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Synthesis and molecular structure of a new class of bi- and ter-dentate palladium complexes with iminophosphorane containing ligands †

Mateo Alajarín,*[a] Carmen López-Leonardo,[a] Pilar Llamas-Lorente,[a] Delia Bautista ‡[b] and Peter G. Jones §[c]

[a] *Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30100 Murcia, Spain. E-mail: alajarin@um.es*

[b] *Servicio Universitario de Instrumentación Científica, Edificio SACE, Universidad de Murcia, Campus de Espinardo, E-30100 Murcia, Spain. E-mail: dbc@um.es*

[c] *Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de*

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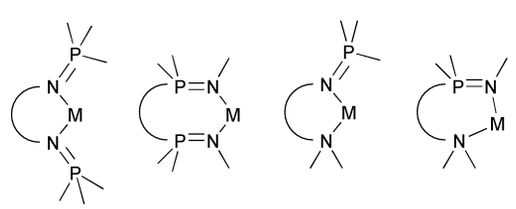
The Michael-type addition of a range of amines to the C=C bond of *P*,*P*,*P*-diphenylvinyl iminophosphoranes yielded a new class of *N*,*N*-bidentate ligands R^1–N=P(Ph_2)CH_2CH_2–NR^2R^3 (**2**). These mixed nitrogen–nitrogen donor ligands react with stoichiometric amounts of $PdCl_2(PhCN)_2$ to give $\sigma N,\sigma N$-palladium complexes **3** containing an iminophosphorane moiety. From primary amines and two vinyl iminophosphorane units, either identical or different, the new terdentate ligands R^1–N=P(Ph_2)CH_2CH_2–N(R^3)–CH_2CH_2P(Ph_2)=N–R^2 (**4**), where $R^1 = R^2$ or $R^1 \neq R^2$, could be efficiently synthesized. Reaction of these ligands with 1.5 equiv. of $PdCl_2(PhCN)_2$ yielded the cationic complexes **5** with the ligands coordinating in a *N*,*N*′,*N*′-terdentate fashion. Additionally, by the use of other nucleophiles such as diphenylphosphane and thiophenol this methodology has been applied to the synthesis of the new *N*,*P*-(R–N=P(Ph_2)$CH_2CH_2PPh_2$) (**9**) and *N*,*S*-bidentate (R–N=P(Ph_2)CH_2CH_2SPh) (**10**) ligands, respectively, and of their corresponding Pd(II) complexes (**11** and **12**). All compounds have been characterized by spectroscopic methods and the X-ray crystal structures of **3c**, **5b** and **11b** are reported.

Introduction

In recent years, bidentate donor species containing sp^2-hybridised nitrogen atoms have attracted much attention as ligands for transition-metal-catalyzed transformations.[1]

Iminophosphoranes (λ^5-phosphazenes), compounds with the general structure R_3P=N–R, date back to 1919,[2a] but their chemistry has been explored mainly in the last three decades. They have found numerous applications, which include their use as ylides in organic synthesis (aza-Wittig reaction) or as building blocks for P–N-backbone polymers (polyphosphazenes).[2] Iminophosphoranes possess a highly polarized P=N bond and have been shown to coordinate to transition metals *via* the approximately sp^2-hybridized nitrogen atom to give stable complexes.[2,3] The most studied complexes incorporating the iminophosphorane moiety are the homobidentate derivatives of type I and II (see below).



There are only a few reports of transition metal complexes of type I.[4] In contrast, derivatives of type II have been studied in depth, with bis(iminophosphoranyl)methane derivatives proving to be versatile ligands.[5] Another class of well-studied ligands are difunctional compounds that contain an iminophosphorane function and a second donor site, in most cases a phosphorus atom from a phosphino group.[6] However, examples of transition metal complexes of type III, that incorporate a nitrogen atom of an amine function as second donor site, are scarce,[7] and to the best of our knowledge there is only one report[7d] on the structurally related complexes of type IV, where the phosphorus atom occupies an endocyclic position.

The small number of examples of type IV $\sigma N,\sigma N$-complexes led us to undertake the study of this poorly explored area. In this communication we present our results on the synthesis of *N*,*N*-ligands with an iminophosphorane unit and an amino group separated by an ethylene tether and their corresponding palladium-complexes.

In common with other electron-withdrawing groups, diphenylphosphinoyl and diphenylthiophosphinoyl groups activate an olefinic residue to nucleophilic (Michael-type) additions with simple nucleophilic species, such as phosphanes,[8] alcohols[9] or amines.[10] The polarity of the P=N bond of an iminophosphorane derived from diphenylvinylphosphane makes the C=C bond of these substrates a potential Michael acceptor unit. In fact, the addition of amines to species of the type CH_2=CH–P(Ph_2)=N–P(X)R_2 has been described recently in the context of the synthesis of dendrimers,[11] and we have reported the addition of diphenylphosphane to CH_2=CH–P(Ph_2)=N–R as a method for the synthesis of monoiminophosphoranes derived from 1,2-bis(diphenylphosphino)ethane.[12]

† Electronic supplementary information (ESI) available: ligand synthesis details. See http://www.rsc.org/suppdata/dt/b2/b209242e/

‡ Corresponding author regarding the X-ray diffraction studies of complexes **3c** and **11b**.

§ Corresponding author regarding the X-ray diffraction studies of complex **5b**.

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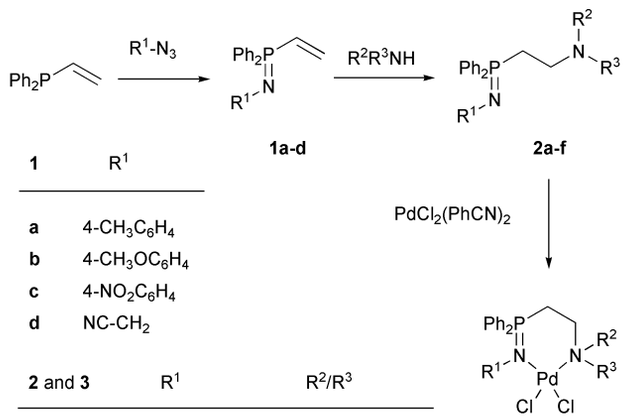
Results and discussion

In the context of our investigations and in conjunction with the literature background in our hands, we envisaged that the Michael-type additions of amines to *P*,*P*,*P*-diphenylvinyl iminophosphoranes could be a potential source of *N*,*N*-ligands for an easy access to complexes of type IV.

The iminophosphoranes **1a**–**c** are readily prepared from the stoichiometric reaction of aryl azides and diphenylvinylphosphane under the standard conditions of the Staudinger imination reaction[2a,c] (Scheme 1). They were isolated after a simple work-up and obtained as crystalline solids in good yields (79–92%, see ESI).†

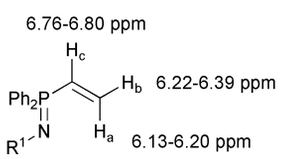


1	R^1
a	4-$CH_3C_6H_4$
b	4-$CH_3OC_6H_4$
c	4-$NO_2C_6H_4$
d	NC-CH_2

2 and 3	R^1	R^2/R^3
a	4-$CH_3C_6H_4$	CH_3/CH_3
b	4-$CH_3C_6H_4$	$(CH_2)_4$
c	4-$CH_3OC_6H_4$	CH_3CH_2/CH_3CH_2
d	4-$CH_3OC_6H_4$	$(CH_2)_5$
e	4-$CH_3OC_6H_4$	$H/CH_3CH_2CH_2$
f	4-$NO_2C_6H_4$	$(CH_2)_5$

Scheme 1

The characterization of **1** was straightforward following their analytical and spectral data. The $^{31}P\{^1H\}$ NMR spectra of **1a**–**c** show a singlet in the range −0.77 to 6.13 ppm. In their ^1H NMR spectra, the signals attributed to the vinylic protons appear as the ABM portion of an ABMX system, due to their coupling with the phosphorus nucleus (Fig. 1).



J_{HH} (Hz)	J_{HP} (Hz)
H_aH_b = 1.3-1.6	H_aP = 21.8-22.5
H_aH_c = 18.3-18.4	H_bP = 36.6-42.9
H_bH_c = 12.4-12.6	H_cP = 22.4-24.0

Fig. 1 ^1H NMR data of *P*-vinyl iminophosphoranes **1**.

The Michael-type addition over the vinyl group of compounds **1** could be carried out efficiently with primary and secondary amines. Thus, refluxing a benzene solution of compounds **1** containing 1.1 equiv. of the cyclic amines pyrrolidine and piperidine or an excess (10 equiv.) of volatile amines such as dimethylamine (2 M solution in THF, bp 60 °C), diethylamine (bp 55 °C) or propylamine (bp 48 °C) the corresponding *N*,*N*-ligands **2a**–**f** were obtained in practically quantitative yields (Scheme 1). After the removal of the solvent and the excess of amine under reduced pressure the residue was washed with n-hexane and the crude **2** so obtained were not submitted to further purification since NMR analysis showed a high degree of purity. The occurrence of the addition was corroborated by the disappearance of the signals of the $CH{=}CH_2$ group in the ^1H and $^{13}C\{^1H\}$ NMR spectra of **2**, as well as by the appearance of the ones corresponding to the new ethylenic group. Thus, in the $^{13}C\{^1H\}$ NMR spectra of **2a**–**f** two methylene resonances are detected, one in the interval δ 24.94–28.68 with a coupling constant ($^1J_{CP}$) of 66.7–72.0 Hz and the other in the interval δ 43.17–52.13, with a $^2J_{CP}$ of 0–1.3 Hz that are assigned to the CH_2P and CH_2N carbons, respectively. These data are in agreement with others previously published, showing that in P(v)-alkyl substituted compounds the value of $^1J_{CP}$ coupling constant is of the order of 60–70 Hz, whereas $^2J_{CP}$ is very small or non-observable.[10g,11b,c] The ^1H NMR spectra of **2a**,**b**,**d** show a multiplet in the range δ 2.45–2.73 as a result of the overlapping of the signals corresponding to the methylene groups of the PCH_2CH_2N backbone, whereas compounds **2c**,**e**,**f** show two separated multiplets centered close to δ 2.60 and 2.80. A bidimensional ^{13}C–^1H COSY NMR experiment on compound **2e** show that the multiplet at lower field is due to the CH_2N group, whereas that at higher field corresponds to the CH_2P group. The nucleophilic addition also induced the deshielding of the signal corresponding to the Ph_2P=NAr phosphorus in the ^{31}P NMR spectra of **2a**–**f** when compared with that of compounds **1** ($\Delta\delta$ = 5.58–5.94 for R^1 = 4-$CH_3C_6H_4$, $\Delta\delta$ = 6.33–7.26 for R^1 = 4-$CH_3OC_6H_4$ and $\Delta\delta$ = 4.93 for R^1 = 4-$NO_2C_6H_4$).

