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Substitution reactions of *trans*-[$PdXPh(SbPh_3)_2$J (X=Cl or Br) with nitrogen, phosphines and arsenic donor ligands. Crystal structures of *trans*-[$PdClPh(PPh_3)_2$], [PdClPh(bipy)], $[PdClPh(dppm)]_2$, and $[PdBrPh(dppm)]_2$

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Abstract

Exchange reactions of *trans*-[$PdXPh(SbPh_3)_2$] (1) (X=Cl or Br) with ligands L in refluxing dichloromethane give the palladium phenyl complexes [$PdXPhL_2$] (X=Cl, L=PPh_3, $AsPh_3$, L_2=2,2′-bipyridine (bipy), 4,4′-dimethyl-2,2′-bipyridine (dmbipy), 1,10-phenanthroline (phen); X=Br, L=PPh_3, L_2=bipy). Treatment of the complexes with *bis*(diphenylphosphino)methane (dppm) in refluxing dichloromethane gives $[PdXPh(dppm]_2$. These complexes have been characterised by microanalysis, IR and ^{1}H NMR spectroscopic data together with single crystal X-ray determinations of the phenyl palladium complexes, *trans*-[$PdClPh(PPh_3)_2$], [PdClPh(bipy)], $[PdClPh(dppm)]_2$, and $[PdBrPh(dppm)]_2$. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Palladium; Bipyridyl; Diphenylphosphinomethane; Crystal structure

We have previously reported the synthesis and characterisation of the complexes *trans*-[$PdClPh(SbPh_3)_2$] (**1a**), and [$PdBrPh(SbPh_3)_2$] (**1b**), [1]. We now report that the triphenylantimony ligands in these complexes can be readily displaced by nitrogen, phosphorus and arsenic donor ligands to afford a convenient synthesis of a variety of palladium phenyl complexes including the new dinuclear *bis*(diphenylphosphino)methane complexes $[PdXPh(dppm)]_2$, (X=Cl or Br). Some nitrogen donor ligand complexes of the type [PdXPh(bipy)], (X=Cl, 2d; X=Br, 2e, X=I), has been previously synthesised using [$Pd_2(dba)_3$] (dba=dibenzylideneacetone, PhCH=CHC(O)CH=CHPh) [2], [3] and [PdClPh(dmphen)] (dmphen=2,9-dimethyl-1,10-phenanthroline), has recently been prepared by reaction of [Pd(dimethylmaleate)(dmphen)] with $PbPh_2Cl_2$ [4].

1. Results and discussion

Exchange reactions of triphenylantimony in complexes (**1**) with a variety of donor ligands in dichloromethane afforded the phenyl-palladium complexes (**2**), Scheme 1. The dimeric *bis*(diphenylphosphino)methane bridged complexes of palladium are also conveniently prepared using this method, Scheme 2.

The molecular structure of the complex (**2a**) is shown in Fig. 1 which also gives the crystallographic numbering scheme. Selected bond distances and angles are given in Table 1. The geometry at the palladium in (**2a**) is square planar with *trans* phosphine donors and phenyl *trans* to chlorine. The Pd–P distances (2.314 (1) and 2.322 (1) Å) are similar to those in the palladium(II) phosphine complexes [$PdBr(3,5\text{-}F_2C_6H_2CH{=}NC_6H_5)(PPh_3)_2$] (2.32 3(3) and 2.336(2) Å) [5]. The Pd–C(1) distance (2.005(3) Å) is also similar to that found in the related complex (**1a**) (2.016(7) Å), but the Pd–Cl distance in (**2a**) (2.4002(8) Å) is longer than that found in the complex (**1a**) (2.373(2) Å) [1]. These Pd–Cl distances are longer than those found in the ion $[PdCl_4]^{2-}$ (2.318 Å), consistent with the *trans* influence of a phenyl group [6].

