Chemistry of Bridging Phosphanes: Pd^{I} Dimers Bearing 2,5-Dipyridylphosphole Ligands

François Leca,[a] Mathieu Sauthier,[a] Valérie Deborde,[a] Loïc Toupet,[b] and Régis Réau*[a]

Abstract: Two synthetic routes to Pd^{I} dimers that feature a bridging 1-phenyl- and 1-cyclohexyl-2,5-di(2-pyridyl)-phosphole ligand, **3a** and **3b**, respectively, are described. The first involves a conproportionation process between Pd^{II} and Pd^{0} complexes, while the second involves ligand displacement from a preformed Pd^{I} dimer. Both routes are operable for 1-phenylphosphole **1a**, whereas the former failed with 1-cyclohexylphosphole **1b**. A mechanistic study revealed that the conproportionation pathway implies a reversible oxidative addition of the P–C(phenyl) bond of Pd^{II}-coordinated **1a** to Pd^{0} leading to a bimetallic Pd^{II} complex **5**. The structures of complexes **3a** and **3b** were studied by means of X-ray diffraction. The similarity of these solid-state structures suggests that the bridging mode of the P atom is due to μ-1κN:1,2κP:2κN coordination of ligands **1a**, **b**. The electrochemical behaviour and UV/Vis absorption properties of complexes **3a**, **b** are reported. Complex **3a** is inert towards CO, PPh_3 and 1,3-dipoles. It reacted with dimethylacetylene dicarboxylate to give complex **6** as a result of insertion of the alkyne into the Pd–Pd bond. X-ray diffraction studies of complexes **5** and **6** are also presented.

Keywords: bridging ligands · coordination mode · palladium · phosphorus heterocycles · P ligands

Introduction

Tertiary phosphanes are probably the most common ligands associated with late transition metals in coordination chemistry and homogeneous catalysis.[1] In contrast to other classical ligands (e.g. CO, carbenes, hydrides, alkyl groups, etc.), their coordination chemistry was thought to be quite invariant: they act as terminal ligands. The possibility that these sp^3-hybridised donors can adopt a bridging bonding mode was, however, predicted in 1989.[2a] Shortly thereafter, a semi-bridging bonding mode was described for secondary and tertiary phosphanes (complexes **A**[3a] and **B**,[4a] Scheme 1). Note that in both cases, this bonding mode is enforced by an agostic interaction involving a P–H or a P–C(sp^2) moiety. Although several more examples of this coordination mode have been described,[3b–d, 4b] it remains rare. A breakthrough in phosphane coordination chemistry was recently achieved by Werner et al. who employed rhodium dimers as templates. The seminal discovery was the synthesis of rhodium dimers featuring a bridging stibane ligand.[5a] Following an elegant tailoring of the Rh ligands, stibane–phosphane exchange became possible; this allowed access to complex **C** (Scheme 1).[5b] This derivative features a symmetrically bridging PMe_3 ligand, the first example of this type of coordination mode for a tertiary phosphane.[2b] It is noteworthy that bridging arsanes have recently been obtained by means of the same strategy.[5c]

The only other example of a bridging phosphane known to date, is found in the dimetallic complex **D** of 1-phenylphosphole (Scheme 1).[6] Herein, we report the full, detailed chemistry of derivatives of type **D** including different methodologies for their preparation, crystal structures, physical properties and reactivity towards alkynes.

Results and Discussion

Synthesis of a Pd^{I} dimer bearing a bridging 1-phenylphosphole ligand: The discovery that 1-phenylphosphole **1a** (Scheme 2) can adopt a bridging coordination mode was made serendipitously during the evaluation of 2-(2-pyridyl)-phospholes as ligands for Pd-catalysed olefin–CO copolymerisation.[7a] With the cationic Pd^{II} precursor **2a**, no catalytic activity was observed owing to the formation of the inactive dimer **3a** (Scheme 2).[7a] This new species was isolated as an air-stable red powder in 95% yield by precipitation from the reaction media. The $^{31}P\{^{1}H\}$ NMR spectrum of **3a** exhibits a

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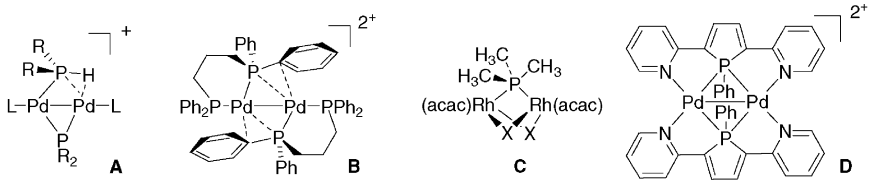
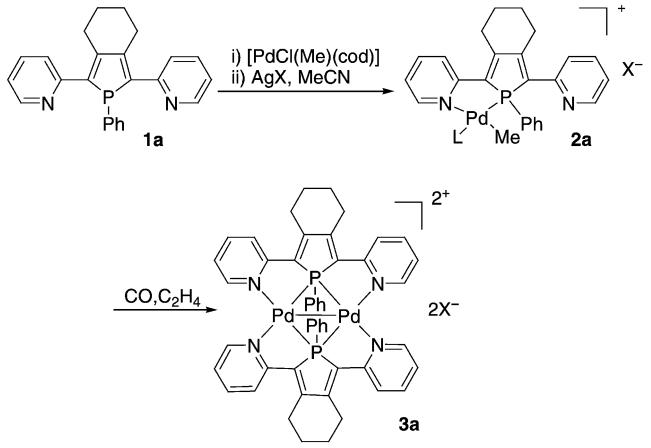


Scheme 1. Complexes bearing semi-bridging phosphane ligands (derivatives **A** and **B**) and bridging phosphane ligands (derivatives **C** and **D**). R = *t*Bu,; L = HP*t*Bu$_2$; X = CPh$_2$.



Scheme 2. Serendipitous discovery of a Pd^{I} dimer bearing a bridging phosphole ligand. cod = 1,5-cyclooctadiene, L = CH_3CN, X = SbF_6.

sharp singlet at $\delta = 69.9$ ppm, which is at a relatively low field for a Pd-coordinated 1-phenylphosphole (for comparison: **2a**, $\delta = 55.2$ ppm). No signal corresponding to a Pd-CH_3 fragment nor a coordinated acetonitrile was observed in either the ^{1}H or ^{13}C{^{1}H} NMR spectra. The ^{13}C NMR{^{1}H}{^{31}P} spectrum of **3a** is extremely simple with one set of signals assignable to a 1-phenyl-2,5-di(2-pyridyl)phosphole moiety (Figure 1, Table 1). These spectroscopic data are indicative of

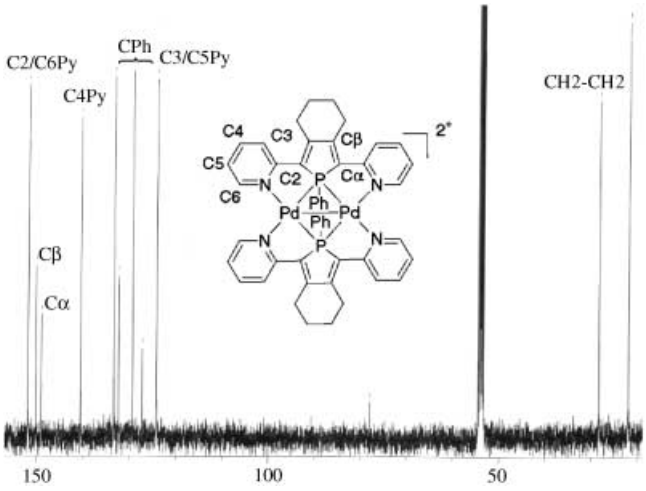


Figure 1. ^{13}C{^{1}H}{^{31}P} NMR spectra of complex **3a** in CD_2Cl_2.

a highly symmetric structure. Notably, these spectra remain unchanged over the temperature regime $-80\,^{\circ}$C to room temperature (solution in CD_2Cl_2), suggesting that the NPN ligand **1a** is strongly bonded and not fluxional in complex **3a**.

High-resolution mass spectrometry and elemental analyses are consistent with the general formula $[Pd_2(\mathbf{1a})_2][(SbF_6)_2]$.

The exact structure of **3a** was established by an X-ray diffraction study[6] (Tables 2 and 3). The pseudo-centrosymmetric dication of **3a** consists of two planar Pd atoms capped by two 2,5-bis(2-pyridyl)phospholes (**1a**) acting as six-electron μ-1κN:1,2κP:2κN donors. The structure will be discussed in detail below, but it is noteworthy that the two Pd–P bond lengths are almost equal (2.349(2), 2.358(2) Å). This solid-state structure, which is consistent with the spectroscopic data obtained in solution, revealed that the σ^3-phosphorus atom of

Table 1. Selected NMR Data for complexes **3a**, **b** and **4a**, **b**.[a]

	δ^{31}P	δ^{13}C{^{1}H}{^{31}P}				
		$PC_\alpha{=}C_\beta$	$PC_\alpha{=}C_\beta$	C_3/C_5 Py	C_4 Py	C_2/C_6 Py
3a	69.9	149.0	150.2	124.1, 124.2	140.6	151.7, 151.8
4a	55.2	136.1	151.9	122.7, 123.7	136.8	149.1, 150.2
		137.0	151.5	123.5, 127.6	139.4	153.6, 156.3
3b	87.2	146.1	149.4	123.8, 124.5	141.1	151.8, 152.8
4b	73.6	133.3	152.2	122.7, 122.9	136.7	149.4, 150.2
		135.1	152.4	123.6, 125.2	139.8	153.2, 154.7

[a] Measured in CD_2Cl_2 at 298 K.

Table 2. Selected bond lengths [Å] and angles [°] for phosphole **1a**,[7c] complexes **3a** (X = SbF_6[7a] and PF_6) and **3b**.