Although the addition of secondary aliphatic amines to the vinyl group of **1** took place successfully, the less basic *N*-substituted anilines did not add under the same conditions.

The ligands **2a**–**f** were allowed to react with an equimolar amount of $PdCl_2(PhCN)_2$ in dichloromethane at room temperature to give the σN,σN-complexes **3a**–**f**, as orange crystalline solids in very good yields (92–98%), the first Pd(II) compounds built on an iminophosphorane-amine skeleton with the atomic connectivity as shown in complexes of type IV (Scheme 1).

An unequivocal proof of that coordination to palladium took place involving the iminophosphorane group is provided by the $^{31}P\{^1H\}$ NMR spectra of complexes **3**. A signal is observed in the range δ 24.44–30.26, remarkably deshielded in relation to the corresponding ligands **2** ($\Delta\delta$ = 18.64–20.07). These chemical shifts are in agreement with the ones described for other iminophosphorane-palladium complexes.[4d,6e,f] On the other hand, differences in chemical shifts and coupling constant values are observed in the $^{13}C\{^1H\}$ NMR spectra of complexes **3** when compared with those of ligands **2**. The doublet assigned to the CH_2P carbon in **3a**–**e** is shifted downfield ($\Delta\delta$ 1.98–3.97) and show a larger coupling constant (Δ^1J_{CP} = 10.3–15.7 Hz) than in the corresponding free ligands **2a**–**e**. The signals attributable to the *ipso* carbons of the Ph_2P group move to lower field on going from **2** to **3** and their *J* values are smaller (Δ^1J_{CP} = 3.0–4.4 Hz). Another notorius difference between **2** and **3** is the splitting of the signal due to the CH_2N group of **3**, with values of $^2J_{CP}$ = 5.4–8.4 Hz, whereas for the free ligands no such coupling constant is observed, with the exception of **2e**.

The chiral nature of complex **3e** due to its stereogenic amine N atom is shown by the magnetic non-equivalence of its diastereotopic phenyl groups of the Ph_2P moiety in its $^{13}C\{^1H\}$ NMR spectrum (for instance C_i: δ 124.18, $^1J_{CP}$ 87.3 Hz and δ 127.22, $^1J_{CP}$ 89.0 Hz).

Crystals of **3c** (R^1 = 4-$CH_3OC_6H_4$, R^2 = R^3 = CH_3CH_2) were grown from dichloromethane–n-hexane and its solid-state structure was clarified by X-ray analysis (Fig. 2). Selected crystallographic data are summarized in Table 3 (see Experimental). In complex **3c** the ligands coordinates in a bidentate manner as a σN,σN-donor forming a puckered six-membered chelate ring, showing a *cis* geometry around the metal with an almost perfect square-planar structure; the mean deviation from the plane Pd, N(1), N(2), Cl(1) and Cl(2) is 0.025 Å. The Pd–Cl bond lengths [2.3109(13) and 2.3166(13) Å] and the Pd–N distances [2.124(4) and 2.063(4) Å] are normal. The natural bite angle of 92.8(2)° for N–Pd–N is larger than the ideal value of 90°. The *trans* angles N(1)–Pd–Cl(1) and N(2)–Pd–Cl(2) of 178.66(11) and 176.75(12)°, respectively, show nearly no deviation from ideality. In the asymmetric unit, molecules

Table 1 Hydrogen bonds (Å and °)

Compound	D–H ··· A	*d*(D ··· H)	*d*(H ··· A)	*d*(D ··· A)	∠(DHA)
3c	C(6)–H(6A) ··· Cl(2)#1	0.99	2.622(0.005)	3.510(0.05)	149.32(0.12)
5b	C(345)–H(345) ··· O(12)#2	0.95	2.56	3.353(7)	141.0
	C(546)–H(546) ··· O(12)#3	0.95	2.57	3.298(6)	133.8
	C(514)–H(514) ··· O(21)#4	0.95	2.45	3.277(7)	145.0
	C(246)–H(246) ··· O(32)#5	0.95	2.47	3.270(6)	141.4
	C(513)–H(513) ··· O(32)#5	0.95	2.41	3.290(6)	154.0
	C(213)–H(213) ··· O(51)	0.95	2.40	3.206(7)	141.4
11b	C(98)–H(98A) ··· Cl(2)#6	0.99	2.654(0.005)	3.633(0.05)	169.97(0.12)

[a] Symmetry transformations used to generate equivalent atoms: #1 x, $1-y$, $-0.5+z$; #2 $-x+1/2$, $y-1/2$, $-z-1/2$; #3 $x+1/2$, $-y+5/2$, $z+1/2$; #4 $-x+1/2$, $y+1/2$, $-z+1/2$; #5 $-x+1$, $-y+2$, $-z$; #6 $-x$, $-y$, $2-z$.

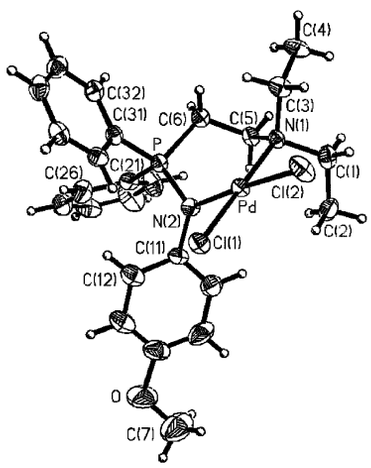


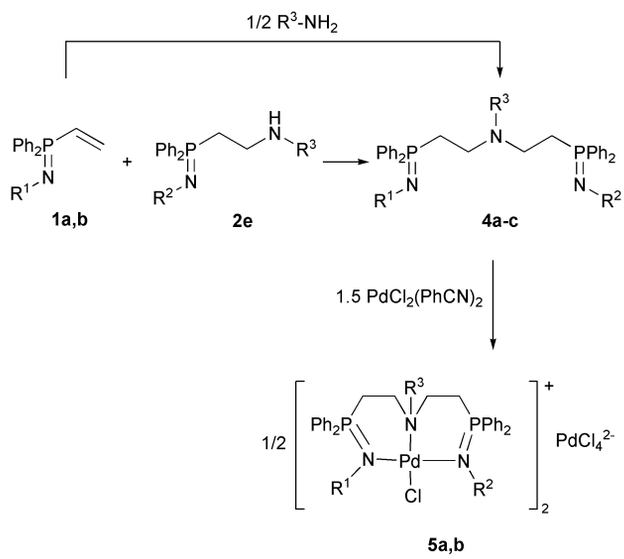
Fig. 2 Thermal ellipsoid plot (50% probability level) of **3c**. Selected bond lenghts (Å) and angles (°): Pd–N(2), 2.063(4), Pd–N(1), 2.124(4), Pd–Cl(1), 2.3109(13), Pd–Cl(2), 2.3166(13), P–N(2), 1.610(4); N(2)–Pd–N(1), 92.8(2), N(2)–Pd–Cl(1), 88.51(12), N(1)–Pd–Cl(1), 178.66(11), N(2)–Pd–Cl(2), 176.75(12), N(1)–Pd–Cl(2), 89.36(11), Cl(1)–Pd–Cl(2), 89.36(5), C(11)–N(2)–P, 124.0(3), C(11)–N(2)–Pd, 119.7(3), P, N(2)–Pd, 114.1(2).

of **3c** associate through intermolecular C–H ··· Cl hydrogen bonding chains parallel to the *y* axis (Table 1).

The iminophosphorane-amine **2e**, obtained by reaction of *P*,*P*,*P*-diphenylvinyl iminophosphorane **1b** and propylamine, was able of adding to a second molecule of *P*-vinyl iminophosphorane **1**, to give the bis(iminophosphoranes) **4a** and **4b**, that can be symmetrically or unsymmetrically substituted depending on the substituents at the iminophosphorane function of each starting material. Thus, reaction of **1a** and **1b** with **2e** in refluxing benzene solution for 5 days afforded **4a** and **4b** in 77 and 80% yield, respectively (Scheme 2).† Alternatively, symmetrically substituted **4** could also be prepared in only one step by treatment of two equiv. of **1** with one equiv. of a primary amine under the above reaction conditions. For example, the addition of benzylamine to **1b** (R^1 = 4-$CH_3OC_6H_4$) afforded the corresponding bis(iminophosphorane) **4c** (R^1 = R^2 = 4-$CH_3OC_6H_4$, R^3 = $C_6H_5CH_2$) in 72% yield.