The molecular structure of the complex (**2d**) is shown in Fig. 2 which also gives the crystallographic numbering scheme. Selected bond distances and angles are given in Table 1. The geometry at the palladium in (**2d**) is square planar. Pd–N bond distances (2.057(6)–2.121(6) Å) are similar to those in the complex [PdIPh(bipy)] (2.070(8)–

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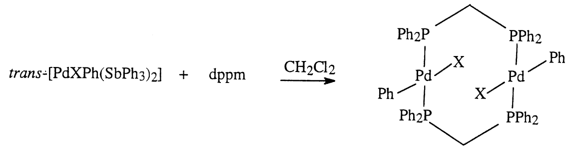
trans-[PdXPh(SbPh$_3$)$_2$] + 2L $\rightarrow$ [PdXPhL$_2$]

	L or L$_2$	X
2a	PPh$_3$	Cl
2b	PPh$_3$	Br
2c	AsPh$_3$	Cl
2d	bipy	Cl
2e	bipy	Br
2f	dmbipy	Cl
2g	phen	Cl

Scheme 1.



3a, X = Cl
3b, X = Br

Scheme 2.

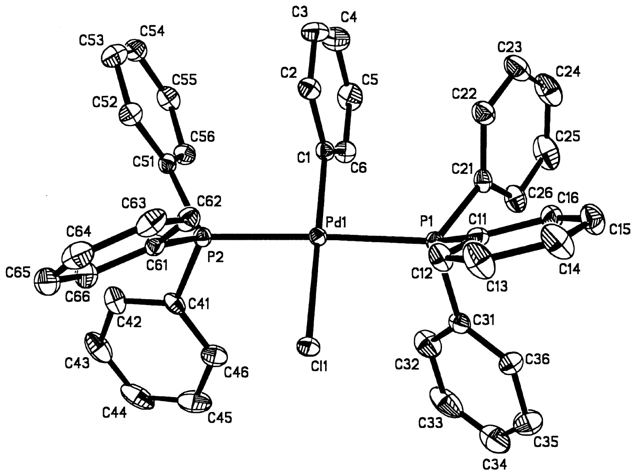


Fig. 1. Molecular structure of **2a** showing the atom numbering scheme. Displacement parameters are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances [Å] and bond angles [°] with estimated standard deviations in parenthesis for (**2a**) and (**2d**)

Complex (**2a**)		Complex (**2d**)	
Bond distances		Bond distances	
Pd–P(1)	2.3144(9)	Pd–N(1)	2.057(6)
Pd–P(2)	2.3223(9)	Pd–N(2)	2.121(6)
Pd–C(1)	2.005(3)	Pd–C(11)	1.970(7)
Pd–Cl	2.4002(8)	Pd–Cl	2.305(2)
Bond angles		Bond angles	
P(1)–Pd–P(2)	177.42(3)	N(1)–Pd–N(2)	78.5(2)
P(1)–Pd–C(1)	90.29(9)	N(1)–Pd–C(11)	94.1(3)
P(2)–Pd–C(1)	91.50(9)	N(2)–Pd–C(11)	171.1(3)
Cl–Pd–P(1)	89.50(9)	N(1)–Pd–Cl	173.7(2)

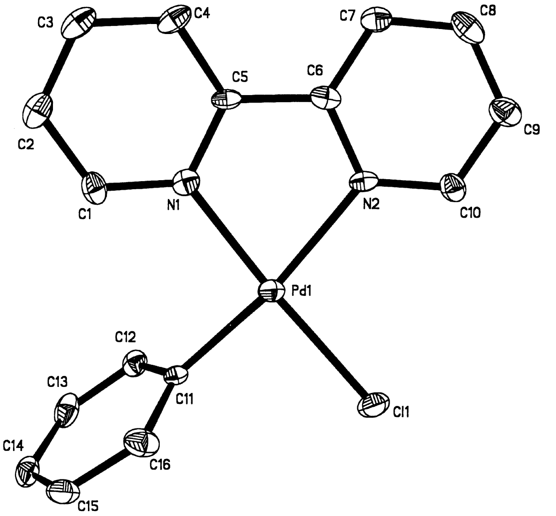


Fig. 2. Molecular structure of **2d** showing the atom numbering scheme. Displacement parameters are shown at the 30% probability level. Hydrogen atoms are omitted for clarity.