	1a	**3a** (X = SbF_6)	**3a** (X = PF_6)	**3b**
Pd1–Pd2	–	2.787(1)	2.767(1)	2.781(1)[b]
P1–Pd1	–	2.358(2)	2.363(2)	2.349(1)
P1–Pd2	–	2.349(2)	2.330(2)	2.349(1)[b]
Pd1–N1	–	2.177(6)	2.155(7)	2.165(4)
Pd2–N2	–	2.162(6)	2.153(7)	2.165(4)[b]
P1–C1	1.806(6)	1.830(8)	1.841(8)	1.844(5)
C1–C2	1.365(9)	1.36(1)	1.36(1)	1.354(7)
C2–C7	1.478(9)	1.48(1)	1.46(1)	1.480(7)
C7–C8	1.354(8)	1.33(1)	1.35(1)	1.357(7)
C8–P1	1.806(6)	1.833(7)	1.826(8)	1.842(5)
P1–C19	1.831(4)	1.816(8)[a]	1.839(8)[b]	1.857(5)
C1–C14	1.467(5)	1.45(1)	1.48(1)	1.453(7)
C8–C9	1.464(5)	1.44(1)	1.465(1)	1.456(7)
N1-Pd1-P1	–	81.5(1)	81.3(2)	80.05(1)
P1-Pd1-P2	–	107.40(6)	107.72(6)	107.43(4)[b]
N1-Pd1-N3	–	91.02(2)	91.2(3)	91.21(16)[b]
N3-Pd1-P2	–	80.5(1)	80.3(1)	80.0(1)[b]
C19-P1-C1	103.3(1)	103.8(3)[a]	103.7(4)[b]	108.1(3)
C19-P1-C8	103.3(2)	104.8(3)[a]	105.9(4)[b]	104.2(2)
C1-P1-C8	90.5(3)	88.8(8)	88.0(4)	87.8(2)
C19-P1-Pd1	–	111.3(3)[a]	110.1(3)[b]	106.6(1)
C19-P1-Pd2	–	109.7(2)[a]	111.1(3)[b]	113.1(2)[b]
Pd1-P1-Pd2	–	72.60(6)	72.28(6)	72.57(4)
P1-C1-C2	110.7(3)	111.8(6)	111.9(7)	112.4(4)
C1-C2-C7	113.7(3)	113.0(7)	113.0(7)	113.3(5)
C2-C7-C8	113.4(4)	114.3(7)	114.0(7)	113.5(4)
C7-C8-P1	110.5(3)	111.7(5)	112.4(6)	112.3(4)

[a] C19 is the *ipso*-carbon atom of the P–Ph moiety in complexes **3a**. [b] Because of the centrosymmetry of the cation of **3b**, Pd2 = Pd1′, P2 = P1′, N3 = N2′.

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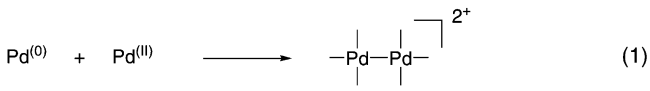
Table 3. Structure determination summary of **3a** (X = PF_6 and SbF_6), **3b**, **5b** and **6**.

	3a	**3a**	**3b**	**5b**	**6**
formula	$C_{48}H_{42}N_4P_2Pd_2 \cdot 2SbF_6 \cdot 2CH_3CN \cdot 2C_6H_{12}$	$C_{48}H_{42}N_4P_2Pd_2 \cdot 2PF_6 \cdot 2CH_2Cl_2$	$C_{48}H_{54}N_4P_2Pd_2, \cdot 2BF_4 \cdot 3CH_2Cl_2$	$C_{42}H_{36}Cl_2Pd_2N_2P_2$	$C_{54}H_{48}N_4P_2Pd_2O_4 \cdot 2PF_6 \cdot 4C_2H_4Cl_2$
M_r	793.69	647.69	1390.09	914.37	1777.45
T[K]	293(2)	110(2)	110(2)	110(2)	120(2)
crystal system	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	*Pbca*	*C*2/*c*	$P2_1/c$	$P2_1/c$
a[Å]	9.389(2)	14.809(5)	23.3370(4)	17.820(4)	16.1111(1)
b[Å]	11.793(6)	15.689(5)	10.3080(2)	11.533(2)	30.3561(3)
c[Å]	14.079(4)	21.536(8)	23.9710(5)	19.6334(5)	16.3044(1)
α[°]	70.33(3)	90	90	90	90
β[°]	88.03(2)	90	95.4400(6)	112.238(1)	118.929(1)
γ[°]	79.50(3)	90	90	90	90
V[Å^3]	1442.8(11)	5003.9(3)	5740.44(19)	3734.9(11)	6978.99(9)
Z	1	4	4	4	4
colour	red	red	red	yellow	yellow
crystal size[mm]	0.38 × 0.21 × 0.18	0.24 × 0.23 × 0.21	0.34 × 0.22 × 0.22	0.35 × 0.28 × 0.20	0.32 × 0.32 × 0.18
ρ_{calcd}[Mg m^{-3}]	1.827	1.720	1.608	1.626	1.692
F(000)	782	2592	2800	1832	3568
μ ($Mo_{K\alpha}$)[cm^{-1}]	16.79	11.24	10.27	12.25	9.95
λ[Å]	0.71073	0.71073	0.71073	0.71073	0.71073
diffractometer	NONIUS CAD4	NONIUS Kappa CCD	NONIUS Kappa CCD	NONIUS CAD4	NONIUS Kappa CCD
hkl range	0/7, −14/15, −17/17	−19/−18, −20/−21, −25/−27	0/30, 0/13, −31/30	0/23, 0/14, −25/23	0/20; 0/39, −21/18
scan range (2θ)[°]	54	60	60	54	55
reflns collected/unique	4710	5756	6530	8569	15884
R(int)	0.161	0.135	0.170	0.092	0.118
data with $I > 2\sigma(I)$	3468	3584	5323	6147	12884
data/restrains/parameters	4710/0/620	5756/0/334	6530/0/344	8569/0/452	15884/0/873
goodness-of-fit on F^2	1.037	1.043	1.042	1.064	0.971
final R indices [$I > 2\sigma(I)$]; $R1/wR2$	0.0556/0.1429	0.0842/0.2246	0.0646/0.1702	0.0418/0.0921	0.0501/0.1178
R indices (all data) $R1/wR2$	0.0882/0.1640	0.1353/0.2564	0.0763/0.1802	0.0740/0.1058	0.0674/0.1294
largest diff. peak/hole [e Å^{-3}]	1.241/−1.535	1.416/−1.144	2.697/−1.132	0.677/−0.680	1.788/−1.513

1-phenylphosphole **1a** can adopt a bridging coordination mode to give a very stable complex.

Since complex **3a** is amongst the very few examples to present this particular phosphane binding mode, it was of primary importance to develop straightforward synthetic routes for its preparation. Dimer **3a** contain two formal Pd^I centres, hence its formation implies the reduction of Pd^{II} complex **2a** (Scheme 2). The formation of Pd^I dimers from the reaction of monocationic alkyl Pd^{II} complexes with CO is known.[8a] This process is believed to involve a reduction of a Pd^{II} salt leading to a Pd^0 complex, followed by a conproportionation process [Eq. (1)].



(1)

This proposal is entirely reasonable, since the reduction of Pd^{II} precursors to give Pd^I dimers according to Equation (1) is well documented.[4a, 8]

Thus, we investigated a conproportionation route to **3a** from the readily accessible precursor **4a** (Scheme 3). This latter air-stable complex was obtained in near quantitative yield by reacting one equivalent of 2,5-di(2-pyridyl)phosphole **1a**[7b] with [$PdCl_2(CH_3CN)_2$] (Scheme 3). The large downfield chemical shift ($\delta \approx 40$ ppm) observed by $^{31}P\{^1H\}$ NMR spectroscopy confirms the formation of a five-membered palladacycle.[7a] In the ^1H NMR spectrum, the chemical shift of H6 of the pyridyl group is also sensitive to coordination and has a downfield shift of $\delta \approx 0.6$ ppm. As expected for an unsymmetrical complex, two sets of signals are observed at low field in the $^{13}C\{^1H\}$ NMR spectrum for the pyridyl and the phosphole P-C_α-C_β moieties (Table 1). Under classical reducing conditions (20 bar H_2, 25 °C, trimethylorthoformate),[4a] in the presence of two equivalents of $NaPF_6$ or $NaSbF_6$, **2a** afforded the target dication **3a** as either the PF_6^- or the SbF_6^- salt in high yields (Scheme 3, route A). It is noteworthy that the multinuclear NMR spectroscopic data for the dication of **3a** are insensitive to the nature of the counter-anion. Similarly, the geometric data obtained by X-ray diffraction studies for the PF_6^- and SbF_6^- salts are very similar, although they crystallise in different space groups (Tables 2 and 3). Therefore, the symmetrically bridging bonding mode of the

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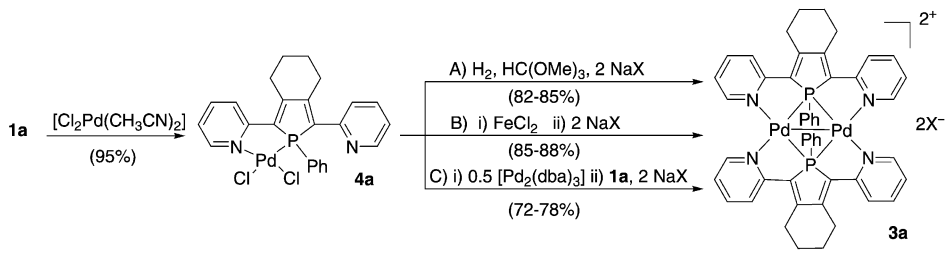


Scheme 3. Synthesis of a Pd^{I} dimer bearing bridging 1-phenylphosphole ligand by means of a conproportionation process. $X = SbF_6$ or PF_6.

phosphorus centre in **3a** is clearly not imposed by packing effects in the solid state.