The addition of **2e** to vinyliminophosphoranes **1** took longer reaction times (5 days) for completion than the addition of simple secondary amines, such as pyrrolidine and piperidine (6 h). The spectroscopic data of the symmetrically substituted adducts **4b**,**c** are very similar to those of **2**, whereas those unsymmetrical, *e.g.* **4a** (R^1 = 4-$CH_3C_6H_4$, R^2 = 4-$CH_3OC_6H_4$, R^3 = $CH_3CH_2CH_2$) displayed the expected splitting of signals due to the presence of two different iminophosphoranylethylene arms. Thus two signals for the CH_2P carbons are observed in the $^{13}C\{^1H\}$ NMR spectrum of **4a**, at δ 24.82 and 24.90, with $^1J_{CP}$ of 65.9 and 66.1 Hz respectively, whereas its $^{31}P\{^1H\}$ NMR spectrum shows two singlets at δ 5.16 and 5.52.

When ligands **4a** and **4b** were reacted with 1 equiv. of $PdCl_2(PhCN)_2$ in dichloromethane solution the cationic Pd



4 and **5**	R^1	R^2	R^3
a	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	$CH_3CH_2CH_2$
b	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	$CH_3CH_2CH_2$
c	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	$C_6H_5CH_2$

Scheme 2

complexes **5a** and **5b** were obtained, as expected for terdentate coordination of **4**, but only in 50 and 60% yield, respectively. After essaying different ratios between both reactants, the best results (87% for **4a** and 92% yield for **4b**) were obtained when 1.5 equiv. of $PdCl_2(PhCN)_2$ were used per equivalent of **4** (Scheme 2). Complexes **5** were isolated as its $[PdCl_4]^{2-}$ salts by crystallization of a dichloromethane solution layered with n-pentane. The formation of **5** took place by means of triple nitrogen coordination of the ligands **4** to palladium with displacement of a chlorine atom from the Pd coordination sphere, and two chloride anions so generated displaced the benzonitrile ligands of a second molecule of $PdCl_2(PhCN)_2$ to form the $[PdCl_4]^{2-}$ anion. Compound **5b** was also characterized by X-ray diffraction. Selected crystallographic data are sumarized in Table 3. The structure consists of four independent cations of **5b**, one $[PdCl_4]^{2-}$ and two ½$[PdCl_4]^{2-}$. The structure of one cation is presented in Fig. 3. A selection of bond lengths and angles is given in Table 2. In the four cations, the Pd-atom [Pd(1), Pd(2), Pd(3) or Pd(5)] is bound to one Cl [Cl(11), Cl(21), Cl(31) or Cl(51)] and to the three N-atoms of the **5b** [N(11), N(12), and N(13), N(21), N(22), and N(23), N(31), N(32), and N(33) or N(51), N(52), and N(53)]. In each cation, the Pd-atom is in a slightly distorted square-planar environment (the mean deviation from the palladium-coordination plane is 0.0074 Å cation I, 0.0448 Å cation II, 0.0467 Å cation III and 0.0512 Å cation IV). Bonds angles around the Pd-atoms range from 177.87(11)–174.85(11)° *trans* NPdCl, 91.06(11)–88.43(11)° *cis*

Table 2 Selected bond lengths (Å) and angles (°) of **5b**

Pd(1)–N(11)	2.059(4)	Pd(5)–N(52)	2.042(4)
Pd(1)–N(12)	2.061(4)	Pd(5)–N(51)	2.071(4)
Pd(1)–N(13)	2.125(4)	Pd(5)–N(53)	2.126(4)
Pd(1)–Cl(11)	2.2996(11)	Pd(5)–Cl(51)	2.2935(12)
Pd(2)–N(22)	2.059(4)	P(11)–N(11)	1.611(4)
Pd(2)–N(21)	2.068(4)	P(12)–N(12)	1.623(4)
Pd(2)–N(23)	2.119(4)	P(21)–N(21)	1.613(4)
Pd(2)–Cl(21)	2.2982(11)	P(22)–N(22)	1.612(4)
Pd(3)–N(32)	2.050(4)	P(31)–N(31)	1.609(4)
Pd(3)–N(31)	2.059(4)	P(32)–N(32)	1.613(4)
Pd(3)–N(33)	2.129(4)	P(51)–N(51)	1.596(5)
Pd(3)–Cl(31)	2.2970(12)	P(52)–N(52)	1.606(4)
N(11)–Pd(1)–N(12)	178.36(15)	C(131)–N(11)–P(11)	125.0(3)
N(11)–Pd(1)–N(13)	88.95(14)	C(131)–N(11)–Pd(1)	119.5(2)
N(12)–Pd(1)–N(13)	92.03(14)	P(11)–N(11)–Pd(1)	112.3(2)
N(11)–Pd(1)–Cl(11)	89.01(11)	C(161)–N(12)–P(12)	121.3(2)
N(12)–Pd(1)–Cl(11)	90.00(11)	C(161)–N(12)–Pd(1)	117.5(2)
N(13)–Pd(1)–Cl(11)	177.87(11)	P(12)–N(12)–Pd(1)	114.7(2)
N(22)–Pd(2)–N(21)	176.21(15)	C(231)–N(21)–P(21)	125.4(3)
N(22)–Pd(2)–N(23)	87.94(14)	C(231)–N(21)–Pd(2)	116.0(2)
N(21)–Pd(2)–N(23)	92.86(14)	P(21)–N(21)–Pd(2)	114.3(2)
N(22)–Pd(2)–Cl(21)	88.93(11)	C(261)–N(22)–P(22)	126.1(3)
N(21)–Pd(2)–Cl(21)	90.41(11)	C(261)–N(22)–Pd(2)	117.4(2)
N(23)–Pd(2)–Cl(21)	176.20(11)	P(22)–N(22)–Pd(2)	109.6(2)
N(32)–Pd(3)–N(31)	175.83(16)	C(331)–N(31)–P(31)	128.2(3)
N(32)–Pd(3)–N(33)	92.76(14)	C(331)–N(31)–Pd(3)	117.4(2)
N(31)–Pd(3)–N(33)	88.10(15)	P(31)–N(31)–Pd(3)	110.2(2)
N(32)–Pd(3)–Cl(31)	90.67(11)	C(361)–N(32)–P(32)	123.0(3)
N(31)–Pd(3)–Cl(31)	88.61(11)	C(361)–N(32)–Pd(3)	116.6(2)
N(33)–Pd(3)–Cl(31)	176.16(11)	P(32)–N(32)–Pd(3)	116.0(2)
N(52)–Pd(5)–N(51)	176.62(16)	C(531)–N(51)–P(51)	123.7(3)
N(52)–Pd(5)–N(53)	87.88(15)	C(531)–N(51)–Pd(5)	116.6(3)
N(51)–Pd(5)–N(53)	92.82(15)	P(51)–N(51)–Pd(5)	116.0(2)
N(52)–Pd(5)–Cl(51)	88.43(11)	C(561)–N(52)–P(52)	127.4(3)
N(51)–Pd(5)–Cl(51)	91.06(11)	C(561)–N(52)–Pd(5)	115.6(2)
N(53)–Pd(5)–Cl(51)	174.85(11)	P(52)–N(52)–Pd(5)	110.0(2)

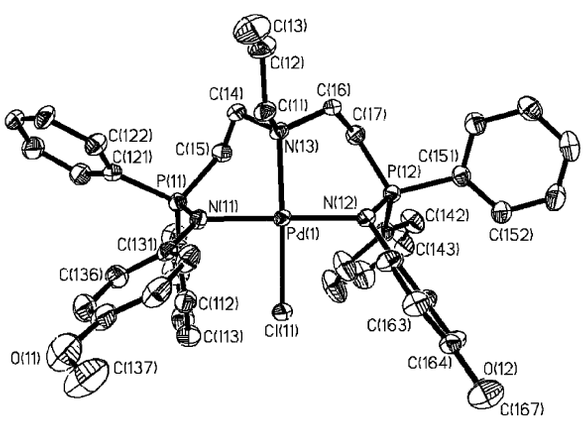


Fig. 3 Thermal ellipsoid plot (50% probability level) of one of the four independent cations of **5b**. Hydrogen atoms are omitted for clarity.

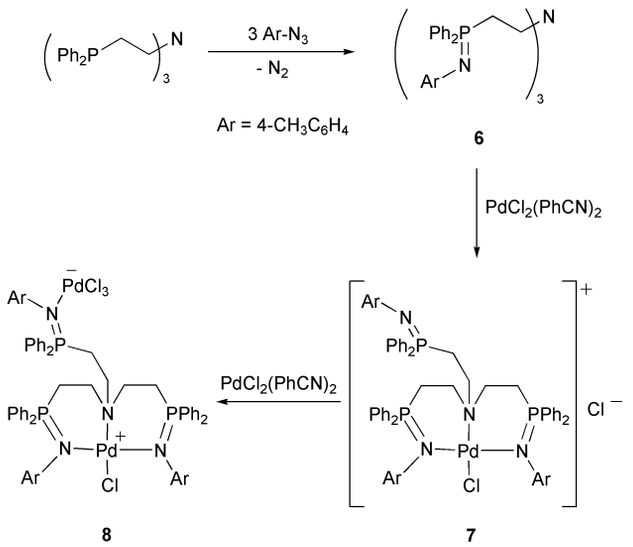
NPdCl, 178.36(15)–175.83(16)° *trans* NPdN, and 92.86(14)–87.88(15)° *cis* NPdN.

The crystal structure of compound **5b** shows a bicyclic system arising from the fusion of the two six-membered rings in the four cations. The metallocycles adopt a boat conformation. Hydrogen bond data are included in Table 1.

