. P. Delis, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Vrieze, N. Veldman, A. L. Spek, K. Goubitz and J. Fraanje, *J. Chem. Soc., Dalton Trans.*, 1997, 1839–1849.
9 H. Bahrmann, K. Bergrath, H.-J. Kleiner, P. Lappe, C. Naumann, D. Peters and D. Regnat, *J. Organomet. Chem.*, 1996, **520**, 97–100.
10 See, for instance: B. L. Shaw, *J. Organomet. Chem.*, 1980, **200**, 307–318; N. A. Al-Salem, H. D. Empsall, R. Markham, B. L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans.*, 1979, 1972; N. A. Al-Salem, W. S. McDonald, R. Markham, M. C. Norton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 59; C. Crocker, R. J. Errington, R. Markham, C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1982, 387.
11 R.-X. Li, N.-B. Wong, X.-J. Li, T. C. W. Mak, Q.-C. Yang and K.-C. Tin, *J. Organomet. Chem.*, 1998, **571**, 223–229.
12 Y. Yamamoto, Y. Fukui, K. Matsubara, H. Takeshima, F. Miyauchi, T. Tanase and G. Yamamoto, *J. Chem. Soc., Dalton Trans.*, 2001, 1773–1781.
13 W. Clegg, G. R. Eastham, M. R. J. Elsegood, R. P. Tooze, X. L. Wang and K. H. Winston, *Chem. Commun.*, 1999, 1877.
14 *Encyclopaedia of Reagents for Organic Synthesis*, ed. L. A. Paquette, J. Wiley & Sons, Chichester, 1995, vol. 2, p. 923.
15 *SHELXTL 6.01*, G. M. Sheldrick, Bruker AXS, Madison, 2001.