A more convenient preparation of **3a** that avoids the use of high H_2 pressures, consists of the addition of $FeCl_2$ to **4a** followed by anion exchange (Scheme 3, route B). Alternatively, **3a** can be isolated following consecutive addition of 0.5 equivalents of $[Pd_2(dba)_3]$, 1-phenylphosphole **1a** and two equivalents of $NaPF_6$ (72% yield) or $NaSbF_6$ (78% yield) to the Pd^{II} complex **4a** (Scheme 3, route C). Hence, little doubt remains that routes A and B (Scheme 3) involve a first reduction of Pd^{II} to Pd^{0}, followed by a conproportionation process illustrated by route C.

Synthesis of a Pd^{I} dimer bearing bridging 1-cyclohexylphosphole ligands: Three efficient and reliable routes to complexes **3a** bearing a bridging 1-phenylphosphole were available to us. The next step was to apply these methods to other P-substituted phospholes in order to evaluate the impact of the steric and electronic properties of the P donor on the characteristics of bridging phospholes. Therefore, we investigated the preparation of complex **3b** bearing 1-cyclohexylphosphole ligand **1b**[7a] (Scheme 4). The Pd^{II} complex **4b** was isolated in excellent yield as an air-stable powder. This complex decomposed both under an atmosphere of H_2 (route A) or in the presence of $FeCl_2$ (route B) and proved to be inert towards $[Pd_2(dba)_3]$ (route C). These failures are very surprising; the synthetic route A–C that work with 1-phenylphosphole complexes (Scheme 3) appear inoperative for their 1-cyclohexyl analogues. Initially, this failure was tentatively attributed to the instability of the Pd^{I} dimer **3b**. In order to check this hypothesis, we envisaged a new route to **3b** that involved the substitution of labile acetonitrile ligands of a preformed Pd^{I} dimer, namely $[Pd_2(CH_3CN)_6]^{2+}$.[4b, 8c–e] This pathway (route D, Scheme 4) afforded derivative **3b** as an air-stable solid in 92% yield after crystallisation from a CH_2Cl_2/Et_2O solution. This route appears to be the most simple and convenient route to Pd^{I} dimers bearing phosphole ligands since 1-phenylphosphole **1a** reacted with $[Pd_2(CH_3CN)_6]^{2+}$ to give complex **3a** in 92% yield.

As observed for the corresponding dichloropalladium complexes **4a** and **4b**, the ^{31}P NMR chemical shift of the P-alkyl complex **3b** is more deshielded than that of its P-aryl analogue **3a** (Table 1). The ^{1}H and ^{13}C NMR data of the 2,5-di(2-pyridyl)phosphole moiety of the new complex **3b** compare well with those of **3a** (Table 1) and support a highly symmetric structure. Finally, the proposed structure was confirmed by an X-ray diffraction study (Table 2 and Table 3, Figure 2). The bridging coordination mode of the P atom is clearly demonstrated by the equivalence of the Pd–P bond lengths (2.349(1) Å). In this case, the dicationic core is centrosymmetric.

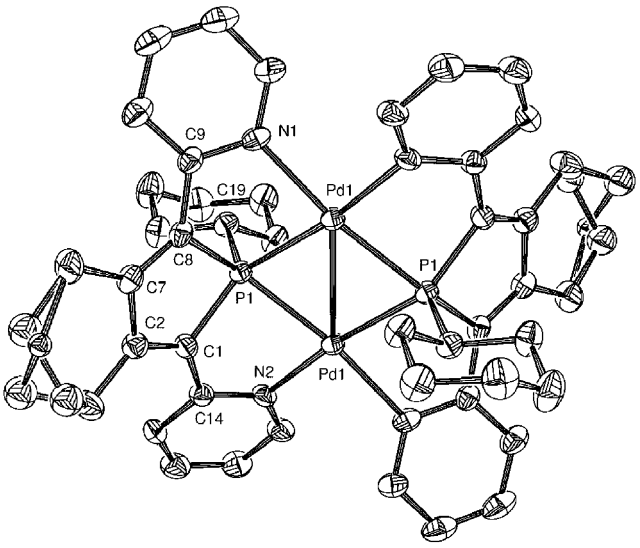
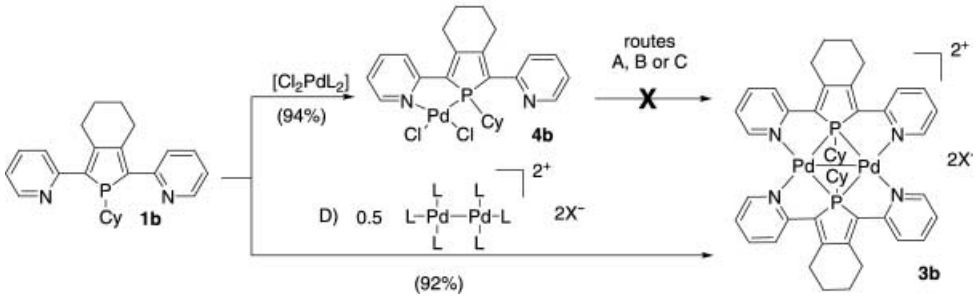


Figure 2. Molecular structure of the dication of complex **3b** in the solid state (hydrogen atoms and solvent molecules have been omitted for clarity).

Study of the mechanism of the formation of 3a by means of a conproportionation processes: At this point, the question of why conproportionation methods A–C (Scheme 3) work with P-arylphosphole **1a**, but fail with its P-alkyl analogue **1b**, still remained. Therefore, we investigated the pathway of route C step-by-step. This pathway can be regarded as a



Scheme 4. Synthesis of a Pd^{I} dimer bearing bridging 1-cyclohexylphosphole ligand by means of ligand exchange. $L = CH_3CN$,; $X^{-} = BF_4$.

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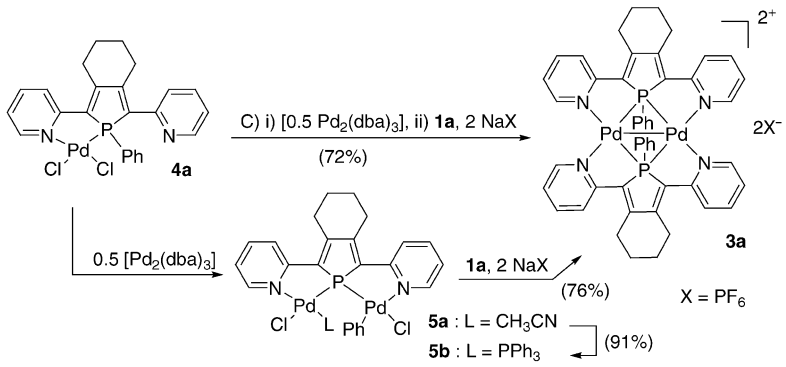
model reaction for the conproportionation process. Compound **4a** reacted rapidly with 0.5 equivalents of $[Pd_2(dba)_3]$ in acetonitrile to afford, quantitatively, a unique P-containing species **5a** (Scheme 5) that presented a sharp $^{31}P\{^1H\}$ NMR signal at $\delta = 115$ ppm. This chemical shift appears at an unusually low field for a Pd-coordinated phosphole (see Table 1) and suggests a profound modification of the P ring.[9, 10a,b] Subsequent addition of one equiv of 1-phenylphosphole **1a** and two equivalents of $NaPF_6$ to the solution of **5a** in CH_3CN gave rise to the Pd^I dimer **3a** in 76% overall yield (Scheme 5). Thus, it appears that derivative **5a** is a key intermediate in the conproportionation route C. Disappointingly, all attempts to isolate compound **5a** failed; nevertheless, addition of one equiv of PPh_3 to an acetonitrile solution of **5a** afforded the new complex **5b**, isolated in 91% yield (Scheme 5). Its $^{31}P\{^1H\}$ NMR spectrum shows a pair of doublets at $\delta = 99.0$ ppm and 25.9 ($J(P,P) = 15.0$ Hz). The doublet at high field has been assigned to the PPh_3 ligand while the phosphole signal of **5b** appears at a low field, similar to that observed for compound **5a**. This data indicates that the two complexes have a similar structure: a labile acetonitrile ligand has been simply substituted by PPh_3. The small magnitude of the $J(P,P)$ coupling constant (15.0 Hz) favours a *cis* arrangement of the two P ligands. The ^{13}C NMR$\{^1H\}$ spectrum for **5b** showed two sets of signals for the pyridyl groups indicating an unsymmetrical structure. Remarkably, three singlets assignable to CH groups of a phenyl ring are observed ($\delta = 128.5, 128.6, 131.0$ ppm). The absence of P–C coupling constants suggests that this phenyl ring is not bound to a P atom.