The conformation of the C_{2h} symmetrically substituted **5b** in the solid state seems to be kept in solution at 278 K, as shown by its NMR data in $CDCl_3$ at that temperature. The inequivalence of the methylenic pairs of protons of the ethylene fragments is observed in its ^{1}H NMR spectrum where a complex system of multiplets, centered at δ 3.57, 4.05 and 4.55, is clearly shown. The first one is attributed to H_A of each methylene group, CH_2P and CH_2N, whereas the second and third ones are due to H_B of CH_2P and CH_2N, respectively. This assignment has been made on the basis of bidimensional ^{13}C–^{1}H COSY NMR experiments. In the ^{13}C{^{1}H} NMR spectra of **5b** two sets of signals are observed for the two phenyl groups in each arm, that adopt differentiated positions (axial and equatorial) in the six-membered rings. Similar observations are made in the NMR spectra of **5c**. The chiral nature of unsymmetrically substituted **5a** is shown in its NMR spectra in $CDCl_3$. For instance, in its ^{1}H MNR spectrum the methylenic protons of the propyl group are observed as diastereotopic, and in its ^{13}C{^{1}H} NMR spectrum two signals for CH_2P carbons at δ 31.40 and 32.45, with a coupling constant of 78.9 Hz in both cases, are clearly differentiated, as well as four signals for the *ipso* carbons of the Ph_2P phenyl groups (124.51, $^1J_{CP}$ = 87.6 Hz; 124.89, $^1J_{CP}$ = 88.2 Hz; 127.07, $^1J_{CP}$ = 97.9 Hz, and 127.54, $^1J_{CP}$ = 87.0 Hz).

As a further step in the study of ligands combining amine and iminophosphorane functions we next prepared the tris(iminophosphoranyl)amine **6**, whose structure is closely related to its mono (**2**) and bis (**4**) analogous ligands prepared above. The potentially tetradentate ligand **6** was prepared in 90% yield following a completely different method: the Staudinger imination reaction[2a,c] of tris(diphenylphosphinoethyl)amine with 3 equiv. of 4-tolylazide (Scheme 3).†

The reaction between ligand **6** and $PdCl_2(PhCN)_2$ in dichloromethane solution in different stoichiometric combinations was first studied by ^{31}P{^{1}H} NMR spectroscopy and revealed the following trends: (A) When the ratio of reactants is 1 : 1, in addition to the signal at δ 5.39 due to the starting material (**6**), two sets of signals in an approximate 1 : 1 ratio are observed which we attributed to species **7** and **8** (Scheme 3). Putative complex **7** exhibits two phosphorus environments at δ 4.37 and 25.44 in a 1 : 2 intensity ratio, respectively. The high-field resonance falls in the usual range for free iminophosphorane and is therefore assigned to a dangling iminophosphorane arm, while the low-field one is attributed to both equivalent arms coordinated to palladium. On the other hand, the two signals attributed to **8** appear at δ 27.82 and 29.51 in a 2 : 1 intensity ratio. In this binuclear complex the three



Scheme 3

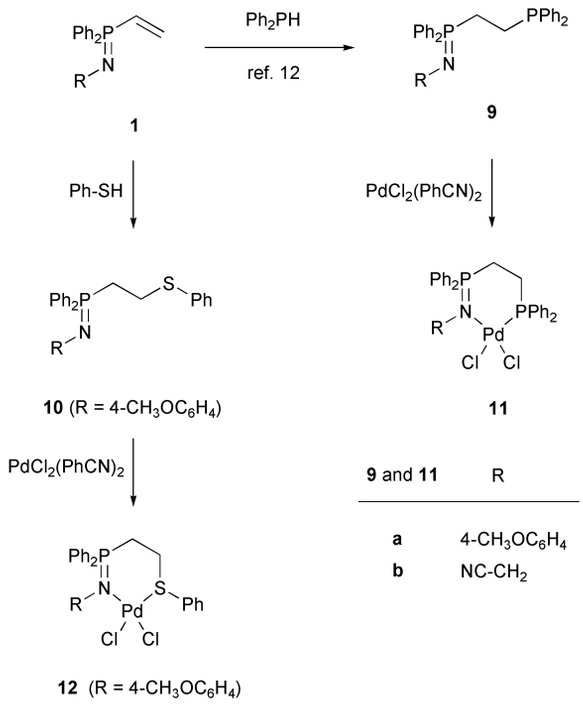
iminophosphorane groups are coordinated to palladium(II), but two arms are equivalent (δ 27.82) and different in nature from the third one (δ 29.51). (B) By increasing the amount of $PdCl_2(PhCN)_2$ to 1.5 equiv., the ratio of products **7/8** was approximately 1 : 2. (C) When the ratio of reactants is 1 : 2, the exclusive formation of complex **8** is observed, which could be isolated as a crystalline solid.

Microanalytical and spectroscopic data support the formulation of complex **8**. Its FAB^+-MS shows a peak corresponding to the fragmentation $M^+ - PdCl_3$ in 48% relative intensity, whereas the molecular ion is detected by the FAB^--MS technique. Its NMR spectra show that the bicyclic moiety keeps a close structural relation with **5b**. In addition to the signals corresponding to the bicyclic framework present in **5b**, others assignable to the dangling $CH_2CH_2P(Ph_2)$=N(Ar)–$PdCl_3$ moiety are observed. Thus, in its $^{13}C\{^1H\}$ NMR spectrum a doublet at δ 33.47 with $^1J_{CP}$ = 79.5 Hz corresponding to the CH_2P carbon, and another at δ 60.30 assignable to the CH_2N carbon, both due to the dangling arm are observed, besides those of the bicycle.

On the other hand, we have previously communicated the synthesis of the $\sigma N,\sigma P$-ligand **9a**, containing iminophosphorane and phosphane units, by means of the Michael-type addition reaction of diphenylphosphane to the vinyliminophosphorane **1b**.[12] Here we now describe the preparation of new examples of similar ligands, and the application of the same methodology for obtaining new $\sigma N,\sigma S$-ligands.

The clean and fast addition of thiophenol to **1b** in benzene provided the iminophosphorane-sulfide **10** in quantitative yield and a high degree of purity (Scheme 4).† The spectroscopic data of **10** are comparable to that of ligands **2** and **9**, with the presumed differences caused by the variation of the heteroatom placed on the ethyl chain (S, N or P). In the $^{13}C\{^1H\}$ NMR spectrum of **10** the doublets at δ 26.05 with $^2J_{CP}$ = 2.1 Hz and δ 28.58 with $^1J_{CP}$ = 63.2 Hz are attributed to the CH_2S and CH_2P methylene groups, respectively. Its $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ 4.97.

The effective coordination of palladium to bidentate ligands **9** and **10** allowed access to the new Pd(II) complexes **11** and **12**, respectively. The reaction of **9a** or **9b** with 1 equiv. of $PdCl_2(PhCN)_2$ at room temperature in dichloromethane led to the formation of $\sigma N,\sigma P$-complexes **11a** (R = 4-$CH_3OC_6H_4$, 92% yield) and **11b** (R = NC–CH_2, 95% yield). A similar transformation converted **10** into the $\sigma N,\sigma S$-complex **12** in 91% yield. These complexes (**11** and **12**) are obtained as stable solids that can be stored for months under a nitrogen atmosphere without noticeable decomposition. There are only a few six-membered cyclic *N,P*-complexes constituted by iminophosphorane and



Scheme 4

phosphane units. In most of the cases the carbon portion on the cycle is derived from a vinylene fragment (–CH=CH–)[6k,n,q] and only in one case is derived from an ethylene fragment (–CH_2–CH_2–).[6e] The absence of crystallographic data for this last example, a *N*-trimethylsilyl derivative of **11**, led us to study the structure in the solid state of **11b** (R = $NCCH_2$) by X-ray diffraction (Fig. 4). Selected crystallographic data are summarized

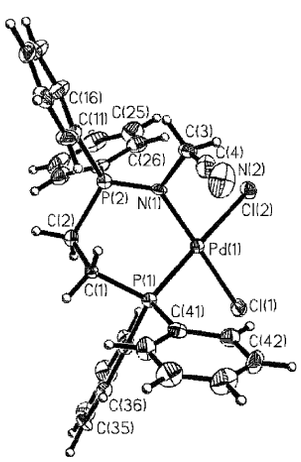


Fig. 4 Thermal ellipsoid plot (50% probability level) of **11b**. Selected bond lenghts (Å) and angles (°): Pd(1)–N(1), 2.046(3), Pd(1)–P(1), 2.2248(12), Pd(1)–Cl(1), 2.2992(10), Pd(1)–Cl(2), 2.3773(11); N(1)–Pd(1)–P(1), 89.22(9), N(1)–Pd(1)–Cl(1), 178.12(9), P(1)–Pd(1)–Cl(1), 89.51(4), N(1)–Pd(1)–Cl(2), 90.27(9), P(1)–Pd(1)–Cl(2), 177.31(4), C(3)–N(1)–P(2), 122.7(3), C(3)–N(1)–Pd(1), 117.0(2), P(2)–N(1)–Pd(1), 117.7(2).

in Table 3. The mean deviation from the plane Pd, N(1), P(1), Cl(1) and Cl(2) is 0.017 Å. The difference between the palladium–chlorine bond lengths Pd(1)–Cl(1) [2.2992(10) Å] and Pd(1)–Cl(2) [2.3773(11) Å] of 0.0781 Å reflects the stronger *trans* influence of the tertiary phosphine compared with the *N*-donor iminophosphorane group. The Pd–N bond length of 2.046(3) and the Pd–P of 2.2248(12) Å are common for this type of complexes. The N–Pd–P bite angle is close to 90° [89.22(9)°]. Hydrogen bond data are included in Table 1.