2.144(8) Å) [2]. The Pd–N(2) bond length in (**2d**) (2.121(6) Å) is longer than the Pd–N(1) bond length (2.057(6) Å), consistent with the *trans* influence of a phenyl group. The Pd–Cl bond distance (2.305(2) Å) is similar to that reported for [PdPhCl(dmphen)] (2.306(1) Å) [4].

The reaction of [PdXPh(SbPh$_3$)$_2$] (X=Cl or Br) with *bis*(diphenylphosphino) methane in dichloromethane afforded the dimeric σ-phenyl complexes [PdXPh(dppm)]$_2$. The structure determinations of the compounds showed them to be isostructural both being centrosymmetric molecules. The geometry at palladium is square planar with *trans* phosphorus donors and with each diphosphine bridging to two palladium atoms. Selected bond distances and angles are given in Table 2 for (**3a**) and (**3b**). The molecular structures are shown in Figs. 3 and 4, respectively. The Pd–P distances in complex (**3a**) (2.300(2) and 2.329(2) Å) are similar to those found in [PdClMe(dppm)]$_2$ (2.314(1) and 2.329(1) Å) [7]. The

Table 2
Selected bond distances [Å] and bond angles [°] with estimated standard deviations in parenthesis for (**3a**) and (**3b**)

Complex (**3a**)		Complex (**3b**)	
Bond distances		Bond distances	
Pd–P(1)	2.300(2)	Pd–P(1)	2.331(2)
Pd–P(2)	2.329(2)	Pd–P(2)	2.306(2)
Pd–C(11)	2.012(7)	Pd–C(11)	2.041(7)
Pd–Cl	2.427(2)	Pd–Br	2.5510(11)
Bond angles		Bond angles	
P(1)–Pd–P(2)	167.09(6)	P(1)–Pd–P(2)	170.74(7)
P(1)–Pd–C(11)	85.2(2)	P(1)–Pd–C(11)	88.6(2)
P(2)–Pd–C(11)	90.0(2)	P(2)–Pd–C(11)	90.8(2)
Cl–Pd–P(1)	92.90(6)	Br–Pd–P(1)	94.231(6)

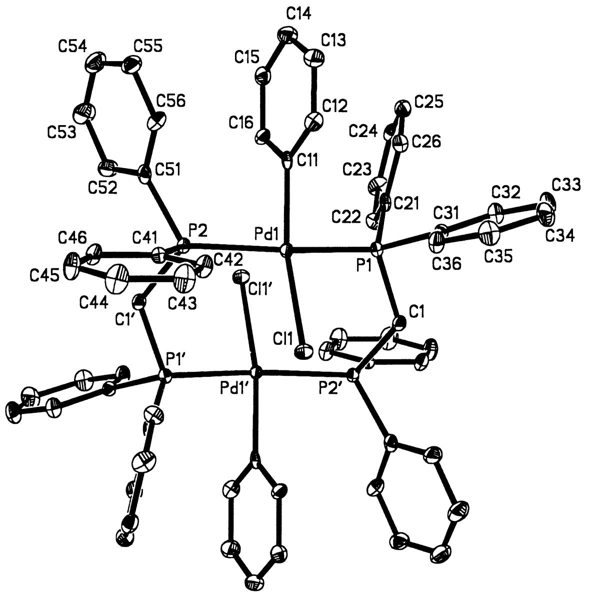


Fig. 3. Molecular structure of **3a** showing the atom numbering scheme. Displacement parameters are shown at the 30% probability level. Primed atoms are generated by a centre of symmetry (symmetry code: $-x$, $-y$, $1-z$). Hydrogen atoms are omitted for clarity.

Pd–C and Pd–Cl distances in complex (**3a**) (2.012(7) and 2.427(2) Å) are similar to those found in $[PdClPh(Ph_2SbCH_2SbPh_2)]_2$ (2.023(5) and 2.411(1) Å) [8].

The X-ray structure results show that the phenyl group is always nearly perpendicular to the coordination plane around palladium. Deviations from 90° are 20.5° (**3b**), 18.4° (**2d**), 14.5° (**2a**), and 8.4° (**3a**).