An X-ray diffraction study (Table 3 and Table 4) revealed that complex **5b** is a bimetallic complex in which two palladium centres are bridged by a phospholyl ligand (Figure 3). The coordination spheres of the metal centres are completed by a pyridyl group and either a triphenylphosphine (Pd2) or a phenyl (Pd1) ligand. This solid-state structure is consistent with the spectroscopic data. The two five-membered metallacycles adopt a slightly distorted envelope conformation with the P atoms out of the Pd-N-C-C planes (C-N-Pd-P 10.5–35.0°; N-C-C-P 21.1–29.5°). The N-Pd-P bite angles (81.8(1)°, 83.4(1)°) are acute, but similar to those recorded for Pd^{II} complexes bearing 2-pyridylphosphole ligands.[7a] The two Pd–N bond lengths are different (Pd1–N2 2.204(3), Pd2–N1 2.138(3)). This is probably the consequence of different *trans* influences of the phenyl and triphenylphosphine ligands. The two Pd–P bond lengths are also different (Pd1–P 2.197(1), Pd2–P 2.285(1) Å), but lie in the range observed for phosphole–Pd^{II} complexes.[7a, 10d] The phosphole ring is almost planar (C7-C2-C1-P1 0.4°, C2-C7-C8-P1 6.3°), the P–C and C–C bond lengths of the P ring being unremarkable and close to those recorded for the free phosphole **1a**[7b,c] (Table 2). The two square-planar palladium centres are formally in oxidation state II since the complex is both diamagnetic and the Pd–Pd separation (3.880(1) Å) is long, discounting any intermetal interaction.[11] These data strongly suggest that the phosphorus atom of the phosphole ring behaves as a 3-electron phosphido ligand, formally donating two electrons to Pd1 and one electron to Pd2. Note that complexes **5a**, **b** are exceptions to the empirical rule that phosphorus nuclei in R_2P groups bridging nonbonding metal centres generally give signals at low field.[12]

Table 4. Selected bond lengths [Å] and angles [°] for complex **5b**.

P1–Pd1	2.197(1)	N2-Pd1-P1	83.44(9)
P1–Pd2	2.285(1)	N2-Pd1-Cl2	96.2(1)
Pd1–N2	2.204(3)	P1-Pd1-C19	88.2(1)
Pd1–C19	2.014(4)	C19-Pd1-Cl2	92.2(1)
Pd1–Cl2	2.376(1)	N1-Pd2-P1	81.80(9)
Pd2–N1	2.138(3)	N1-Pd2-Cl1	89.7(1)
Pd2–P2	2.253(1)	P1-Pd2-P2	94.53(4)
Pd2–Cl1	2.374(1)	P2-Pd2-Cl1	94.02(4)
P1–C1	1.791(4)	C1-P1-Pd1	100.5(1)
C1–C2	1.362(5)	C1-P1-Pd2	125.8(1)
C2–C7	1.473(6)	C1-P1-C8	90.8(2)
C7–C8	1.351(6)	Pd1-P1-Pd2	119.90(5)
C8–P1	1.793(4)	Pd1-P1-C8	129.6(1)
C1–C14	1.475(5)	Pd2-P1-C8	89.4(1)
C8–C9	1.454(6)		

The phospholyl anion exhibits a rich coordination chemistry with varied coordination modes, including the bridging phosphido arrangement.[10] However, it is noteworthy that the tetracoordinate P1 atom exhibits a highly distorted tetrahedral geometry. The C-P1-C and C-P1-Pd angles ranging from 89.5(1)° to 100.5(1)° (Table 4) are typical,[7a] while the Pd1-P1-Pd2 angle is unusually large (119.90(5)°). The severely distorted geometry about P1 is clear from the value of the angle between the planes containing the C1-P1-C8 and the Pd1-P1-Pd2 fragments (64.3(2)°) that differs notably from the ideal value of 90° (Figure 3b). The strain in the metallacycles is reflected in the fact that the C1 atom does not possess the expected planar trigonal geometry (C7-C2-C1-C(9), 157.4(1)°, Figure 3b). These structural features result from the formation of two five-membered metallacycles upon coordination, and the rigidity of the 1,4-*P,N* chelate backbones which contain sp^2 atoms. Hence, the phosphorus atom of a bridging phospholyl ligand can accommodate severe



Scheme 5. Stepwise formation of complex **3a** by conproportionation route C.

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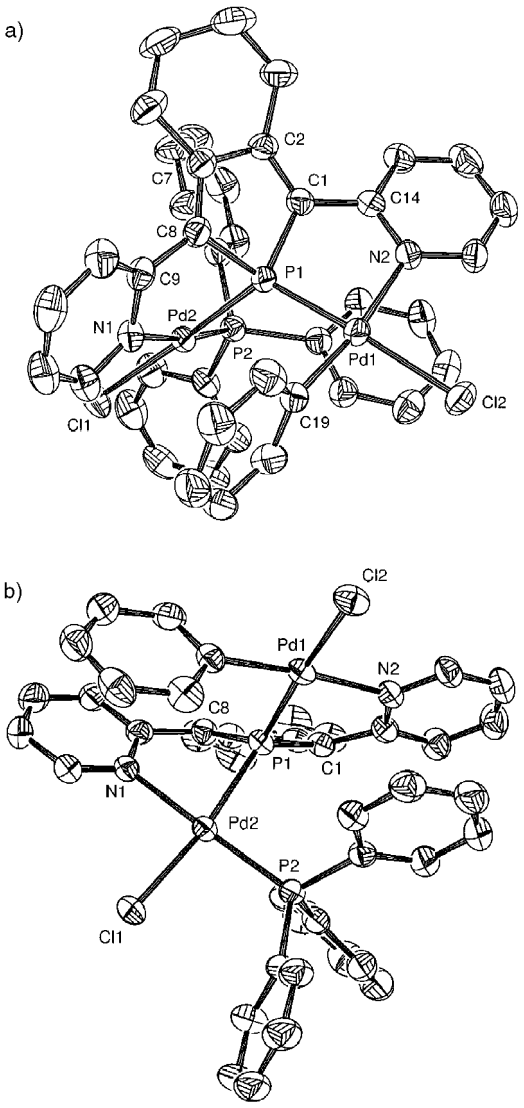

Figure 3. Molecular structure of complex **5b** in the solid state (hydrogen atoms have been omitted for clarity). a) General view. b) View showing the geometry about the phosphorus atom of the phosphole ring.

deviation from an optimal tetrahedral geometry, probably because of the high s character of the lone pair on P.[9, 10a, 13]

From a mechanistic point of view, the key feature associated with the generation of **5b** is that it results formally from an oxidative addition of the phosphole P–C(phenyl) bond of **1a** to a Pd^0 centre. This process is followed by a classical Cl exchange.[14] Although this oxidative addition has been observed on a number of occasions with arylphosphines,[12a, 15] it is unprecedented in phosphole chemistry.[9, 10a,b] It is interesting to note that this oxidative addition process is probably a key step in the thermal reaction of P-arylphospholes with low-valent transition metals leading to phosphametallocenes.[10a,b, 16] The discovery that an oxidative addition occurs in route C (Scheme 3) holds the clue to rationalising why this method is not operative for the P-alkylphosphole **1b**, since P–C(alkyl) bonds are more reluctant to undergo oxidative addition than P–C(aryl) bonds.[15a] Furthermore, the fact that **5a** reacted with an equivalent of free **1a** affording palladium dimer **3a** (Scheme 5) clearly shows that the P–Ph oxidative addition is *reversible*! The pathway depicted in Scheme 5 reveals a series of reactions that break and remake P–C(Ar) bonds under very mild reaction conditions. Since the phosphido ligand formally donates two electrons to the Pd1 centre, the transformation of **5a** into **3a** implies a migratory insertion of the μ^2-coordinated phosphido ligand into the Pd–C(phenyl) bond. To the best of our knowledge, such a mechanism involving a μ^2-phosphido ligand has never been proposed.[17] It is very likely that this new fundamental step could provide insight into other reaction mechanisms, especially phosphine degradation during catalytic reactions[15] or chemical vapour deposition experiments,[11b] and aryl exchange that occurs between P–aryl ligands and Pd-bound aryl or alkyl groups during cross-coupling reactions.[18]

Solid-state structure of complexes 3a and 3b: A comparison of the solid-state structures of complexes **3a**[6] and **3b** is of particular interest since the bridging P atoms possess very different electronic and steric properties. Each palladium atom has a slightly distorted square-planar geometry and the intermetal Pd–Pd bond lengths lie in the same range (**3a**, 2.787(2) Å; **3b**, 2.780(1) Å). For both complexes, the coordination planes about the palladium atoms are nearly coplanar. The angles and the bond lengths of the metallacycles are similar to values reported for Pd^{II} complexes bearing (2-pyridyl)phosphole ligands.[7a] The five-membered metallacycles of complexes **3a** and **3b** have a slightly distorted envelope conformation, with the Pd, N and the two inter-ring C atoms being almost coplanar (maximum deviation: **3a**, 0.068; **3b**, 0.075 Å), and the P atoms lying out of these planes (dihedral NCCP and CNPdP angles: **3a**, 25.6–25.2°; **3b**, 22.6–38.7°). The geometric data of the coordinated phosphole rings are comparable to those observed for the free phosphole **1a** (Table 2). These solid state-studies revealed that the symmetric μ_2-bridging coordination mode of the P atoms does not dramatically perturb the structure of the ligands nor the coordination sphere of the Pd centres. The most remarkable feature is the similarity of the geometric parameters for complexes **3a** and **3b** (Table 2) in spite of the different electronic and steric properties of the P ligands. Hence, the structural parameters associated with this type of bridging phosphanes are imposed by the tridentate coordination mode of the rigid and symmetric 2,5-di(2-pyridyl)phosphole moiety.