Each compound **11** shows two well-differentiated signals in the aliphatic region of its $^{13}C\{^1H\}$ NMR spectrum, correspond-

ing to the P(v)CH_2CH_2P(III) portion. The double doublet assigned to the CH_2P(III) carbon appeared at δ 18.67 ($^1J_{CP(III)}$ = 33.6 and $^2J_{CP(V)}$ = 6.4 Hz) for **11a** and δ 19.81 ($^1J_{CP(III)}$ = 32.5 and $^2J_{CP(V)}$ = 5.7 Hz) for **11b**. The doublet assigned to the CH_2P(v) carbon was shifted downfield, at δ 25.01 for **11a** and 25.29 for **11b**, showing only a ^1J coupling constant with the P(v) atom of 77.1 and 72.5 Hz, respectively. Additionally, in the $^{13}C\{^1H\}$ NMR spectra of complexes **11** two differentiated sets of signals for the phenyl rings of the two Ph_2P groups are observed, which show very similar chemical shifts and coupling constants. The $^{31}P\{^1H\}$ NMR spectrum of **11a** shows two doublets ($^3J_{PP}$ = 11.0 Hz) at δ 23.78 and 27.36, whereas for **11b** these doublets appear at δ 22.49 and 36.95 ($^3J_{PP}$ = 14.9 Hz). Both compounds display phosphorus resonances notably shifted downfield when compared with those of the free ligands **9** [**9a**: δ −12.61 and 6.62 ($^3J_{PP}$ = 46.7 Hz) and **9b**: δ −11.42 and 24.63 ($^3J_{PP}$ = 46.3 Hz)], as expected for the coordination in a σN and σP chelate mode.

Microanalytical and spectroscopic data of **12** are consistent with its formulation. Two multiplets at δ 2.92 and 3.20 in its ^1H NMR spectrum and two doublets at δ 28.41 ($^1J_{CP}$ = 79.5 Hz, CH_2P) and 29.87 ($^2J_{CP}$ = 7.5 Hz, CH_2S) in its $^{13}C\{^1H\}$ NMR spectrum are specially significant. The singlet at δ 25.73 in its $^{31}P\{^1H\}$ NMR spectrum along with the appearance of the peak at *m*/*z* 642 (M^+ + 23) in its FAB^+-MS spectrum further corroborate the proposed structure.

Summary

The present investigation has explored the Michael-type addition reaction of different *N*-, *P*- and *S*- nucleophiles to *P*,*P*,*P*-diphenylvinyl iminophosphoranes. By the concourse of several amines, diphenylphosphane and thiophenol we have prepared different *N*,*N*-, *N*,*P*-, and *N*,*S*-bidentate, and *N*,*N*,*N*-tridentate ligands. The corresponding Pd(II) complexes have been obtained and characterized. We believe that this synthetic strategy could be applicable to varied structural motifs. The assessment of the catalytic activity of these complexes in different processes, and additional experimental refinement to obtain new ligands and their complexes with other metals is in progress in our laboratory.

Experimental

All reactions were carried out under nitrogen and using solvents that were dried by routine procedures. Diphenylvinylphosphane and $PdCl_2(PhCN)_2$ were purchased from Aldrich Chemical Co. and used as received. Ligand **9a**[12] and tris(diphenylphosphinoethyl)amine[13] were prepared as reported. Column chromatography was performed with the use of silica gel (70–200 μm) as the stationary phase. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were determined as Nujol mulls or films on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorder at 25 °C on a Bruker AC200 (200 MHz) or a Varian Unity 300 (300 MHz). ^1H and ^{13}C chemical shifts are reported in ppm downfield of internal tetramethylsilane and ^{31}P chemical shifts were externally referenced to 85% H_3PO_4. The mass spectra were recorded on a Hewlett-Packard 5993C spectrometer (EI) or on a VG-Autospec spectrometer (FAB^+ and FAB^-). Microanalyses were performed on a EA 1108 Carlo Erba instrument. The syntheses and data of ligands **1**, **2**, **4**, **6**, **9** and **10** are given in the ESI.†

Synthesis

General procedure for the synthesis of compounds 3. To a dry dichloromethane solution (15 mL) of the corresponding iminophosphorane-amine **2** (0.3 mmol) was added 1 equiv. of $PdCl_2(PhCN)_2$ (0.115 g, 0.3 mmol) under a nitrogen atmosphere. The solution was stirred at 25 °C for 0.5 h. The solvent was removed under vacuum and the residue was treated with dry diethyl ether to give **3** as a solid which was isolated by filtration and dried under reduced pressure.

3a *(R^1 = 4-$CH_3C_6H_4$, R^2 = R^3 = CH_3).* Orange solid (0.155 g, 96%) that was recrystallized from CH_2Cl_2–n-pentane (orange prisms); mp (decomp.) 167–171 °C. IR (Nujol)/cm^{-1}: 1504, 1440, 1288, 1268, 1112, 1021, 876, 729. ^1H NMR ($CDCl_3$): δ 2.10 (s, 3H, CH_3), 2.98 [s, 6H, $(CH_3)_2N$], 2.84–2.88 (m, 4H, PCH_2CH_2N), 6.76 (d, J = 8.1 Hz, 2H, Ar), 7.19 (d, J = 8.1 Hz, 2H, Ar), 7.25–7.54 (m, 4H, Ph_2), 7.55–7.63 (m, 2H, Ph_2), 7.76–7.83 (m, 4H, Ph_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.83 (CH_3), 29.06 (d, $^1J_{CP}$ = 81.4 Hz, CH_2P), 52.24 (CH_3N), 56.26 (d, $^2J_{CP}$ = 7.0 Hz,CH_2N), 126.91 (d, $^1J_{CP}$ = 88.7 Hz, C_i), 127.30 (d, $^3J_{CP}$ = 10.4 Hz, C_2), 128.74 (C_3), 129.45 (d, $^3J_{CP}$ = 12.2 Hz, C_m), 131.55 (C_4), 132.90 (d, $^2J_{CP}$ = 9.9 Hz, C_o), 133.43 (C_p), 145.01 (C_1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.25. FAB^+-MS *m*/*z* (rel. intensity): 540 (M^+ + 2, 6), 538 (M^+, 6), 364 (M^+ + 2-$PdCl_2$, 31), 363 (M^+ + 1-$PdCl_2$, 100), 362 (M^+ − $PdCl_2$, 31), 361 (M^+ − 1-$PdCl_2$, 94). Anal. calc. for $C_{23}H_{27}Cl_2N_2PPd$: C, 51.18; H, 5.04; N, 5.19. Found: C, 50.99; H, 5.21; N, 5.34%.

3b *[R^1 = 4-$CH_3C_6H_4$, R^2 = R^3 = $(CH_2)_4$].* Orange solid (0.166 g, 98%) that was recrystallized from CH_2Cl_2–n-pentane (orange prisms); mp (decomp.) 158–160 °C. IR (Nujol)/cm^{-1}: 1504, 1437, 1285, 1265, 1114, 1023. ^1H NMR ($CDCl_3$): δ 1.89 (m, 2H, CH_2), 2.10 (s, 3H, CH_3), 2.13 (m, 2H, CH_2), 2.80–3.00 (m, 6H, CH_2), 4.22 (m, 2H, CH_2), 6.76 (d, J = 8.1 Hz, 2H, Ar), 7.18 (d, J = 8.1 Hz, 2H, Ar), 7.47–7.54 (m, 4H, Ph_2), 7.59–7.65 (m, 2H, Ph_2), 7.78–7.84 (m, 4H, Ph_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.82 (CH_3), 22.17 (CH_2), 30.25 (d, $^1J_{CP}$ = 82.3 Hz, CH_2P), 52.17 (d, $^2J_{CP}$ = 8.4 Hz, CH_2N), 60.69 (CH_2), 126.19 (d, $^1J_{CP}$ = 88.1 Hz, C_i), 126.75 (d, $^3J_{CP}$ = 9.9 Hz, C_2), 128.72 (C_3), 129.36 (d, $^3J_{CP}$ = 12.3 Hz, C_m), 131.11 (C_4), 133.01 (d, $^2J_{CP}$ = 10.0 Hz, C_o), 133.35 (d, $^4J_{CP}$ = 2.3 Hz, C_p), 145.05 (C_1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.57. FAB^+-MS *m*/*z* (rel. intensity): 566 (M^+ + 2, 15), 564 (M^+, 16), 563 (M^+ − 1, 12), 390 (M^+ + 2-$PdCl_2$, 54), 389 (M^+ + 1-$PdCl_2$, 100), 388 (M^+ − $PdCl_2$, 62), 387 (M^+ − 1-$PdCl_2$, 96). Anal. calc. for $C_{25}H_{29}Cl_2N_2PPd$: C, 53.07; H, 5.17; N, 4.95. Found: C, 53.24; H, 5.29; N, 5.13%.

3c *(R^1 = 4-$CH_3OC_6H_4$, R^2 = R^3 = CH_3CH_2).* Orange solid (0.16 g, 92%) that was recrystallized from CH_2Cl_2–n-pentane (orange prisms); mp (decomp.) 143–145 °C. IR (Nujol)/cm^{-1}: 1506, 1442, 1234, 1111, 1015, 748, 727. ^1H NMR ($CDCl_3$): δ 1.57–1.60 (m, 6H, CH_3CH_2), 2.90–3.10 (m, 6H, CH_3CH_2 + CH_2), 3.38 (m, 2H, CH_2), 3.59 (s, 3H, OCH_3), 6.45 (d, J = 8.5 Hz, 2H, Ar), 7.15 (d, J = 8.5 Hz, 2H, Ar), 7.43–7.50 (m, 4H, Ph_2), 7.55–7.66 (m, 2H, Ph_2), 7.80–7.86 (m, 4H, Ph_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.94 (CH_2CH_3), 28.91 (d, $^1J_{CP}$ = 82.4 Hz, CH_2P), 47.44 (d, $^2J_{CP}$ = 6.5 Hz,CH_2N), 55.20 (OCH_3), 55.28 (CH_2CH_3), 113.25 (C_3), 126.79 (d, $^1J_{CP}$ = 88.1 Hz, C_i), 128.47 (d, $^3J_{CP}$ = 9.9 Hz, C_2), 129.27 (d, $^3J_{CP}$ = 12.2 Hz, C_m), 132.89 (d, $^2J_{CP}$ = 9.9 Hz, C_o), 133.18 (C_p), 140.69 (C_1), 154.79 (C_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.63. FAB^+-MS *m*/*z* (rel. intensity): 584 (M^+ + 2, 22), 583 (M^+ + 1, 15), 582 (M^+, 18), 408 (M^+ + 2-$PdCl_2$, 91), 407 (M^+ + 1-$PdCl_2$, 65), 406 (M^+ − $PdCl_2$, 100), 405 (M^+ − 1-$PdCl_2$, 72). Anal. calc. for $C_{25}H_{31}Cl_2N_2OPPd$: C, 51.43; H, 5.35; N, 4.80. Found: C, 51.24; H, 5.49; N, 4.66%.