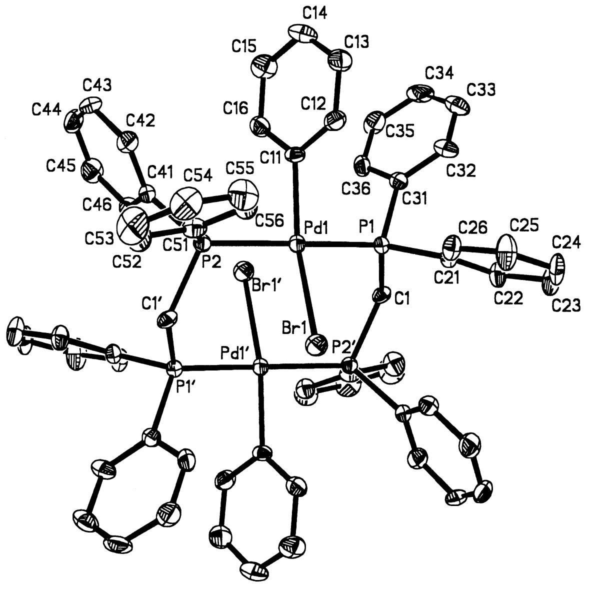


Fig. 4. Molecular structure of **3b** showing the atom numbering scheme. Displacement parameters are shown at the 30% probability level. Primed atoms are generated by a centre of symmetry (symmetry code: $1-x$, $1-y$, $1-z$). Hydrogen atoms are omitted for clarity.

2. Crystallography

Crystals of (**2a**), (**2d**), (**3a**) and (**3b**) suitable for X-ray crystallographic analysis were grown from dichloromethane/diethyl ether at room temperature. The crystal data, a summary of the data collection and structure refinement parameters are given in Table 3. Crystals were glued on glass fibers. Unit cell dimensions were determined by least squares refinement of optimised setting angles. The data were corrected for Lorentz and polarisation effects, and empirical absorption corrections were applied. The structures were solved by Patterson methods (SHELXTL PC) [9], and refined by full matrix least squares using SHELXL 96 [10]. H atoms were included in calculated positions (C–H 0.96 Å). All H atoms had isotropic displacement parameters fixed at 1.2 Ueq of the bonded atom except those of (**2a**) for which $U_{11}=0.05$ Å^2. All non H atoms were refined with anisotropic displacement parameters. Details of the X-ray structure determinations in the form of ClF files for **2a**, **2d**, **3a** and **3b** have been deposited at the Cambridge Crystallographic Data Centre. The deposition numbers are 102989, 102990, 102991 and 102992, respectively.

3. Experimental

All reactions were performed under a dry, oxygen-free, nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. Microanalysis were carried out by Butterworth Laboratories Ltd., 54–56 Waldegrave Road, Teddington, Middlesex TW11 8LG. Melting points were measured on a Reichert Hot stage apparatus and are uncorrected. The FAB mass spectra of the solid complexes were obtained on a Kratos Concept Double Focusing Sector Mass Spectrometer. The ^1H NMR spectra were recorded at room temperature in $[^2H_1]$ chloroform on a BRUKER ARX 250 spectrometer operating at 250.13 MHz with $SiMe_4$ (0.0 ppm) as internal reference. ^{13}C–$\{^1H\}$ NMR spectra were recorded at room temperature in $[^2H_1]$chloroform on a BRUKER ARX 250 spectrometer operating at 62.9 MHz. The ^{31}P–$\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a BRUKER ARX 250 spectrometer operating at 23.1 MHz. The quoted IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer in Nujol mulls between polythene plates in the range 600–200 cm^{-1} or in Nujol mulls between NaCl plates in the range 3000–600 cm^{-1}.

The compounds $[PdXPh(SbPh_3)_2$ I (X=Cl or Br) were prepared as described in the literature [1].