Structural features of the Pd_2P_2 core observed in the solid state merit some discussion. The geometry about the bridging P atoms cannot be regarded as a trigonal bipyramid, since the endocyclic carbon atoms and palladium atoms linked to the P centres lie in the same plane (maximum deviation from the best plane: **3a**, 0.006 Å; **3b**, 0.031 Å; Figure 4). At a first glance, the molecular geometry about the bridging P atoms can be described as square-pyramidal (SP), with the P atom lying 0.68 Å (**3a**) and 0.79 Å (**3b**) out of the plane defined by the palladium and the endocyclic C1 and C8 carbon atoms (Figure 4). However, the C19-P-Pd and Pd-P-Pd angles deviate notably from the values predicted for an SP geometry,[19] with average values at 110° (ideal value, 105°) and 72.5° (ideal value, 86°), respectively. These angular distortions suggest that the geometry about the P atoms can be best

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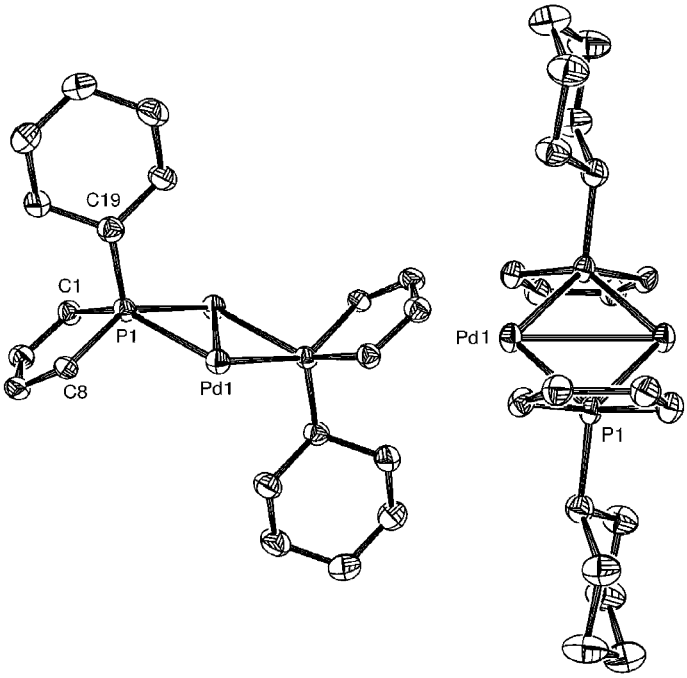

Figure 4. Simplified views of the molecular structure of the dication of complex **3b** in the solid state showing the geometry about the P atoms.

described as a distorted tetrahedron if the midpoint of the Pd–Pd bond is considered as the coordination centre (Figure 4). This view is supported by a theoretical study revealing that the Pd–Pd and Pd–P bonding of derivative **3a** is highly delocalised.[6] In fact, the lines connecting the P and Pd atoms in complexes **3a** and **3b** are topologic lines and not bonds in the Lewis sense. In accordance with this model, the P–Pd bond lengths (**3a**, 2.349(2), 2.358(2) Å; **3b**, 2.349(1) Å) are longer than those measured when phospholes act as classical two-electron donors (≈2.20–2.25 Å),[7a,c] whereas the metal–metal bonds (**3a**, 2.787(2) Å; **3b**, 2.780(1) Å) are rather long compared to those usually observed in a Pd^{I} dimer.[8b] For comparison, the Pd–Pd bond lengths in complexes **A** and **B** (Scheme 1) are 2.611(1)[3b,c] and 2.701(3) Å,[4a] respectively.

These results demonstrate the ability of 2,5-di(2-pyridyl)-phospholes to act as μ-1κN:1,2κP:2κN ligands. The symmetrically bridging bonding mode of the P atom is very probably dictated by the ability of these ligands to act as tridentate pincers toward a bimetallic fragment.

Electrochemical behaviour, electronic absorption spectra and reactivity of complexes 3a and 3b: Complexes **3a** and **3b** exhibit similar electrochemical behaviour. Cyclic voltammetry performed in CH_2Cl_2 (10^{-3} M) at 200 mV s^{-1} showed three irreversible reduction waves for both derivatives (Table 5). The waves are still irreversible at scan rates of 600 mV s^{-1} suggesting that electrochemical-chemical processes take place. The reductive cleavage of the exocyclic P–C(phenyl) bond of phosphole is a favoured process on account of the highly aromatic character of the resulting phospholyl anion.[9, 10a] However, this process can be excluded in the case of **3a** since it showed the same electrochemical behaviour as its P-alkyl analogue **3b**. Considering that the LUMO of these

Table 5. Reduction peak potentials for complexes **3a** (X = PF_6) and **3b**.[a]

	E_1[V]	E_2[V]	E_3[V]
3a	−0.82	−1.13	−1.60
3b	−0.83	−1.20	−1.41

[a] All potentials were obtained during cyclic voltammetric investigations in 0.2 M Bu_4NPF_6 in CH_2Cl_2. Platinum electrode diameter 1 mm, sweep rate :200 mV s^{-1}. Oxidation potential (V versus SCE), measured versus ferrocene as the internal standard ($Ep_{1/2}$ = 0.5 V vs SCE, ΔEp = 70 mV).

complexes is antibonding with respect to the Pd–Pd unit,[6] it is very likely that the primary electron-transfer steps involve metal–metal bond cleavage followed by fast chemical reactions.

The UV/Vis spectra of complexes **3a** and **3b** are also very similar, exhibiting several maxima between λ = 300 and 500 nm (Figure 5). Pd^{I} dimers generally give an ultraviolet

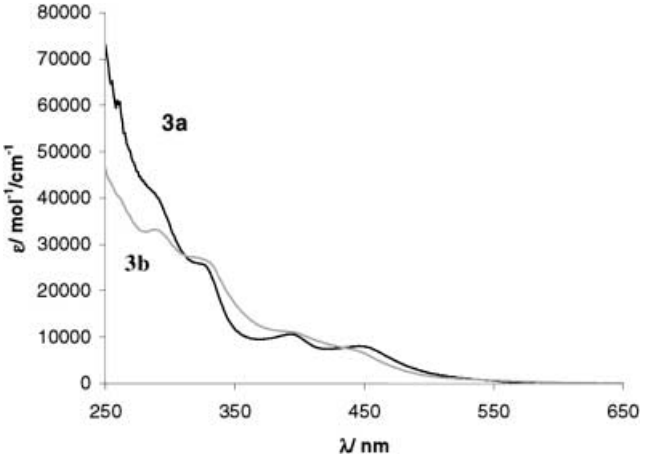

Figure 5. UV/Vis spectra of complexes **3a** and **3b** in CH_2Cl_2.

absorption assigned to σ(Pd–Pd) → σ*(Pd–Pd) excitation.[20] The energy of these bands varies in a large range ($\lambda \approx$ 300–450 nm) depending on the nature of the ligands. In the case of **3a** and **3b**, it is very difficult to assign one of the low-energy UV/Vis absorptions to a σ(Pd–Pd) → σ*(Pd–Pd) transition since coordination of 2-pyridyl ligands to Pd centres results in low-energy UV/Vis absorptions assigned to charge transfer from the metal or the phosphorus-metal fragments to the pyridine ligands.[21]

Complexes **3a**, **b** are air-stable, moisture-insensitive derivatives. They can be stored for months without degradation. Complexes **3a**, **b** do not exhibit the typical reaction pattern of Pd^{I} dimers.[8b] For example, **3a** is inert towards classical two-electron donors (CO, PPh_3) and 1,3-dipoles (trimethylsilylazide, trimethylsilyldiazomethane). Note that **3a** decomposed rapidly in the presence of organic bases (Et_3N, pyridine, etc.). It is known that acetylenes bearing electron-withdrawing substituents insert into Pd^{I}–Pd^{I} bonds to give μ-η^1:η^1-alkyne complexes with an A-frame structure.[22] Indeed, when a solution of **3a** in CH_2Cl_2 was reacted with dimethylacetylene dicarboxylate (DMAD), the original deep red colour of the solution changed to orange over a period of 15 h at 45 °C. The $^{31}P\{^1H\}$ spectrum showed a sharp singlet at δ = 54.3 ppm,

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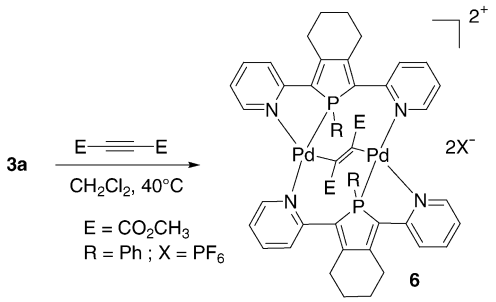
suggesting the formation of a single product. Evaporation of the solvent and precipitation of the residue from a CH_2Cl_2/Et_2O solution afforded the new complex **6** in 73% yield (Scheme 6). The high-resolution mass spectrum confirms that



Scheme 6. Reaction of **3a** with dimethylacetylene dicarboxylate.

6 is the stoichiometric (**3a** · DMAD). Two sets of signals are recorded for the pyridyl groups in the $^{13}C\{^1H\}$ NMR spectra and a single resonance was observed for the OCH_3 moieties in the ^1H ($\delta = 3.81$ ppm) and $^{13}C\{^1H\}$ NMR spectra ($\delta =$ 51.0 ppm). These spectroscopic data fit with an expected basic A-frame structure.[19] Single crystals of **6** were grown from a CH_2Cl_2/pentane solution. They were subjected to an X-ray diffraction study that confirmed the proposed structure and clearly showed that complex **6** possesses an A-frame structure (Figure 6, Table 3 and Table 6). The coordination at each palladium centre is distorted square-planar with acute chelating N-Pd-P angles (82.7(3) – 84.5(3)°), and a *cis* orientation of the carbon and the phosphorus atoms. The Pd–Pd separation (3.6 Å) falls well outside the range considered typical of a Pd–Pd single bond.[8b, 11] The geometric data for the μ-η^1;η^1-alkyne-Pd_2 moiety are typical.[22] The Pd–C bond lengths are similar (1.994(14) – 2.004(12) Å). The C55–C56 bond lengths of 1.34(2) Å with angles around 120° (119.2(11) – 125.8(10)°) indicate an hybridisation close to sp^2 for the two carbons bridging the palladium metal centres. Compound **1a** adopts a bridged position, acting as a bidentate ligand toward one palladium centre and monodentate donor toward the other. A similar coordination was proposed for a Pd^I dimer bearing triphosphine ligands; however, no crystallographic study of this complex has been carried out.[23]

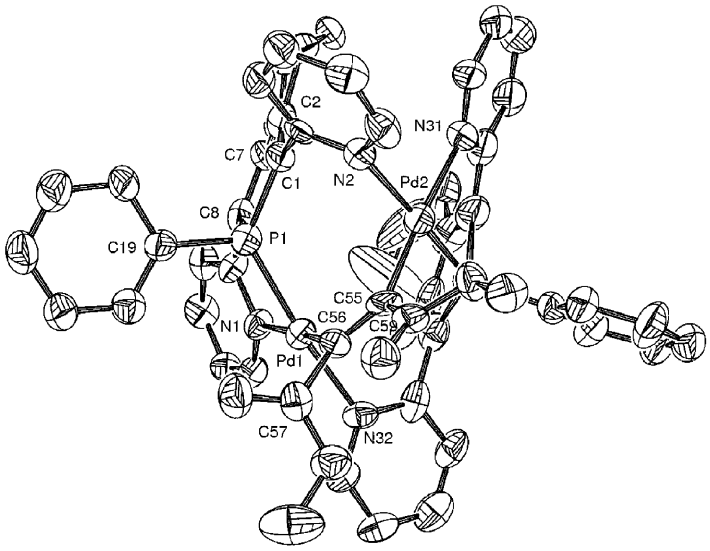


Figure 6. View of the molecular structure of complex **6** in the solid state (hydrogen atoms and solvent molecules have been omitted for clarity).