3d *[R^1 = 4-$CH_3OC_6H_4$, R^2 = R^3 = $(CH_2)_5$].* Orange solid (0.17 g, 96%) that was recrystallized from CH_2Cl_2–n-hexane (orange prisms); mp (decomp.) 172–174 °C. IR (Nujol)/cm^{-1}: 1506, 1436, 1234, 1120, 1023, 859, 732. ^1H NMR (CD_2Cl_2): δ 1.54–1.79 [m, 6H, $N(CH_2CH_2)_2CH_2$], 2.92 (m, 2H, CH_2P), 3.09–3.20 [m, 4H, $N(CH_2CH_2)_2CH_2$], 3.64 (s, 3H, OCH_3), 4.30 (m, 2H, CH_2N), 6.53 (d, J = 8.9 Hz, 2H, Ar), 7.18 (d, J = 8.9 Hz, 2H, Ar), 7.50–7.56 (m, 4H, Ph_2), 7.63–7.68 (m, 2H, Ph_2), 7.76–7.84 (m, 4H, Ph_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 21.09 [$N(CH_2CH_2)_2$-CH_2], 23.39 [$N(CH_2CH_2)_2CH_2$], 29.03 (d, $^1J_{CP}$ = 84.1 Hz, CH_2P), 46.33 (d, $^2J_{CP}$ = 5.4 Hz, CH_2N), 55.32 (OCH_3), 57.41 [$N(CH_2CH_2)_2CH_2$], 113.34 (C_3), 126.65 (d, $^1J_{CP}$ = 87.4 Hz, C_i), 128.05 (d, $^3J_{CP}$ = 10.4 Hz, C_2), 129.42 (d, $^3J_{CP}$ = 12.2 Hz, C_m),

133.03 (d, $^2J_{CP}$ = 9.9 Hz, C_o), 133.60 (br s, C_p), 140.88 (C_1), 155.13 (C_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.28. FAB^+-MS *m/z* (rel. intensity): 596 (M^+ + 2, 8), 594 (M^+, 8), 420 (M^+ + 2-$PdCl_2$, 42), 419 (M^+ + 1-$PdCl_2$, 100), 418 (M^+ − $PdCl_2$, 48), 417 (M^+ − 1-$PdCl_2$, 89). Anal. calc. for $C_{26}H_{31}Cl_2N_2OPPd$: C, 52.41; H, 5.24; N, 4.70. Found: C, 52.59; H, 5.36; N, 4.64%.

3e *(R^1 = 4-$CH_3OC_6H_4$, R^2 = H, R^3 = $CH_3CH_2CH_2$).* Orange solid (0.163 g, 96%) that was recrystallized from CH_2Cl_2–n-hexane (orange prisms); mp (decomp.) 198–200 °C. IR (Nujol)/cm^{-1}: 1504, 1440, 1237, 1114, 1041, 723, 667. ^1H NMR ($CDCl_3$): δ 0.98 (t, J = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 2.12 (sextet, J = 7.3 Hz, 2H, $CH_2CH_2CH_3$), 2.62–2.88 (m, 3H, CH_2), 3.07–3.17 (m, 2H, CH_2), 3.43 (m, 1H, CH_2), 3.62 (s, 3H, OCH_3), 4.84 (m, 1H, NH), 6.50 (d, J = 8.7 Hz, 2H, Ar), 7.13 (d, J = 8.7 Hz, 2H, Ar), 7.31–7.36 (m, 4H, Ph_2), 7.43–7.65 (m, 4H, Ph_2), 8.26–8.33 (m, 2H, Ph_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.57 (CH_2-CH_2CH_3), 22.19 ($CH_2CH_2CH_3$), 30.97 (d, $^1J_{CP}$ = 82.3 Hz, CH_2P), 42.97 (d, $^2J_{CP}$ = 5.8 Hz, CH_2N), 55.26 (OCH_3), 56.49 ($CH_2CH_2CH_3$), 113.45 (C_3), 124.18 (d, $^1J_{CP}$ = 87.3 Hz, C_i), 127.22 (d, $^1J_{CP}$ = 89.0 Hz, C_i), 127.52 (d, $^3J_{CP}$ = 10.8 Hz, C_2), 129.22 (d, $^3J_{CP}$ = 10.9 Hz, C_m), 129.44 (d, $^3J_{CP}$ = 11.3 Hz, C_m), 132.59 (d, $^2J_{CP}$ = 8.9 Hz, C_o), 133.11 (br s, C_p), 133.41 (br s, C_p), 133.52 (d, $^2J_{CP}$ = 10.7 Hz, C_o), 140.53 (C_1), 154.56 (C_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.44. FAB^+-MS *m/z* (rel. intensity): 570 (M^+ + 2, 17), 569 (M^+ + 1, 23), 568 (M^+, 19), 394 (M^+ + 2-$PdCl_2$, 32), 393 (M^+ + 1-$PdCl_2$, 100), 392 (M^+ − $PdCl_2$, 37), 391 (M^+ − 1-$PdCl_2$, 95). Anal. calc. for $C_{24}H_{29}Cl_2N_2OPPd$: C, 50.59; H, 5.13; N, 4.92. Found: C, 50.72; H, 5.40; N, 4.79%.

3f *[R^1 = 4-$NO_2C_6H_4$, R^2 = R^3 = $(CH_2)_5$].* Orange solid (0.17 g, 93%) that was recrystallized from CH_2Cl_2 (orange prisms); mp (decomp.) 195–197 °C. IR (Nujol)/cm^{-1}: 1504, 1497, 1295, 1283, 1112, 732. ^1H NMR ($CDCl_3$): δ 1.46–1.72 [m, 6H, N(CH_2-CH_2)$_2$$CH_2$], 2.95–3.1 [m, 6H, CH_2P + N(CH_2CH_2)$_2$$CH_2$], 4.19 (m, 2H, CH_2N), 7.36 (d, J = 9.0 Hz, 2H, Ar), 7.52–7.55 (m, 4H, Ph_2), 7.63–7.72 (m, 6H, Ph_2), 7.78 (d, J = 9.0 Hz, 2H, Ar). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.26. FAB^+-MS *m/z* (rel. intensity): 611 (M^+ + 2, 5), 609 (M^+, 5), 435 (M^+ + 2-$PdCl_2$, 93), 434 (M^+ + 1-$PdCl_2$, 48), 433 (M^+ − $PdCl_2$, 100), 432 (M^+ − 1-$PdCl_2$, 54). Anal. calc. for $C_{25}H_{28}Cl_2N_3O_2PPd$: C, 49.16; H, 4.62; N, 6.88. Found: C, 49.01; H, 4.49; N, 7.01%.

General procedure for the synthesis of compounds 5. To a dry dichloromethane solution (15 mL) of the corresponding bis(iminophosphorane) **4** (0.3 mmol) was added 1.5 equiv. of $PdCl_2(PhCN)_2$ (0.17 g, 0.45 mmol) under a nitrogen atmosphere. The solution was stirred at 25 °C for 0.5 h. The solvent was removed under vacuum and the residue was treated with dry diethyl ether to give **5** as a red solid which was isolated by filtration and dried under reduced pressure. Analytically pure samples were obtained by recrystallization from CH_2Cl_2–n-pentane (red prisms).