3.1. General procedure

An excess of the ligand (PPh_3, $AsPh_3$, bipy, dmbipy, phen, dppm) in dichloromethane (2 cm^3) was added to a solution of $[PdXPh(SbPh_3)_2]$ (0.1 g) in dichloromethane

Table 3
Crystal data, data collection parameters and refinement details for **2a**, **2d**, **3a** and **3b**

Compound	**2a**	**2d**	**3a**	**3b**
Formula	$C_{42}H_{35}ClP_2Pd$	$C_{16}H_{13}ClN_2Pd$	$C_{31}H_{27}ClP_2Pd$	$C_{31}H_{27}BrP_2Pd$
Mol. wt.	743.49	375.13	603.32	647.78
Lattice	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	*Pbca*	$P2_1/c$	*P*-1	*P*-1
a Å	11.818(2)	9.439(3)	10.181(4)	10.438(2)
b Å	23.594(3)	18.281(3)	11.302(3)	11.709(2)
c Å	25.397(3)	8.738(2)	12.473(5)	12.887(2)
α°	90	90	73.57(2)	72.78(1)
β°	90	112.59(2)	75.79(3)	66.72(1)
γ°	90	90	72.88(3)	66.63(1)
V Å^3, Z	7082(2), 4	1392.1(6), 4	1294.8(8) 2,	1309.9(4), 2
Dc Mg m^3	1.395	1.790	1.547	1.642
μ mm^{-1}	0.719	1.514	0.962	2.375
F(000)	3040	744	612	648
Cell refinement (reflections)	36	26	40	21
Crystal size mm	0.56×0.50×0.46	0.34×0.20×0.07	0.31×0.25×0.21	0.44×0.11×0.10
Crystal colour/shape	Colourless block	Pale yellow plate	Yellow block	Yellow needle
Scan range θ°	2.5–25.0	2.6–25.0	2.5–24.50	2.8–25.0
Scan index limits (*h*, *k*, *l*)	−1 13; −1 28; −1 30	−11 10; −21 1; −1 10	−1	11; −12 12; −14 14
Abs. correction *T* min, max	0.739, 0.768	0.798, 0.912	0.825, 0.878	0.863, 0.975
Data collected	6941	3149	4996	5439
Unique data	5652	2444	4211	4610
Goodness of fit on F^2	1.034	1.023	1.055	1.028
a,*b*[a] in weighting scheme	0.0392, 4.37	0.031, 51.44	0.090, 3.79	0.0496, 1.29
R(int)	0.0217	0.0408	0.0498	0.0479
Observed data [$F>4\sigma(F)$]	4416	1677	3363	2998
*R*1	0.0332	0.0508	0.0563	0.0561
*wR*2(all data)	0.0750	0.1164	0.1610	0.1363
Parameters *n*	415	181	316	316
ΔF e Å^{-3}	0.372, −0.406	1.098, −0.874	1.046, −1.061	0.673, −0.583
Δ/σ	0.002	0.001	0.001	0.001

Details in common: Siemens P4 diffractometer monochromated Mo-Kα radiation (λ=0.7107 Å) omega scans, 190 K.
$R1=\Sigma\|F_o-|F_c\|/\Sigma|F_o|$, $wR2=[w(F_o^2-F_c^2)^2/(F_o^2)^2]^{1/2}$, goodness of fit $s=R[\Sigma w(F_o^2-F_c^2)^2/(n-p)]^{1/2}$ where n=number of reflections and p=total number of parameters.
[a] $w=1/[\sigma^2(Fo^2)+(aP)^2+bP]$ where $P=(Fo^2=Fc_2)$.

(8 cm) and the solution was refluxed for 4 h. The solution was cooled to room temperature and diethyl ether or hexane (10 cm^3) was added. The filtered product was washed with diethyl ether and dried in vacuo.