Table 6. Selected bond lengths [Å] and angles [°] for complex **6**

Pd1–P1	2.221(4)	N1-Pd1-P1	84.5(3)
Pd1–N1	2.115(11)	P1-Pd1-C56	93.0(4)
Pd1–N4	2.124(11)	C56-Pd1-N4	88.8(5)
Pd1–C56	1.994(14)	N1-Pd1-N4	94.2(4)
Pd2–P2	2.229(5)	N3-Pd2-P2	82.7(4)
Pd2–N2	2.129(12)	P2-Pd2-C55	98.9(4)
Pd2–N4	2.176(14)	C55-Pd2-N2	88.3(5)
Pd2–C55	2.004(12)	N2-Pd2-N3	93.6(5)
C55–C56	1.34(2)	C1-P1-N8	92.5(7)
P1–C1	1.834(14)	C55-C56-C57	124.3(13)
C1–C2	1.38(2)	C55-C56-Pd1	125.8(10)
C2–C7	1.46(2)	C57-C56-Pd1	119.8(9)
C7–C8	1.37(2)	C56-C55-C59	119.7(11)
C8–P1	1.802(16)	C56-C55-Pd2	121.0(11)
C1–C19	1.793(15)	C59-C55-Pd2)	119.2(11)

It is worth noting that no alkyne oligomerisation was observed on heating **3a** in neat DMAD at 100 °C, and that **3a** is inert toward other acetylenes which lack electron-withdrawing substituents such as phenylacetylene.

Conclusion

In summary, this study showed that phospholes bearing 2-pyridyl substituents can adopt a bridging coordination mode. This behaviour is probably be attributed to ability of these derivatives to act as tightly bonded tridentate ligands toward the Pd–Pd fragment. The analysis of the solid-state structures of the Pd^I dimers bearing bridging phosphanes shows no destabilising constraints caused by this unusual coordination mode. On the one hand, we believe that these results give the clue to a rational extension of this very rare coordination mode. It is expected that other symmetrically bridging phosphanes should be readily obtained using tridentate μ-1κ:1,2κP:2κ donors able to form five-membered metallacycles. Pd^I dimers are valuable templates in this quest on account of the availability of several different synthetic routes to the target complexes (conproportionation, ligand exchange). On the other hand, the ability of di(2-pyridyl)-phospholes to act as assembling ligands can probably be exploited to prepare dimetallic complexes with unusual metal – metal bonds.

Experimental Section

General: All experiments were performed under an atmosphere of dry argon with standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under argon from sodium/benzophenone (tetrahydrofuran, diethyl

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ether) or from phosphorus pentoxide (pentane, dichloromethane, acetonitrile). ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AM300, DPX200 or ARX400 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported relative to Me_4Si as the external standard. ^{31}P NMR downfield chemical shifts are report relative to external 85 % H_3PO_4. The assignment of carbon atoms was based on HMBC and HMQC experiments. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec-TOF Micromass at CRMPO, University of Rennes. Elemental analyses were performed by the CRMPO or the Centre de Microanalyse du CNRS at Vernaison (France).

Determination of optical data and cyclic voltammetry measurements: UV/Vis spectra were recorded at room temperature on a UVIKON 942 spectrophotometer in freshly distilled solvents at room temperature. Electrochemical measurements were performed in dichloromethane (Puran No. 02910E21) from SDS with less than 100 ppm of water. Tetra-*N*-butylammonium hexafluorophosphate from Fluka was used as received. All the electrochemical investigations were carried out in a conventional three-compartment cell: in all cases, the anode, the cathode and the reference electrode were separated by a glass frit. The working electrode was of polished platinum while the counter-electrode was a glassy carbon rod. The reference electrode was composed of a silver wire in contact with 10^{-1}M $AgNO_3$. Ferrocene was added to each electrolytic solution at the end of a series of experiments. The ferrocene/ferrocenium ($Fc/Fc^{\bullet+}$) couple served as an internal standard and all reported potentials are referenced to its reversible formal potential.

[Bis{1-phenyl-2,5-di(2-pyridyl)phosphole}$_2$Pd$_2$]X$_2$ (3a):

Route A, $X = SbF_6^-$: A solution of **4a** (0.50 g, 0.92 mmol), $NaSbF_6$ (0.49 g, 1.90 mmol) and trimethylorthoformate (1.00 mL, 9.14 mmol) in CH_2Cl_2 (20 mL) and MeOH (10 mL) were placed into a 150-mL stainless steel autoclave equipped with a magnetic stirrer. The autoclave was pressurised with H_2 (10 bar) and the solution was stirred for 12 h at room temperature. The autoclave was vented, and the volatile components were removed in a vacuum. The brown residue was extracted with CH_2Cl_2 (2×25 mL) and the solution was concentrated to $\approx 5-10$ mL. After addition of $CHCl_3$ (40 mL), complex **3a** precipitated at room temperature as an air-stable red solid (0.53 g, 82 %).

Route A, $X = SbF_6^-$: Following this procedure, **3a** ($X = PF_6^-$) was obtained in 85 % yield.

Route B, $X = PF_6^-$: To a solution of **4a** (0.50 g, 0.92 mmol) in CH_2Cl_2 (10 mL) was added, at room temperature, solid [$FeCl_2 \cdot 4H_2O$] (0.18 g, 0.92 mmol). The solution was stirred for 48 h at 45 °C, then KPF_6 (0.80 g, 4.34 mmol) and distilled water (20 mL) were added. The solution was stirred for 1 h at room temperature. After extraction, the organic layer was washed with distilled water (2×10 mL), dried over $MgSO_4$ and the solvent was evaporated. The residue was washed with $CHCl_3$ (2×10 mL) and dried in a vacuum. Complex **3a** was obtained as a red solid (0.50 g, 88 %).

Route B, $X = SbF_6^-$: Following this procedure, **3a** ($X = SbF_6^-$) was obtained in 85 % yield.

Route C, $X = PF_6^-$: A solution of [$Pd_2(dba)_3$] (0.21 g, 0.23 mmol) in CH_3CN (5 mL) was added to a solution of complex **4a** (0.25 g, 0.46 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 0.5 h at room temperature, then neat 1-phenyl-2,5-di(2-pyridyl)phosphole (**1a**, 0.17 g, 0.46 mmol) and $NaPF_6$ (0.15 g, 0.92 mmol) were added. The solution was stirred for 2 h at room temperature and the solvent was removed in vacuo. The residue was washed with $CHCl_3$ (2×10 mL) and dried in a vacuum. Complex **3a** was obtained as a red solid (0.41 g, 72 %).

Route C, $X = PF_6^-$: Following this procedure, **3a** ($X = SbF_6^-$) was obtained in 88 % yield.

3a ($X = SbF_6^-$): ^{1}H{^{31}P} NMR (400 MHz, CD_2Cl_2): $\delta = 1.55-2.20$ (m, 8H; C=CCH$_2$CH_2), 3.20 (m, 6H; C=CCH$_2$), 3.60 (m, 2H; C=CCH$_2$), 7.11 (dd, ^3J(H,H) = 7.4 Hz, ^3J(H,H) = 7.4 Hz, 4H; *m*-H Ph), 7.22 (t, ^3J(H,H) = 7.4 Hz, 2H; *p*-H Ph), 7.30 (m, 8H; *o*-H_O Ph and H5 Py), 7.92 (d, ^3J(H,H) = 5.5 Hz, 4H; H3 Py), 8.00 ppm (m, 8H; H6 and H4 Py); ^{13}C{^{1}H}{^{31}P} NMR (100.622 MHz, CD_2Cl_2): $\delta = 21.9$ (s, C=CCH$_2$*C*H$_2$), 28.3 (s, C=C*C*H$_2$), 124.1 (s, C5 Py or C3 Py), 124.2 (s, C5 Py or C3 Py), 127.2 (s, *ipso*-C Ph), 129.3 (s, *m*-C Ph), 132.3 (s, *P,C* Ph), 133.4 (s, *o*-C Ph), 140.6 (s, C4 Py), 149.0 (s, P*C*$_\alpha$=C), 150.2 (s, PC=*C*$_\beta$), 151.7 (s, C2 Py or C6 Py), 151.8 ppm (s, C2 Py or C6 Py); ^{31}P{^{1}H}NMR (81.014 MHz, CD_2Cl_2): $\delta = 69.9$ ppm; HR-MS (FAB-mNBA): *m*/*z*: 1184.9933 [$M - SbF_6$]$^+$; calcd for $C_{48}H_{42}N_4P_2SbF_6Pd_2$: 1184.9923; elemental analysis calcd (%) for $C_{48}H_{42}N_4P_2Sb_2F_{12}Pd_2$ (1421.167): C 40.57, H 2.98, N 3.94; found: C 40.18, H 2.79, N 3.75.

