

Synthesis of mono-phosphido, mono-dppm bridged Pd(I) cationic dimers. Structure and fluxionality of $[\text{Pd}_2(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})(\eta^1\text{-dppm})_2]\text{CF}_3\text{SO}_3$ (dppm = bis-diphenylphosphinomethane)

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Abstract

The dimer $[\text{Pd}_2(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-P}^t\text{Bu}_2\text{H})(\text{P}^t\text{Bu}_2\text{H})_2]^+\text{X}^-$ [(1)⁺BF₄[−], X = BF₄; (1)⁺Tf[−], X = CF₃SO₃], with two terminal and one bridging weakly bonded di-tert-butylphosphine molecules, proved to be an excellent reagent for the preparation of new mono-phosphido, mono-dppm bridged palladium(I) derivatives of general formula $[\text{Pd}_2(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})(\text{PR}_3)_2]^+\text{X}^-$ [(2)⁺X[−], PR₃ = P^tBu₂H; (3)⁺X[−], PR₃ = PMe₃; (4)⁺X[−], PR₃ = PEt₃; (5)⁺X[−], PR₃ = η¹-dppm]. The cation (5)⁺ has one dppm molecule terminally bonded to each palladium atom in a monodentate fashion. As demonstrated by solution ³¹P{¹H} NMR spectra, the two phosphorus atoms of each η¹-dppm molecule are rapidly scrambled without dissociation through an intermediate chelate coordination of the disphosphine molecule. The same fluxional behavior was observed in the neutral $[\text{Pd}_2(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})(\text{SPh})(\eta^1\text{-dppm})]$ (6) obtained by reaction of (5)⁺BF₄[−] with PhSNa. The solid state structures of complexes (3)⁺Tf[−] and (5)⁺Tf[−] were determined by X-ray diffraction methods.

Keywords: Pd; Phosphido; Dinuclear complexes; Dppm complexes; Fluxionality; X-ray crystal structure