3.1.1. *[PdClPh(PPh$_3$)$_2$], (2a).*

Yield: 70 mg (88%) colourless crystals from CH_2Cl_2/hexane. (Found; C, 67.9; H, 4.6; Cl, 4.5. $C_{42}H_{35}ClP_2Pd$ calc.; C, 67.8; H, 4.7; Cl, 4.5, %). ^{1}H NMR, δ=7.49–7.19 (30H, m, *Ph*–P), 6.63 (2H, d, $H_{2,6}$–Ph), 6.37 (1H, t, *J*=14.5 Hz, H_4–Ph), 6.22 (2H, t, $H_{3,5}$–Ph). ^{31}P–^{1}{H} NMR, 6=23.86 (s) ppm. FAB mass spectrum: *m*/*z*, 707 [M–Cl]$^+$. IR.: 280 ν(Pd–Cl), cm^{-1}. M.p: 218–222°C (decomp.).

3.1.2. *[PdBrPh(PPh$_3$)$_2$, (2b)*

Yield: 50 mg (61 %), flaky crystals from CH_2Cl_2/hexane. ^{1}H NMR δ=7.61–7.13 (30H, m, *Ph*–P), 6.56 (2H, d, $H_{2,6}$–Ph), 6.28 (1H, t, *J*=14.2 Hz, H_4–Ph), 6.14 (2H, t, $H_{3,5}$–Ph). ^{31}P–^{1}{H} NMR=23.84 ppm (s). FAB mass spectrum: *m*/*z*, 707 [M–Br]$^+$. M.p: 210°C (decomp.).

3.1.3. *[PdClPh(AsPh$_3$)$_2$], (2c).*

Yield: 80 mg (89%), pale yellow solid. ^{1}H NMR δ= 7.36–7.18 (30H, m, *Ph*–As), 6.64–6.26 (5H, br, *Ph*–Pd). FAB mass spectrum: *m*/*z*, 795 [M–Cl]$^+$. IR.: 272 ν(Pd–Cl). M.p: 189–190°C (decomp.).

3.1.4. *[PdClPh(bipy)], (2d)*

Yield: 15 mg (37 %), pale yellow solid. (Found; C, 51.0; H, 3.3; N, 7.5. $C_{18}H_{13}ClN_2Pd$, Calc.; C, 51.2: H, 3.5; N, 7.5%). ^{1}H NMR, δ=9.19 (1H, d, H_4–bipy), 8.04–7.88 (5H, m, $H_{1,10}$, $H_{2,9}$ and H_7–bipy), 7.48 (1H, m, H_3–bipy), 7.35 (2H, d, $H_{12,16}$–Ph), 7.23 (1H, m, H_8–bipy), 7.02–6.88 (3H, m, $H_{13,15}$ and H_{14}–Ph). FAB mass spectrum: *m*/*z*, 339 [M–Cl]$^+$ IR.: 1710, 1590, 1555 ν(N=C), cm^{-1}. M.p: 223–224°C (decomp.).

3.1.5. *[PdBrPh(bipy)], (2e)*

Yield: 15 mg (35%), pale yellow solid. ^{1}H NMR, δ= 9.34 (1H, d, H_4–bipy), 8.04–7.88 (4H, m, $H_{1,10}$ and $H_{2,9}$), 7.82 (1H, d, H_7–bipy), 7.48 (1H, m, H_3–bipy), 7.35 (2H, d, $H_{12,16}$–Ph), 7.23 (1H, m, H_8–bipy), 7.02–6.86 (3H, m,

$H_{13,15}$– and H_{14}–Ph). FAB mass spectrum: *m*/*z*, 419 [M–Br]$^+$. IR.: 1710, 1502, ν(N=C), cm^{-1}. M.p: 220–222°C (decomp.).

3.1.6. ***[PdClPh(dmbipy)], (2f)***

Yield: 28 mg (64 %), pale yellow solid. ^{1}H NMR, δ=9.10 (1H, d, H_4–bipy), 7.86 (3H, m, $H_{1,10}$ and H_7), 7.42 (2H, d, $H_{3,8}$–bipy), 7.35 (2H, d, $H_{14,18}$–Ph), 7.10–6.97 (3H, m, $H_{15,17}$ and H_{16}–Ph), 2.53 (3H, s, Me), 2.48 (3H, s, Me). FAB mass spectrum: *m*/*z*, 367 [M–Cl]$^+$. IR.: 1708, 1605, 1553, ν(N=C), cm^{-1}. M.p: 269–270°C (decomp.).