3a ($X = PF_6^-$): ^{31}P{^{1}H}NMR (81.014 MHz, CD_2Cl_2): $\delta = 69.8$ (P-Ph), -141.7 ppm (sept., ^1J(P,F) = 712.7 Hz); HR-MS (FAB-mNBA): *m*/*z*: 1095.0694 [$M - PF_6$]$^+$; calcd for $C_{48}H_{42}N_4P_3F_6Pd_2$: 1095.0621; elemental analysis calcd (%) for $C_{48}H_{42}N_4P_4F_{12}Pd_2$ (1239.598): C 46.51, H 3.42, N 4.52; found: C 46.18, H 3.49, N 4.45.

[{1-Phenyl-2,5-di(2-pyridyl)phosphole}PdCl$_2$] (4a): A solution of 1-phenylphosphole **1a** (0.30 g, 0.81 mmol) in CH_2Cl_2 (5 mL) was added to a solution of [$(CH_3CN)_2PdCl_2$] (0.21 g, 0.81 mmol) in CH_2Cl_2 (10 mL) at room temperature. The solution was stirred for 1 h at room temperature, and the volatile materials were removed under vacuum. The residue was washed with diethyl ether (3×10 mL) and dried under vacuum. Complex **4a** was obtained as an air-stable orange solid (0.42 g, 95 %). ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta = 1.65-2.00$ (m, 4H; C=CCH$_2$CH_2), 2.72 (m, 1H; C=CCH$_2$), 3.02 (m, 2H; C=CCH$_2$), 3.48 (m, 1H; C=CCH$_2$), 7.08 (ddd, ^3J(H,H) = 7.8 Hz, ^3J(H,H) = 4.6 Hz, ^4J(H,H) = 0.9 Hz, 1H; H5 Py), 7.21–7.42 (m, 4H; *m*-/*p*-H Ph and H5 Py), 7.51 (dd, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 0.9 Hz, 1H; H3 Py), 7.61 (ddd, ^3J(H,H) = 7.9 Hz, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.7 Hz, 1H; H4 Py), 7.80–7.93 (m, 3H; *o*-H Ph and H4 Py), 8.20 (d, ^3J(H,H) = 7.9 Hz, 1H; H3 Py), 8.56 (dd, ^3J(H,H) = 4.6 Hz, ^4J(H,H) = 1.7 Hz, 1H; H6 Py), 9.64 ppm (dd, ^3J(H,H) = 5.0 Hz, ^3J(H,H) = 1.7 Hz, 1H; H6 Py); ^{13}C{^{1}H} NMR (50.323 MHz, CD_2Cl_2): $\delta = 21.1$ (s, C=CCH$_2$CH$_2$), 22.3 (s, C=CCH$_2$*C*H$_2$), 27.7 (d, ^3J(P,C) = 8.8 Hz, C=C*C*H$_2$), 30.2 (d, ^3J(P,C) = 9.8 Hz, C=C*C*H$_2$), 122.7 (s, C5 Py), 123.7 (s, C5 Py), 123.5 (d, ^3J(P,C) = 10.8 Hz, C3 Py), 123.6 (d, ^1J(P,C) = 49.1 Hz, *ipso*-C), 127.6 (d, ^3J(P,C) = 2.5 Hz, C3 Py), 129.3 (d, ^3J(P,C) = 12.0 Hz, *m*-C Ph), 132.8 (d, ^4J(P,C) = 2.8 Hz, *p*-C Ph), 133.9 (d, ^2J(P,C) = 13.0 Hz, *o*-C Ph), 136.1 (d, ^1J(P,C) = 48.9 Hz, P*C*$_\alpha$=C), 136.8 (s, C4 Py), 137.0 (d, ^1J(P,C) = 55.0 Hz, P*C*$_\alpha$=C), 139.4 (s, C4 Py), 149.1 (s, C6 Py), 150.2 (d, ^2J(P,C) = 13.0 Hz, C2 Py), 151.5 (d, ^2J(P,C) = 19.5 Hz, PC=*C*$_\beta$), 151.9 (d, ^2J(P,C) = 20.4 Hz, PC=*C*$_\beta$), 153.6 (s, C6 Py), 156.3 ppm (d, ^2J(P,C) = 13.3 Hz, C2 Py); ^{31}P{^{1}H}NMR (81.014 MHz, CD_2Cl_2): $\delta = 55.2$ ppm; HR-MS (FAB-mNBA): *m*/*z*: 509.0177 [$M - Cl$]$^+$; calcd for $C_{24}H_{21}N_2PCl_2Pd$: 509.0172; elemental analysis calcd (%) for $C_{24}H_{21}N_2PCl_2Pd$ (545.74): C 52.82, H 3.88, N 5.13; found: C 52.76, H 3.79, N 5.21.

[{1-cyclohexyl-2,5-di(2-pyridyl)phosphole}PdCl$_2$] (4b): Following the procedure described for the compound **4a**, reaction of 1-cyclohexylphosphole **1b** (0.33 g, 0.90 mmol) and [$(CH_3CN)_2PdCl_2$] (0.23 g, 0.90 mmol) afforded **4b** as an air-stable orange solid (0.48 g, 96 %). ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta = 0.65-1.9$ (m, 14H; CH$_2$), 2.30 (m, 1H; CH$_2$), 2.55–3.15 (m, 4H; CH$_2$), 7.22 (dd, ^3J(H,H) = 7.3 Hz, ^3J(H,H) = 4.5 Hz, 1H; H5 Py), 7.32 (ddd, ^3J(H,H) = 7.4 Hz, ^3J(H,H) = 5.7 Hz, ^4J(H,H) = 1.4 Hz, 1H; H5 Py), 7.58 (br d, 1H, ^3J(H,H) = 7.6 Hz; H3 Py), 7.76 (ddd, ^3J(H,H) = 7.8 Hz, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.8 Hz, 1H; H4 Py), 7.95 (br d, ^3J(H,H) = 7.8 Hz, 1H; H3 Py), 8.00 (ddd, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.4 Hz, 1H; H4 Py), 8.63 (br d, ^3J(H,H) = 4.5 Hz, 1H; H6 Py), 9.49 ppm (br d, ^3J(H,H) = 5.7 Hz, 1H; H6 Py); ^{13}C{^{1}H} NMR (50.323 MHz, CD_2Cl_2): $\delta = 21.6$ (s, C=CCH$_2$*C*H$_2$), 22.2 (s, C=CCH$_2$*C*H$_2$), 25.5 (d, *J*(P,C) = 2.3 Hz, CH$_2$), 26.6 (d, *J*(P,C) = 11.7 Hz, CH$_2$), 26.9 (d, *J*(P,C) = 16.3 Hz, CH$_2$), 27.4 (d, *J*(P,C) = 8.6 Hz, CH$_2$), 27.5 (d, *J*(P,C) = 10.1 Hz, CH$_2$), 29.6 (d, *J*(P,C) = 9.4 Hz, C=C*C*H$_2$), 30.3 (s, CH$_2$), 39.3 (d, ^1J(P,C) = 21.1 Hz, CH), 122.7 (s, C5 Py), 122.9 (d, ^3J(P,C) = 10.2 Hz, C3 Py), 123.6 (s, C5 Py), 125.2 (d, ^3J(P,C) = 4.7 Hz, C3 Py), 133.3 (d, ^1J(P,C) = 44.4 Hz, P*C*$_\alpha$=C), 135.1 (d, ^1J(P,C) = 46.7 Hz, P*C*$_\alpha$=C), 136.7 (s, C4 Py), 139.8 (s, C4 Py), 149.4 (s, C6 Py), 150.2 (d, ^2J(P,C) = 10.2 Hz, C2 Py), 152.2 (d, ^2J(P,C) = 16.0 Hz, PC=*C*$_\beta$), 152.4 (d, ^2J(P,C) = 19.4 Hz, PC=*C*$_\beta$), 153.2 (s, C6 Py), 154.70 ppm (d, ^2J(P,C) = 10.9 Hz, C2 Py); ^{31}P{^{1}H}NMR (81.014 MHZ, CD_2Cl_2): $\delta =$ 73.6 ppm; HR-MS (FAB-mNBA): *m*/*z*: 517.0630 [$M - Cl$]$^+$; calcd for $C_{24}H_{27}N_2PPdCl$: 517.0639; elemental analysis calcd (%) for $C_{24}H_{27}N_2PPdCl_2$ (551.788): C 52.24, H 4.93, N 5.08; found: C 52.06, H 4.95, N 5.15.