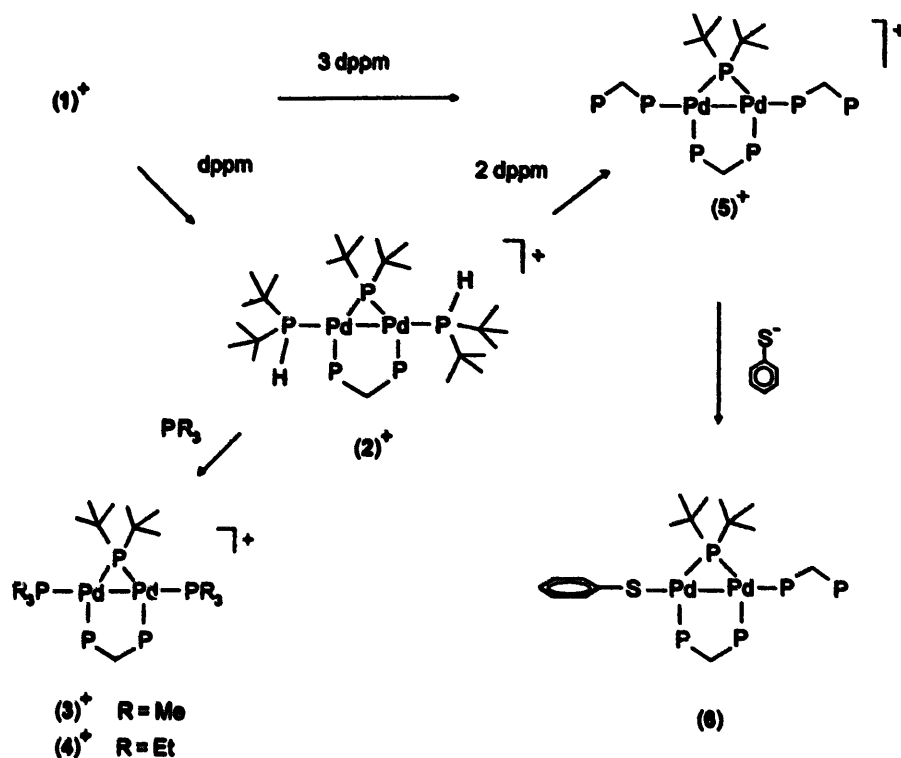
1. Introduction

The chemistry of Pd(I) complexes has received growing interest in the last few years, though it is much less developed than Pd(0)/Pd(II) chemistry. A few examples of mononuclear derivatives [1] apart, it deals mainly with polynuclear compounds. Unsupported metal–metal bonds were observed [2] in some isonitrile derivatives, and the structure of an interesting dimer with the metal–metal bond supported only by semi-bridging phosphorus atoms, $[\text{Pd}(\text{dppp})_2](\text{CF}_3\text{SO}_3)_2$ [dppp = 1,3-bis(diphenylphosphino)propane] [3], has recently been reported. However, the large majority of polynuclear Pd(I) complexes are ligand bridged. Various molecules or ions have been shown to be suitable bridging ligands:

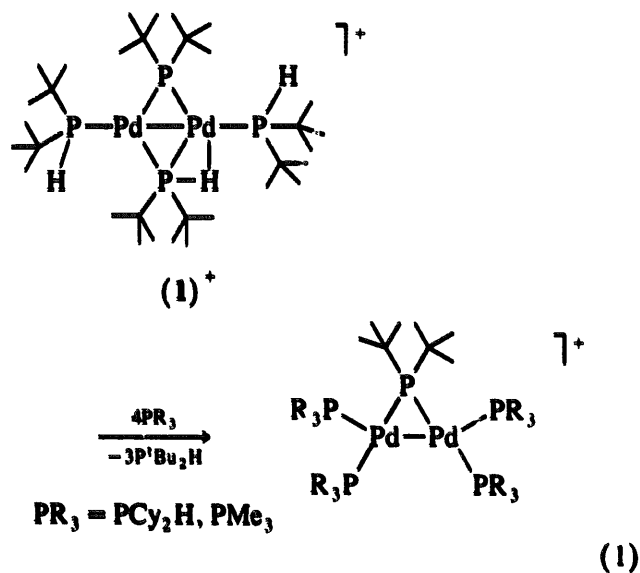
vinylphosphines [4], alkynes [5], hydrides, as in $[(\text{dipp})\text{Pd}(\mu\text{-H})_2]$ [6] or $[(\text{dipp})_2\text{Pd}_2(\mu\text{-H})(\mu\text{-CO})]\text{Cl}$ [7] (dipp = 1,3-bis(diisopropylphosphino)propane), 2-(diphenylphosphino)pyridine (PN), as in $[\text{Pd}(\mu\text{-PN})\text{Cl}]_2$ [8]. Three main classes of ligand bridged Pd(I) dimers have been studied in greater detail and include a relatively large number of compounds. The first one, principally developed by Werner's group, has bridging π-carbon ligands as cyclopentadienyls [9], allyls [10] and arenes [11]. The so-called "A-frame" complexes [12], with two bridging dppm molecules, constitute the second broad class of derivatives. Mono- and di-phosphido bridged derivatives are being developed by our group [13].

We have recently reported the synthesis of complex (1)⁺X[−] [13b]. The three P^tBu₂H molecules bonded to the Pd₂(μ-P^tBu₂) core in the cation (1)⁺ are labile, and can be substituted by four molecules of sterically less demanding phosphines [13f]:

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Scheme 1.



As a straightforward extension of the results of Eq. (1) we investigated the reactions of $(1)^+X^-$ with diphosphines, which afforded a new and practical high yield method for the synthesis of mono-phosphido mono-dppm bridged Pd(I) dinuclear compounds.