3.1.7. ***[PdClPh(phen)], (2g)***

Yield: 28 mg (65 %), pale yellow solid. ^{1}H NMR, δ=9.49 (1H, dd, H_2–phen), 8.44 (2H, m, H_4– and H_7–phen), 8.28 (1H, dd, H_9–phen), 7.95–7.81 (3H, m, H_3– and H_8–phen, and H_6–phen), 7.58 (1H, m, H_5–phen), 7.47 (2H, d, $H_{16,20}$–Ph), 7.09–6.93 (3H, m, $H_{17,19}$ and H_{18}–Ph). FAB mass spectrum: *m*/*z*, 363 [M–Cl]$^+$. *R*.: 1708, 1553, 1502 ν(N=C), cm^{-1}. M.p: (decomp.)>300°C.

3.1.8. ***[PdClPh(dppm)]$_2$, (3a)***

Yield: 45 mg (71 %), pale yellow solid. ^{1}H NMR, δ=7.75–7.03 (40H, m, *Ph*–P), 6.75 (2H, br, $H_{12,16}$–Ph), 6.68 (1H, m, *J*=14.2 Hz, H_{14}–Ph), 6.55 (2H, m, $H_{13,15}$–Ph), 3.86–3.6 (4H, br, CH_2). ^{31}P–^{1}{H} NMR, δ=10.5 (s) ppm. FAB mass spectrum: *m*/*z*, 1171 [M–Cl]$^+$. IR.: 280 ν(Pd–Cl), cm^{-1}. M.p: 196–200°C (decomp.).

3.1.9. ***[PdBrPh(dppm)]$_2$, (3b)***

Yield: 46 mg (69%) pale yellow crystals from CH_2Cl_2/hexane. (Found; C, 56.6; H, 4.3; Br, 12.4. $C_{62}H_{54}Br_2P_4Pd_2$ calc.; C, 57.5; H, 4.2; Br, 12.4, %). ^{1}H NMR, δ=7.35–7.17 (40H, m, Ph–P), 6.65 (2H, br, $H_{12,16}$–Ph), 6.53 (1H, m, *J*=14.0 Hz, H_{14}–Ph), 6.45 (2H, m, $H_{13,15}$–Ph) 4.0 (4H, br, CH_2). ^{31}P–^{1}{H} NMR, δ=11.17 (s) ppm. FAB mass spectrum: *m*/*z*, 1215 [M–Br]$^+$. M.p: 184–5°C (decomp.).

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References

[1] A. Mentes, R.D.W. Kemmitt, J. Fawcett, D.R. Russell, J. Organomet. Chem. 528 (1997) 59.

[2] B.A. Markies, A.J. Canty, W. de Graaf, J. Boersma, M.D. Janssen, M.P. Hogerheide, W.J.J. Smeets, A.L. Spek, G. van Koten, J. Organomet. Chem. 482 (1994) 191.

[3] V. De Felice, M.E. Cucciclito, A. De Renzi, F. Ruffo, D. Tesauro, J. Organomet. Chem. 493 (1995) 1.

[4] M.E. Cucciolito, A. De Renzi, F. Giordano, F. Ruffo, Organometallics 14 (1995) 5410.

[5] J. Albert, J. Granell, R. Moragas, J. Sales, M. Font-Bardía, X. Solans, J. Organomet. Chem. 494 (1995) 95.

[6] R.H.B. Mais, P.G. Owston, A.M. Wood, Acta Crystallogr., Sect. B 28 (1972) 393.

[7] S.J. Young, B. Kellenberger, J.H. Reibenspies, S.E. Himmel, M. Manning, O.P. Anderson, J.K. Stille, J. Am. Chem. Soc. 110 (1988) 5744.

[8] A.F. Chiffey, J. Evans, W. Levason, M. Webster, Organometallics 14 (1995) 1522.

[9] G.M. Sheldrick SHELXTL PC, Release 4.2, Siemens Analytical X-Ray Instruments, Madison, WI, 1991.

[10] G.M. Sheldrick, SHELXL 96, Program for Crystal Structure Refinement, University of Göttingen, 1996.