[{1-cyclohexyl-2,5-di(2-pyridyl)phosphole}$_2$Pd$_2$][BF$_4$]$_2$ (3b): A solution of [$(CH_3CN)_6Pd_2$][BF_4]$_2$ (0.29 g, 0.46 mmol) in CH_2Cl_2 (10 mL) was added to a solution of 1-cyclohexylphosphole **1b** (0.34 g, 0.92 mmol) in CH_2Cl_2 (5 mL) at room temperature. The solution was stirred for 0.5 h at room temperature, filtered, and the volatile materials were removed under vacuum. The residue was crystallised from a CH_2Cl_2/Et_2O mixture at room temperature. Complex **3b** was obtained as air-stable red crystals (0.48 g, 92 %). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 0.35-0.85$ (m, 8H; CH$_2$), 1.20–2.10 (m, 22H; CH$_2$), 2.95–3.3 (m, 8H; CH$_2$), 7.48–7.78 (m, 8H; H5 Py and H3 Py), 8.03

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(d, ^3J(H,H) = 5.8 Hz, 4H; H6 Py), 8.18 ppm (d, ^3J(H,H) = 7.2 Hz, ^3J(H,H) = 7.3 Hz, 4H; H4 Py); ^{13}C{^{1}H} NMR (75.469 MHz, CD_2Cl_2): δ = 21.9 (s, C=CCH$_2$CH$_2$), 25.8 (s, CH$_2$), 27.3 (m, CH$_2$), 28.1 (m, CH$_2$), 31.0 (s, C=CCH$_2$), 41.0 (d, ^1J(P,C) = 22.5 Hz, CH), 123.8 (m, C3 Py), 124.5 (s, C5 Py), 141.1 (s, C4 Py), 146.1 (dd, ^1J(P,C) = 47.2 Hz, ^3J(P,C) = 3.5 Hz, PC_α=C), 149.4 (m, PC=C_β), 151.8 (s, C6 Py), 152.8 ppm (m, C2 Py); ^{31}P{^{1}H} NMR (81.014 MHz, CD_2Cl_2): δ = 87.2 ppm; HR-MS (FAB-mNBA): *m*/*z*: 1049.1962 [*M* − BF_4]$^+$; calcd for $C_{48}H_{54}N_4P_2F_4Pd_2B$: 1049.1955; elemental analysis calcd (%) for $C_{48}H_{54}N_4P_2F_8Pd_2B_2$(1135.37): C 50.78, H 4.79, N 4.93; found: C 50.62, H 4.36, N 4.72.

Bimetallic complex (5b): Neat [Pd$_2$(dba)$_3$] (0.25 g, 0.27 mmol) was added to a solution of complex **4a** (0.29 g, 0.54 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 0.5 h at room temperature before PPh_3 (0.14 g, 0.54 mmol) was added as a solid to the solution. The orange solution was stirred for 1 h at room temperature, and concentrated ≈5–10 mL. After addition of diethyl ether (20 mL), complex **5b** precipitated as an orange solid (0.41 g, 83%). ^{1}H NMR (200 MHz, CD_2Cl_2 MHz): δ = 1.40 (m, 4H; CH$_2$), 2.40 (m, 2H; CH$_2$), 2.90 (m, 2H; CH$_2$), 6.40 (d, ^3J(H,H) = 6.4 Hz, 1H; H arom), 6.56 (m, 2H; H arom), 6.94 (dd, ^3J(H,H) = 7.0 Hz, ^3J(H,H) = 6.0 Hz, 1H; H5 Py); 7.07 (dd, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 6.0 Hz, 1H; H5 Py), 7.13 (m, 2H; H arom), 7.30–7.55 (m, 18H; H arom), 7.81 (ddd, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 6.0 Hz, 1H; H arom), 8.54 (d large, ^3J(H,H) = 6.0 Hz, 1H; H6 Py), 8.63 ppm (s large, 1H; H6 Py); ^{13}C{^{1}H} NMR (50.323 MHz, CD_2Cl_2): δ = 22.8 (s, =CCH$_2$CH$_2$), 23.2 (s, =CCH$_2$CH$_2$), 28.1 (s,=CCH$_2$), 28.7 (s,=CCH$_2$), 121.7 (s, C5 Py), 121.7 (d, ^1J(P,C) = 74.2 Hz, *ipso*-C PPh_3), 122.9 (s, C5 Py), 128.5 (s, *m* or *p*-C Ph), 128.6 (s, *m* or *p*-C Ph), 128.7 (d, ^3J(P,C) = 8.1 Hz, *m*-C PPh_3), 128.9 (d, ^3J(P,C) = 11.6 Hz, C3 Py), 131.0 (s, *o*-C Ph), 131.7 (d, ^3J(P,C) = 2.8 Hz, C3 Py), 134.9 (s, C4 Py), 135.2 (d, ^2J(P,C) = 11.6 Hz, *o*-C PPh_3), 135.5 (s, *p*-C PPh_3), 135.6 (s, C4 Py), 137.3 (d, ^1J(P,C) = 55.9 Hz, PC_α=C); 138.2 (d, ^1J(P,C) = 41.72 Hz, PC_α=C), 151.4 (s, C6 Py), 152.1 ppm (s, C6 Py); the Pd-*ipso*-C carbon atom is not observed; ^{31}P{^{1}H} NMR (81.014 MHz, CD_2Cl_2): δ = 29.5 (d, ^2J(P,P) = 15.0 Hz, PPh_3), 99.0 ppm (d, ^2J(P,P) = 15.0 Hz, phospholyl); HR-MS (FAB-mNBA): *m*/*z*: 915.9839 [*M*]$^+$; calcd for $C_{42}H_{36}N_2P_2Pd_2Cl_2$: 915.9808; elemental analysis calcd (%) for $C_{42}H_{36}N_2P_2Pd_2Cl_2$(914.448): C 55.17, H 3.97, N 3.06; found: C 55.11, H 3.90, N 3.12.

Complex 6: To a solution of complex **3a** (X = PF_6^-), (0.42 g, 0.34 mmol) in CH_2Cl_2 (5 mL) was added an excess of dimethylacetylene dicarboxylate (0.05 mL). The solution was stirred for 15 h at 40 °C and diethyl ether (40 mL) was added. The solution was filtered and the precipitate was washed with pentane (2 × 10 mL). Complex **6** was obtained by crystallisation from a CH_2Cl_2/pentane solution at room temperature (0.34 g, 73%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 1.40–1.90 (m, 8H; C=CCH$_2$CH$_2$), 2.20–2.5 (m, 4H; C=CCH$_2$CH$_2$), 2.90 (m, 4H; C=CCH$_2$), 3.81 (s, 6H; OCH$_3$), 7.38–7.6 (m, 10H, H arom), 7.70–7.87 (m, 8H, H arom), 8.02–8.18 (m, 4H; H arom), 8.95 ppm (d large, ^3J(H,H) = 5.5 Hz, 4H; H6 Py); ^{13}C{^{1}H} NMR (75.469 MHz, CD_2Cl_2): δ = 20.1 (s, C=CCH$_2$CH$_2$), 20.7 (s, C=CCH$_2$CH$_2$), 26.4 (m, C=CCH$_2$), 27.6 (m, C=CCH$_2$), 51.0 (s, OCH$_3$), 120.9 (s, C=C-Pd), 124.1 (d, ^1J(P,C) = 37.4 Hz, *ipso*-C),124.5 (d, ^3J(P,C) = 4.6 Hz, C3 Py), 125.8 (s, C5 Py),129.1 (m, *m*-C Ph), 132.7 (m, *o*-C Ph), 132.8 (s, *p*-C Ph), 140.2 (s, C4 Py), 149.2 (s, C6 Py), 149.8 (d, ^2J(P,C) = 18.7 Hz, C2 Py), 164.6 ppm (s, C=O); ^{31}P{^{1}H}NMR (81.014 MHz, CD_2Cl_2): δ = 54.3 ppm; HR-MS (FAB-mNBA): *m*/*z* 1235.0890 [*M* − PF_6]$^+$ calcd for $C_{54}H_{48}N_4P_4F_{12}Pd_2O_4$: 1235.0890; elemental analysis calcd (%) for $C_{54}H_{48}N_4P_4F_{12}Pd_2O_4$ (1381.710): C 46.94, H 3.50, N 4.05; found: C 46.93, H 3.54, N 4.10.

X-ray crystal structure analysis: Single crystals suitable for X-ray crystal analysis were obtained by crystallisation from a CH_2Cl_2/CH_3CN/heptane solution at −20 °C for **3a** (X = SbF_6), from a CH_2Cl_2/Et_2O solution at room temperature for **3a** (X = PF_6), from a CH_2Cl_2/Et_2O solution at room temperature for **3b** (X = BF_4), from a CH_2Cl_2 solution at room temperature for **5b**, from a CH_2Cl_2/pentane solution at room temperature for **6**. The unit cell constant, space group determination and the data collection were carried out on an automatic NONIUS CAD4 diffractometer (compound **3a** (X = SbF_6)) or a NONIUS Kappa CCD (compounds **3a** (X = PF_6), **5b**, **6**) with graphite-monochromated $Mo_{K\alpha}$ radiation.[24a] The cell parameters were obtained by fitting a set of 25 high-theta reflections. After Lorentz and polarization corrections, absorption corrections with ψ scan,[24b] the structures were solved with SIR-97[24c] which reveals the non-hydrogen atoms of the structure. After anisotropic refinement, all hydrogen atoms may be found with a Fourier difference. The whole structures were refined with SHELXL 97[24d] by the full-matrix least-squares techniques (use of *F* magnitude; *x*, *y*, *z*, β_{ij} for C, O, N, P, Cl, F, Sb and Pd atoms), *x*, *y*, *z* in riding mode for the H atoms. Atomic scattering factors were obtained from *International Tables for X-ray Crystallography*.[24e] ORTEP views were prepared with PLATON 98.[24f] All calculations were performed on a Silicon Graphics Indy computer. Crystal refinement parameters are given in Table 3. The carbon atoms of the ethyl bridges of **3a** (X = SbF_6 or PF_6) and **3b** appear as disordered. Further studies in space group *P*1 for **3a** and *Cc* for **3b** unambiguously showed that there is no disorder but a difference in the conformation of the six-membered ring. In the space group *P*1, the pseudo-symmetry of all the other atoms of **3a** leads to important correlations giving unsatisfactory geometry and e.s.d.s.

CCDC-149074 (**3a** (X = SbF_6)), CCDC-203511 (**3a** (X = PF_6)), CCDC-195446 (**3b**), CCDC-195447 (**5b**) and CCDC-204729 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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