2. Results and discussion

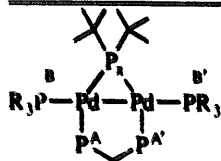
2.1. Complexes with μ -dppm

A violet suspension of $(1)^+BF_4^-$ was reacted with an equimolar amount of dppm, after workup $[\text{Pd}_2(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})(\text{P}^t\text{Bu}_2\text{H})_2]^+BF_4^-$, $(2)^+BF_4^-$, was isolated as a yellow microcrystalline solid in 70% yield (Scheme 1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $(2)^+BF_4^-$ (CH_2Cl_2 , 293 K) consisted of a triplet of triplets at low

Table 1

P labelling scheme, chemical shift and coupling constants in $^{31}\text{F}\{^1\text{H}\}$ NMR spectra of complexes $(2)^+X^-$ and $(3)^+X^-$

Complex	δ_A	δ_B	δ_X	$J_{AA'}$	$J_{BB'}$	J_{AB}	J_{AX}	J_{BX}	$J_{AB'}$
$(2)^+X^-$	-3.36	24.2	340.1	60	205	-35	195	-26	10
$(3)^+X^-$	2.98	-33.3	342.8	60	205	-40	199.5	-26	20



field (340 ppm), assigned to the bridging phosphide, with a large *trans* and a smaller *cis* coupling ($^2J_{PP} = 195$ and 26 Hz). The high field zone showed two signals at ca. 24.2 and -3.36 ppm. The first one was split in a broad doublet ($^1J_{PH} = 290$ Hz) in the corresponding proton coupled spectrum, and was therefore assigned to the P^tBu_2H molecules; the second signal was a doublet of multiplets with the large *trans* coupling and was assigned to the μ -dppm phosphorus nuclei. The spectrum, owing to the $AA'BB'X$ [$A = \mu$ -P(dppm), $B = P^tBu_2H$, $X = \mu$ -P tBu_2] spin system, is not first order, and its simulation gave the set of parameters reported in Table 1.

Two types of tert-butyl proton were observed in the 1H NMR spectrum at 1.54 (d, $^3J_{PH} = 13$ Hz, 36H) and 0.95 ppm (d, $^3J_{PH} = 13.5$ Hz, 18H); other signals in the spectrum were a multiplet at 7.2 ppm (20H, C_6H_5), a triplet at 4.5 ppm ($^2J_{PH} = 9$ Hz, PC_6H_5P) and a doublet of multiplets centered at 4.9 ppm ($^1J_{PH} = 290$ Hz, 2H, PH), in good agreement with the structure suggested for $(2)^+BF_4^-$. Satisfactory analytical results were obtained and significant IR absorptions were observed at 3040 m (ν_{CH}), 1585 m, 1475 m ($\nu_{C=C}$) and 1050 br, vs (ν_{BF} of uncoordinated BF_4^-) cm^{-1} . Analogous results were obtained starting from the triflate salt of $(1)^+$ (see Experimental section).

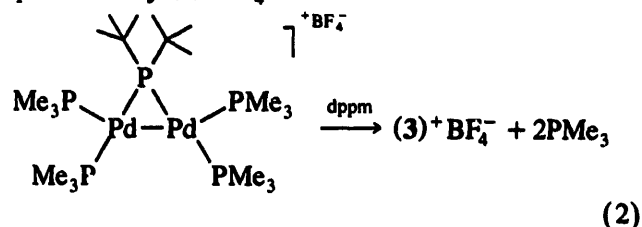
The $Pd_2(\mu$ -P tBu_2)(μ -dppm) core of complex $(2)^+X^-$ is stable towards substitution while the two P tBu_2H molecules are labile and were substituted by reaction with a slight excess of PMe_3 yielding $[Pd_2(\mu$ -P tBu_2)(μ -dppm)(PMe_3) $_2$] X [(3) BF_4^- (90%); (3) $CF_3SO_3^-$ (70%)] (Scheme 1).

Complex (3) $CF_3SO_3^-$ was characterized by single crystal X-ray diffraction (see below) and by the usual analytical and spectroscopic methods. Its $^{31}P\{^1H\}$ NMR spectrum was very similar to the one observed for $(2)^+BF_4^-$, except for the chemical shift of the terminally bonded phosphines, and will not be discussed in detail. Measured and calculated spectra are shown in Fig. 1, and the set of parameters used in the simulation are listed in Table 1.

1H NMR and IR spectra and elemental analyses were as expected (see Experimental section).

The triethylphosphine derivative $[Pd_2(\mu$ -P tBu_2)(μ -dppm)(PEt_3) $_2$] BF_4^- [(4) $^+BF_4^-$ (80%)] was obtained by the same procedure (Scheme 1).