5a *(R^1 = 4-$CH_3C_6H_4$, R^2 = 4-$CH_3OC_6H_4$, R^3 = $CH_3CH_2CH_2$).* Yield (0.51 g, 87%); mp 170–172 °C. IR (Nujol)/cm^{-1}: 1504, 1439, 1265, 1241, 1114, 996, 834, 666 (m). ^1H NMR ($CDCl_3$): δ 1.18 (t, J = 7.2 Hz, 3H, $CH_2CH_2CH_3$), 2.11 (s, 3H, CH_3), 2.59 (m 1H, $CH_2CH_2CH_3$), 2.73 (m, 1H, $CH_2CH_2CH_3$), 3.45–3.77 (m, 6H, $CH_2CH_2CH_3$+ 2 CH_AH_BP + 2 CH_AH_BN), 3.61 (s, 3H, OCH_3), 3.88–4.17 (m, 2H, 2 CH_AH_BP), 4.40–4.60 (m, 2H, 2 CH_AH_BN), 6.52 (d, J = 8.8 Hz, 2H, H-3), 6.76 (d, J = 8.2 Hz, 2H, H-3′), 7.06 (d, J = 8.2 Hz, 4H, H-2 + H-2′), 7.23–7.30 (m, 8H, Ph_2), 7.38–7.46 (m, 2H, Ph_2), 7.51–7.64 (m, 6H, Ph_2), 8.17–8.32 (m, 4H, Ph_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 11.97 ($CH_2CH_2CH_3$), 20.54 ($CH_2CH_2CH_3$), 20.72 (CH_3), 31.40 (d, $^1J_{CP}$ = 78.9 Hz, CH_2P), 32.45 (d, $^1J_{CP}$ = 78.9 Hz, CH_2P), 54.48 (2 CH_2N), 55.26 (OCH_3), 68.56 ($CH_2CH_2CH_3$), 113.70 (C_3), 124.51 (d, $^1J_{CP}$ = 87.6 Hz, C_i), 124.89 (d, $^1J_{CP}$ = 88.2 Hz, C_i), 126.10 (d, $^3J_{CP}$ = 11.6 Hz, $C_{2'}$), 127.07 (d, $^1J_{CP}$ = 97.9 Hz, C_i), 127.54 (d, $^1J_{CP}$ = 87.0 Hz, C_i), 128.05 (d, $^3J_{CP}$ = 10.4 Hz, C_2), 128.98 ($C_{3'}$)129.02 (d, $^3J_{CP}$ = 12.2 Hz, 2 C_m), 129.36 (d, $^3J_{CP}$ = 14.5 Hz, 2 C_m), 130.87 ($C_{4'}$), 132.58 (d, $^2J_{CP}$ = 8.7 Hz, 2 C_o), 132.86–133.02 (4 C_p), 133.63 (d, $^2J_{CP}$ = 10.4 Hz, 2 C_o), 140.40 (C_1), 144.97 ($C_{1'}$), 154.81 (C_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.75, 25.98. FAB^+-MS *m/z* (rel. intensity): 852 [½(M^+–$PdCl_4$) + 2, 99], 851 [½(M^+ − $PdCl_4$) + 1, 61], 850 [½(M^+ − $PdCl_4$), 100], 849 [½(M^+ − $PdCl_4$) − 1, 65], 815 [½(M^+ − $PdCl_4$) − Cl, 22], 306 (12), 290 (16). Anal. calc. for $C_{90}H_{98}Cl_6N_6O_2P_4Pd_3$: C, 55.39; H, 5.06; N, 4.21. Found: C, 55.25; H, 4.92; N, 4.31%.

5b *(R^1 = R^2 = 4-$CH_3OC_6H_4$, R^3 = $CH_3CH_2CH_2$).* Yield (0.55 g, 92%); mp 184–186 °C. IR (Nujol)/cm^{-1}: 1506, 1437, 1240, 1112, 1042, 669. ^1H NMR ($CDCl_3$): δ 1.16 (t, J = 7.2 Hz, 3H, $CH_2CH_2CH_3$), 2.66 (m, 2H, $CH_2CH_2CH_3$), 3.48–3.65 (m, 6H, $CH_2CH_2CH_3$+ 2 CH_AH_BP + 2 CH_AH_BN), 3.60 (s, 6H, OCH_3), 4.05 (m, 2H, 2 CH_AH_BP), 4.55 (m, 2H, 2 CH_AH_BN), 6.50 (d, J = 8.7 Hz, 4H, H-3), 7.04 (d, J = 8.7 Hz, 4H, H-2), 7.22–7.26 (m, 8H, Ph_2), 7.36–7.42 (m, 2H, Ph_2), 7.49–7.61 (m, 6H, Ph_2), 8.20–8.27 (m, 4H, Ph_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 12.00 ($CH_2CH_2CH_3$), 20.59 ($CH_2CH_2CH_3$), 31.68 (d, $^1J_{CP}$ = 80.6 Hz, CH_2P), 54.53 (d, $^2J_{CP}$ = 6.4 Hz, CH_2N), 55.27 (OCH_3), 68.46 ($CH_2CH_2CH_3$), 113.70 (C_3), 124.68 (d, $^1J_{CP}$ = 88.2 Hz, C_i), 127.68 (d, $^3J_{CP}$ = 11.0 Hz, C_2), 128.20 (d, $^1J_{CP}$ = 89.9 Hz, C_i), 128.90 (d, $^3J_{CP}$ = 12.2 Hz, C_m), 129.40 (d, $^3J_{CP}$ = 12.8 Hz, C_m), 132.62 (d, $^2J_{CP}$ = 9.3 Hz, C_o), 132.88 (br s, C_p), 133.01 (br s, C_p), 133.62 (d, $^2J_{CP}$ = 11.0 Hz, C_o), 140.46 (C_1), 154.75 (C_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.89. FAB^+-MS *m/z* (rel. intensity): 868 [½(M^+ − $PdCl_4$) + 2, 99], 867 [½(M^+ − $PdCl_4$) + 1, 67], 866 [½(M^+ − $PdCl_4$), 100], 865 [½(M^+ − $PdCl_4$) − 1, 64], 833 [½(M^+ − $PdCl_4$) − Cl, 18], 417 (35), 334 (96), 322 (26). Anal. calc. for $C_{90}H_{98}Cl_6N_6O_4P_4Pd_3$: C, 54.49; H, 4.98; N, 4.24. Found: C, 54.61; H, 5.11; N, 4.32%.

Synthesis of complex 8. A solution of 2 equiv. of $PdCl_2(PhCN)_2$ (0.23 g, 0.6 mmol) in dry dichloromethane was added slowly, under a nitrogen atmosphere, to a dry dichloromethane solution (15 mL) of tris(iminophosphorane) **6** (0.29 g, 0.3 mmol). The solution was stirred at 25 °C for 0.5 h. The solvent was removed under vacuum and the residue was treated with dry diethyl ether to give **8** as a red solid which was isolated by filtration and dried under reduced pressure. An analytically pure sample was obtained by recrystallization from CH_2Cl_2–n-pentane (red prisms). Yield (0.37 g, 94%); mp 199–201 °C. IR (Nujol)/cm^{-1}: 1504, 1439, 1252 (m), 1111, 845, 722, 692. ^1H NMR (CD_2Cl_2): δ 2.09 (s, 6H, CH_3), 2.12 (s, 3H, CH_3), 2.97–3.07 (m, 2H, CH_2), 3.45–3.58 (m, 2H, CH_2), 3.69–3.83 (m, 2H, CH_2), 4.03–4.27 (m. 4H, CH_2), 5.40 (m, 2H, CH_2), 6.66 (d, J = 8.1 Hz, 4H, Ar), 6.77 (d, J = 8.4 Hz, 2H, Ar), 6.96 (d, J = 8.1 Hz, 4H, Ar), 7.25–7.39 (m, 8H, Ph_2), 7.41–7.48 (m, 6H, Ph_2), 7.54–7.75 (m, 8H, Ph_2), 7.73 (d, J = 8.4 Hz, 2H, Ar), 7.99–8.15 (m, 8H, Ph_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 20.26 (CH_3), 20.46 (2 CH_3), 32.18 (d, $^1J_{CP}$ = 82.4 Hz, 2 CH_2P), 33.47 (d, $^1J_{CP}$ = 79.5 Hz, CH_2P), 57.26 (d, $^2J_{CP}$ = 6.4 Hz, 2 CH_2N), 60.30 (CH_2N), 123.44 (d, $^1J_{CP}$ = 89.9 Hz, 2 C_i), 125.03 (d, $^1J_{CP}$ = 87.6 Hz, 2 C_i), 125.39 (d, $^3J_{CP}$ = 12.2 Hz, C_2), 126.77 (d, $^2J_{CP}$ = 11.0 Hz, 2 C_2), 127.02 (d, $^1J_{CP}$ = 86.5 Hz, 2 C_i), 128.62 (br s, 3 C_3), 129.12–129.69 (m, C_m), 131.50 (br s, 3 C_4), 133.06–133.92 (m, C_o + C_p), 144.67 (2 C_1), 145.93 (C_1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.82 (2 P), 29.51 (1 P). FAB^+-MS *m/z* (rel. intensity): 1109 (M^+ − $PdCl_3$, 48), 1074 (M^+ − $PdCl_4$, 15), 307 (100). FAB^--MS *m/z* (rel. intensity): 1320 (M^-, 3), 188 (100). Anal. calc. for $C_{63}H_{63}Cl_4N_4P_3Pd_2$: C, 57.16; H, 4.80; N, 4.23. Found: C, 57.06; H, 4.68; N, 4.12%.

General procedure for the synthesis of compounds 11. To a dry dichloromethane solution (15 mL) of the corresponding iminophosphorane-phosphane **9** (0.3 mmol) was added 1 equiv. of $PdCl_2(PhCN)_2$ (0.115 g, 0.3 mmol) under a nitrogen atmosphere. The solution was stirred at 25 °C for 0.5 h. The solvent was removed under vacuum and the residue was treated with dry diethyl ether to give **10** as a yellow solid which was isolated by filtration and dried under reduced pressure. Analytically

Table 3 Crystallographic data for compounds **3c**, **5b** and **11b**

	3c·0.5CH_2Cl_2	**5b**·10CH_2Cl_2	**11b**·2CH_2Cl_2
Empirical formula	$C_{25.50}H_{32}Cl_3N_2OPPd$	$C_{95}H_{108}Cl_{16}N_6O_4P_4Pd_3$	$C_{30}H_{30}Cl_6N_2P_2Pd$
Formula weight	626.25	2408.15	799.60
Temperature/K	173(2)	133(2)	173(2)
Wavelength/Å	0.71073	0.71073 Å	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*C*2/*c*	*P*21/*n*	*Pbca*
a/Å	21.920(2)	22.316(2)	13.6655(12)
b/Å	19.798(2)	25.460(3)	22.307(2)
c/Å	16.2440(10)	36.865(4)	22.333(2)
β/°	129.06	101.293(5)	90
Volume/Å^3	5473.8(8)	20540(4)	6808.1(10)
Z	8	8	8
Absorption coefficient/mm^{-1}	1.051	1.051	1.134
F(000)	2552	9776	3216
Crystal size/mm	0.38 × 0.25 × 0.11	0.55 × 0.28 × 0.10	0.30 × 0.20 × 0.10
Reflections collected	5260	277026	6894
Independent reflections	4821 [*R*(int) = 0.0361]	50104 [*R*(int) = 0.0505]	5990 [*R*(int) = 0.0317]
Refinement method	Full-matrix least-squares on F^2	Full-matrix-block least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4820/250/323	50104/1858/2306	5990/0/360
Final *R* indices [$I > 2\sigma(I)$][a]	*R*1 = 0.0458, *wR*2 = 0.1151	*R*1 = 0.0598, *wR*2 = 0.1470	*R*1 = 0.0378, *wR*2 = 0.0510
R indices (all data)[b]	*R*1 = 0.0685, *wR*2 = 0.1252	*R*1 = 0.1069, *wR*2 = 0.1777	*R*1 = 0.0852, *wR*2 = 0.0585
Absorption correction	Psi-scans	Semi-empirical from equivalents	—

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

pure samples were obtained by recrystallization from dichloromethane (yellow prisms).