The high affinity of dppm for the fragment $Pd_2(\mu$ -P tBu_2) was confirmed by its reaction with $[Pd_2(\mu$ -P tBu_2)(PMe_3) $_4$] BF_4^- [13f]. This complex reacts immediately at room temperature with an equimolar amount of dppm which substitutes two molecules of PMe_3 giving quantitatively $(3)^+BF_4^-$:



2.2. Complexes with μ - and η^1 -dppm

The reaction of $(2)^+X^-$ with a two-fold excess of dppm gave $[Pd_2(\mu$ -P tBu_2)(μ -dppm)(η^1 -dppm) $_2$] X

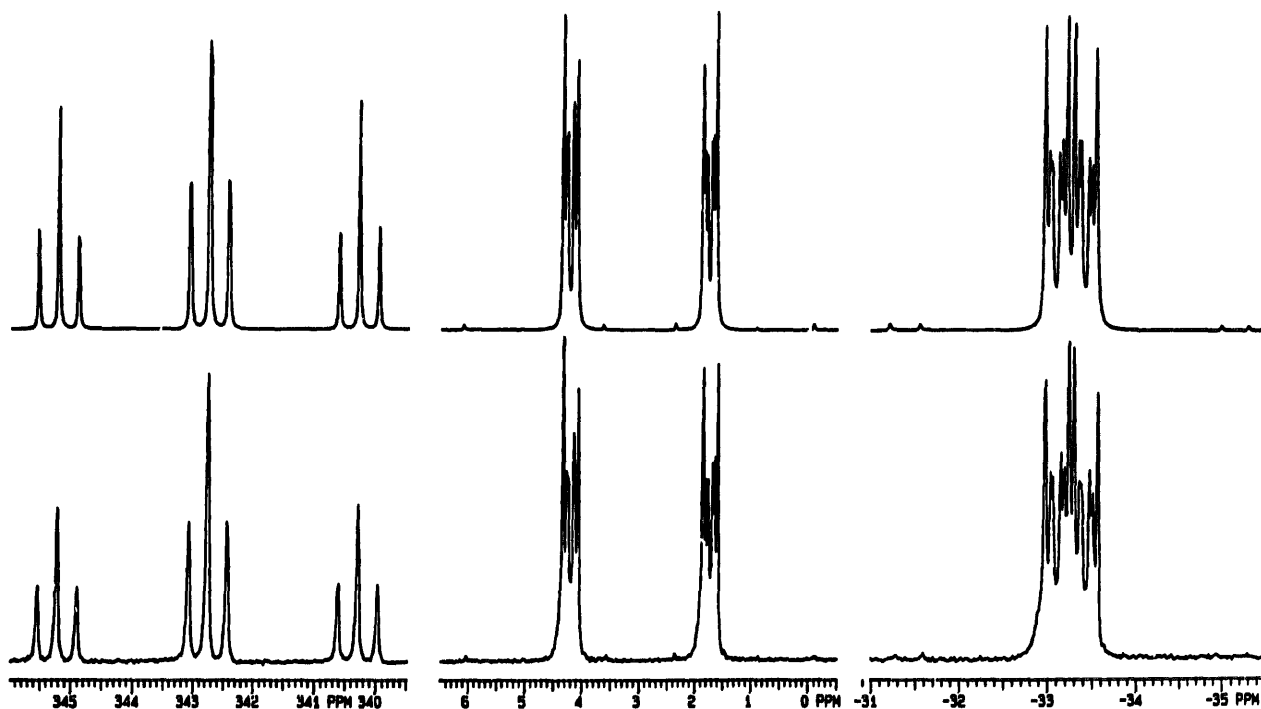


Fig. 1. Calculated (upper) and measured (lower) ($CDCl_3$, 298 K) $^{31}P\{^1H\}$ NMR spectra of complex $(3)^+ Tf^-$.

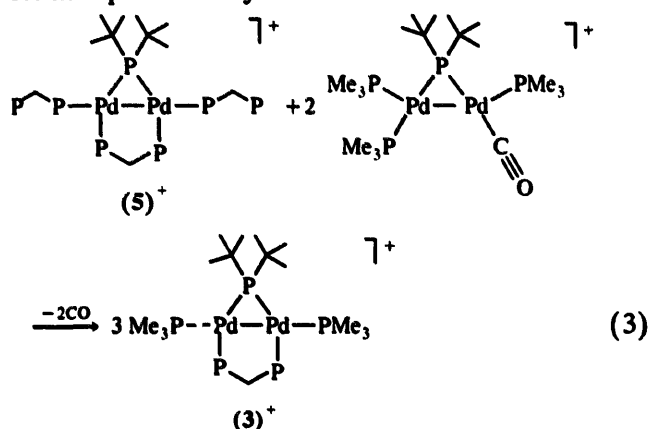
[(5)BF₄ (85%); (5)CF₃SO₃ (68%)]. The triflate salt was characterized by single crystal X-ray diffraction (see below). The same complex was also obtained by the direct reaction of (1)⁺X[−] with an excess of dppm.

The ³¹P{¹H} NMR spectrum (CD₂Cl₂, 298 K, Fig. 2) of complex (5)⁺BF₄[−] consisted of a triplet of quintets at 337.4 ppm for the bridging phosphido P₁, with the usual large *trans* coupling with the two equivalent nuclei P₂ and P₂' (²J_{PH} = 195 Hz). The main triplet is split into quintets owing to the coupling with the four P atoms of the η¹-dppm ligands; the small coupling (*J*_{PP} = 16 Hz) is therefore a mean value of the ²J_{PP} with P₃ and P₃' and ⁴J_{PP} with P₄ and P₄', suggesting a dynamic process which scrambles these nuclei without cleavage of the Pd–P bonds. This is confirmed by the appearance of the signals in the high field zone. In fact, while P₂ and P₂' of the μ-dppm molecule give a well-resolved doublet of multiplets at −3.62 ppm (*trans* ²J_{PP} = 195 Hz), the four P nuclei of the η¹-dppm molecules give a broad absorption centered at −11.5 ppm which splits into two broad signals at 1.5 and −29 ppm when the spectrum is

registered at 193 K. The signal at −29 ppm, very close to the resonance of free dppm (−30.9 ppm), can be assigned to the uncoordinated P₄ and P₄' and, consequently, the signal at 1.5 ppm must be assigned to P₃ and P₃'.

¹H and IR spectra and elemental analyses were consistent with the structure (5)BF₄.

However, the bridging coordination mode of the dppm molecule is highly preferred in these systems and the two η¹-dppm molecules can be easily transferred. In fact, a ligand redistribution takes place immediately when (5)BF₄ is reacted with two equivalents of [Pd₂(μ-P^tBu₂)(CO)(PMe₃)₃]BF₄, and the known (3)BF₄ is formed quantitatively with loss of carbon monoxide:



2.3. Reaction of (5)⁺ with PhS[−]

The stability of the Pd₂(μ-P^tBu₂)(μ-dppm) core towards substitution was confirmed by the reaction of the cation (5)⁺ with an anionic nucleophile. Complex (5)⁺BF₄[−] was reacted with a stoichiometric amount of PhS[−] which substituted one of the terminal diphosphines and gave the neutral derivative [Pd₂(μ-P^tBu₂)(μ-dppm)(η¹-dppm)(SPh)] (6). This compound exhibited the same type of fluxionality observed in the cation (5)⁺. The resonance due to the bridging phosphido P₁ appeared in the ³¹P{¹H} NMR spectrum of (6) (Fig. 3) as a doublet of doublets of triplets at 307 ppm. Two large *trans* couplings (²J_{PP} = 259 and 186 Hz), responsible for the double doublet splitting, were assigned to the coupling with the two unequivalent phosphorus nuclei of the μ-dppm molecule. Each line of the dd is further split into triplets by a small *cis* coupling [(²J_{P₁P₃} + ⁴J_{P₁P₄})/2 = 9.4 Hz] with the two nuclei (P₄ and P₃) of the η¹-dppm molecule in rapid interchange. The high field portion of the spectrum exhibits three signals. The P nuclei of the μ-dppm molecule (P₂ and P₃) resonate at −7.48 and −0.08 ppm; both of them appear as doublets of doublets of triplets having the following coupling constants: *J*_{PP} = 259, 74.7, 3.8 Hz and *J*_{PP} = 136, 74.7, 10.3 Hz respectively. The multiplicity of the signals is due to the large *trans* coupling