11a *(R = 4-$CH_3OC_6H_4$)*. Yield (0.19 g, 92%); mp 202–204 °C. IR (Nujol)/cm^{-1}: 1504, 1436, 1239, 1113, 724, 693, 665. ^{1}H NMR ($CDCl_3$): δ 2.66 (m, 2H, CH_2), 2.88 (m, 2H, CH_2), 3.61 (s, 3H, OCH_3), 6.43 (dd, $^3J_{HH}$ = 8.9 Hz, J_{HP} = 0.5 Hz, 2H, Ar), 6.84 (dd, $^3J_{HH}$ = 8.9 Hz, J_{HP} = 1.3 Hz, 2H, Ar), 7.44–7.58 (m, 10H, Ph_2), 7.61–7.67 (m, 2H, Ph_2), 7.81–7.96 (m, 8H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 18.67 [dd, $^1J_{CP(III)}$ = 33.6 Hz, $^2J_{CP(V)}$ = 6.4 Hz, CH_2P(III)], 25.01 [d, $^1J_{CP(V)}$ = 77.1 Hz, CH_2P(V)], 55.16 (OCH_3), 113.14 (C_3), 126.94 (d, $^1J_{CP}$ = 92.8 Hz, C_i), 128.83 (d, $^3J_{CP}$ = 11.6 Hz, C_m), 129.30 (d, $^3J_{CP}$ = 12.2 Hz, C_m), 129.43 (d, $^3J_{CP}$ = 7.5 Hz, C_2), 131.70 (d, $^4J_{CP}$ = 2.3 Hz, C_p), 132.91 (d, $^2J_{CP}$ = 9.9 Hz, C_o), 133.42 (d, $^4J_{CP}$ = 2.3 Hz, C_p), 133.60 (d, $^2J_{CP}$ = 10.4 Hz, C_o), 139.98 (C_1), 155.39 (C_4). One C_i not observed. ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.78 [d, $^3J_{PP}$ = 11.0 Hz, P(III)], 27.36 [d, $^3J_{PP}$ = 11.0 Hz, P(V)]. FAB$^+$-MS *m*/*z* (rel. intensity): 662 (M^+ + 2-Cl, 97), 661 (M^+ + 1 − Cl, 50), 660 (M^+ − Cl, 100), 659 (M^+ − 1 − Cl, 66), 625 (M^+ − 2Cl, 69), 519 (M^+ − $PdCl_2$, 15). Anal. calc. for $C_{33}H_{31}Cl_2NOP_2Pd$: C, 56.88; H, 4.48; N, 2.01. Found: C, 57.02; H, 4.63; N, 2.15%.

11b *(R = NC–CH_2)*. Yield (0.18 g, 95%); mp 212–214 °C. IR (Nujol)/cm^{-1}: 2342, 1438, 1158, 1119, 1102, 869, 724, 665. ^{1}H NMR ($CDCl_3$): δ 2.60–2.71 (m, 4H, PCH_2CH_2P), 4.06 (d, $^3J_{HP}$ = 19.2 Hz, 2H, CH_2N), 7.31–7.37 (m, 4H, Ph_2), 7.43–7.49 (m, 2H, Ph_2), 7.53–7.59 (m, 4H, Ph_2), 7.65–7.79 (m, 10H, Ph_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 19.81 [dd, $^1J_{CP(III)}$ = 32.5 Hz, $^2J_{CP(V)}$ = 5.7 Hz, CH_2P(III)], 25.29 [d, $^1J_{CP(V)}$ = 72.5 Hz, CH_2P(V)], 38.65 (CH_2N), 120.29 [d, $^3J_{CP(V)}$ = 5.0 Hz, CN], 126.55 (d, $^1J_{CP}$ = 132.8 Hz, C_i), 127.57 (d, $^1J_{CP}$ = 95.3 Hz, C_i), 128.81 (d, $^3J_{CP}$ = 11.6 Hz, C_m), 129.93 (d, $^3J_{CP}$ = 12.8 Hz, C_m), 131.92 (d, $^4J_{CP}$ = 2.9 Hz, C_p), 132.66 (d, $^2J_{CP}$ = 10.4 Hz, C_o), 134.01 (d, $^2J_{CP}$ = 10.4 Hz, C_o), 134.34 (d, $^4J_{CP}$ = 2.9 Hz, C_p). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 22.49 [d, $^3J_{PP}$ = 14.9 Hz, P(III)], 36.95 [d, $^3J_{PP}$ = 14.9 Hz, P(V)]. FAB$^+$-MS *m*/*z* (rel. intensity): 595 (M^+ + 2 − Cl, 95), 594 (M^+ + 1 − Cl, 60), 593 (M^+ − Cl, 100), 592 (M^+ − 1 − Cl, 83), 558 (M^+ − 2Cl, 62), 452 (M^+–$PdCl_2$, 32). Anal. calc. for $C_{28}H_{26}Cl_2N_2P_2Pd$: C, 53.40; H, 4.16; N, 4.45. Found: C, 53.32; H, 4.29; N, 4.58%.

Synthesis of complex 12. A solution of $PdCl_2(PhCN)_2$ (0.115 g, 0.3 mmol) in dry dichloromethane (5 mL) was added to a dry dichloromethane solution (15 mL) of the iminophosphorane-sulfide **10** (0.133 g, 0.3 mmol) under a nitrogen atmosphere. The solution was stirred at 25 °C for 0.5 h. The solvent was removed under vacuum and the residue was treated with dry diethyl ether to give **12** as a red solid which was isolated by filtration and dried under reduced pressure. After recrystallization from dichloromethane–n-pentane an analytically pure sample was obtained in 91% yield. Mp 154–156 °C. IR (Nujol)/cm^{-1}: 1503, 1441, 1236, 1120, 753, 720. ^{1}H NMR ($CDCl_3$): δ 2.92 (m, 2H, CH_2), 3.20 (m, 2H, CH_2), 3.60 (s, 3H, OCH_3), 6.46 (d, *J* = 8.9 Hz, 2H, Ar), 6.98 (dd, $^3J_{HH}$ = 8.9 Hz, H_{Ar}, J_{HP} = 1.3 Hz, 2H, Ar), 7.38–7.50 (m, 7H, Ph_2 + PhS), 7.56–7.61 (m, 2H, Ph_2), 7.69–7.76 (m, 4H, Ph_2), 8.03–8.06 (m, 2H, PhS). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 28.41 (d, $^1J_{CP}$ = 79.5 Hz, CH_2P), 29.87 (d, $^2J_{CP}$ = 7.5 Hz, CH_2S), 55.34 (OCH_3), 114.46 (C_3), 126.67 (d, $^1J_{CP}$ = 92.2 Hz, C_i), 129.53 (d, $^3J_{CP}$ = 12.8 Hz, C_m), 129.75 (d, $^3J_{CP}$ = 7.0 Hz, C_2), 129.80 (CH), 130.80 (CH), 132.97 (d, $^2J_{CP}$ = 9.9 Hz, C_o), 133.19 (CH), 133.74 (d, $^4J_{CP}$ = 2.5 Hz, C_p), 139.71 (C_1'), 152.47 (C_1), 155.83 (C_4).^{31}P{^{1}H} NMR ($CDCl_3$): δ 25.73. FAB$^+$-MS *m*/*z* (rel. intensity): 642 (M^+ + Na, 6), 640 (M^+ + Na − 1, 8), 444 (M^+ + 1 − $PdCl_2$, 16), 289 (22), 136 (100). Anal. calc. for $C_{27}H_{26}Cl_2NOPPdS$: C, 52.23; H, 4.22; N, 2.26. Found: C, 52.31; H, 4.08; N, 2.12%.

X-Ray structure determinations

X-Ray intensities of compounds **3c** and **11b** were measured on a Siemens P4 instrument with a LT2 low-temperature attachment. Compound **5b** was measured on a Bruker SMART 1000 CCD/LT3 machine. Data were collected using monochromated Mo-Kα radiation in ω (**3c** and **5b**) and ω/θ (**11b**) modes.

The structures were solved by direct methods, and all were refined anisotropically on F^2 (compound **5b** program SHELX-97; **3c** and **11b** program SHELX-93, G. M. Sheldrick. University of Göttingen). Restraints to local aromatic ring symmetry or light atom displacement factor components were applied in some cases. Hydrogens were refined using a riding method. Full details are given in Table 3.

Particular features: **3c** contains half a disordered dichloromethane molecule; **5b** contains ten dichloromethane molecules, one of them disordered; and **11b** contains two dichloromethane molecules.

CCDC reference numbers 194361–194363.

See http://www.rsc.org/suppdata/dt/b2/b209242e/ for crystallographic data in CIF or other electronic format.

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