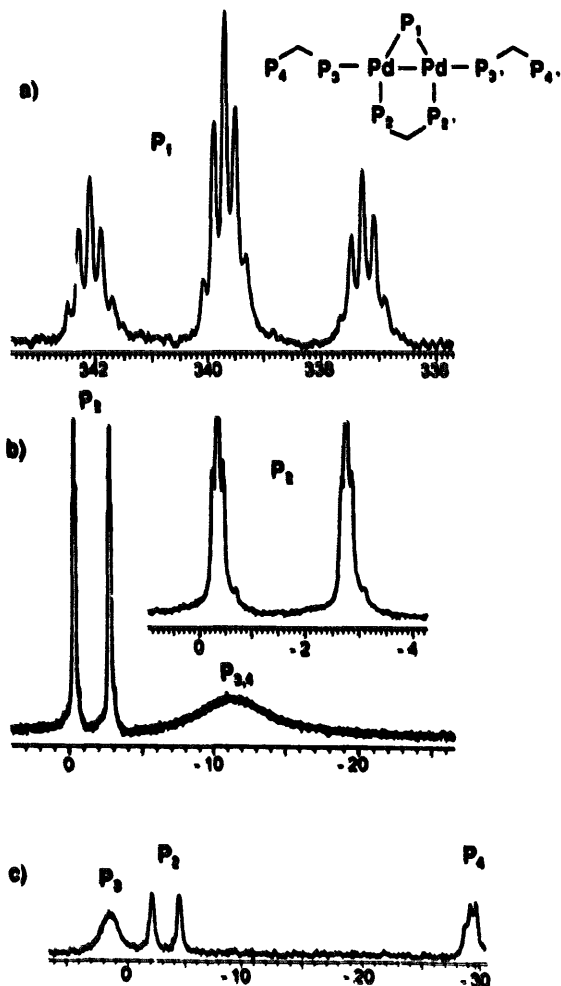
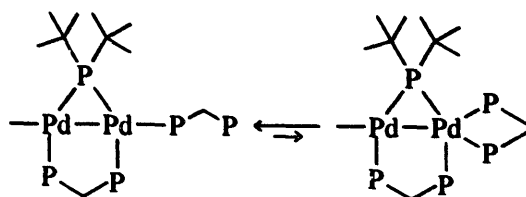


Fig. 2. ³¹P{¹H} NMR spectra (CD₂Cl₂) of complex (5)⁺ Tf[−]: (a) and (b) 298 K; (c) 193 K.

with the bridging phosphide, to the mutual coupling ($^2J_{P_2P_3} = 74.7$ Hz), and to the small average coupling with P_4 and P_5 of the η^1 -dppm molecule. The last coupling is greater [$(^2J_{P_3P_4} + ^4J_{P_3P_5})/2 = 10.3$ Hz] for the phosphorus *cis* to η^1 -dppm and smaller [$(^3J_{P_2P_4} + ^5J_{P_2P_5})/2 = 3.8$ Hz] for the phosphorus *cis* to the thiophenoxide ligand. The two phosphorus nuclei of the η^1 -dppm molecule (P_4 and P_5) give a single broad singlet at -16 ppm.

1H NMR and IR spectra and elemental analyses were consistent with the structure (6).

A reasonable explanation of the fluxionality observed in the spectra of complexes $(5)^+X^-$ and (6) is that the phosphorus atoms of the η^1 -dppm molecules exchange their position in solution through a pentacoordinate intermediate of the type shown in Scheme 2.



Scheme 2.

No signal attributable to an intermediate could be observed in the low temperature spectra of $(5)^+$, and this intermediate should therefore be present in low concentration (or as a transition state). This is not surprising, however, since pentacoordinated palladium complexes are known but are stable only when supported by nitrogen and/or carbon ligands [14], no ex-

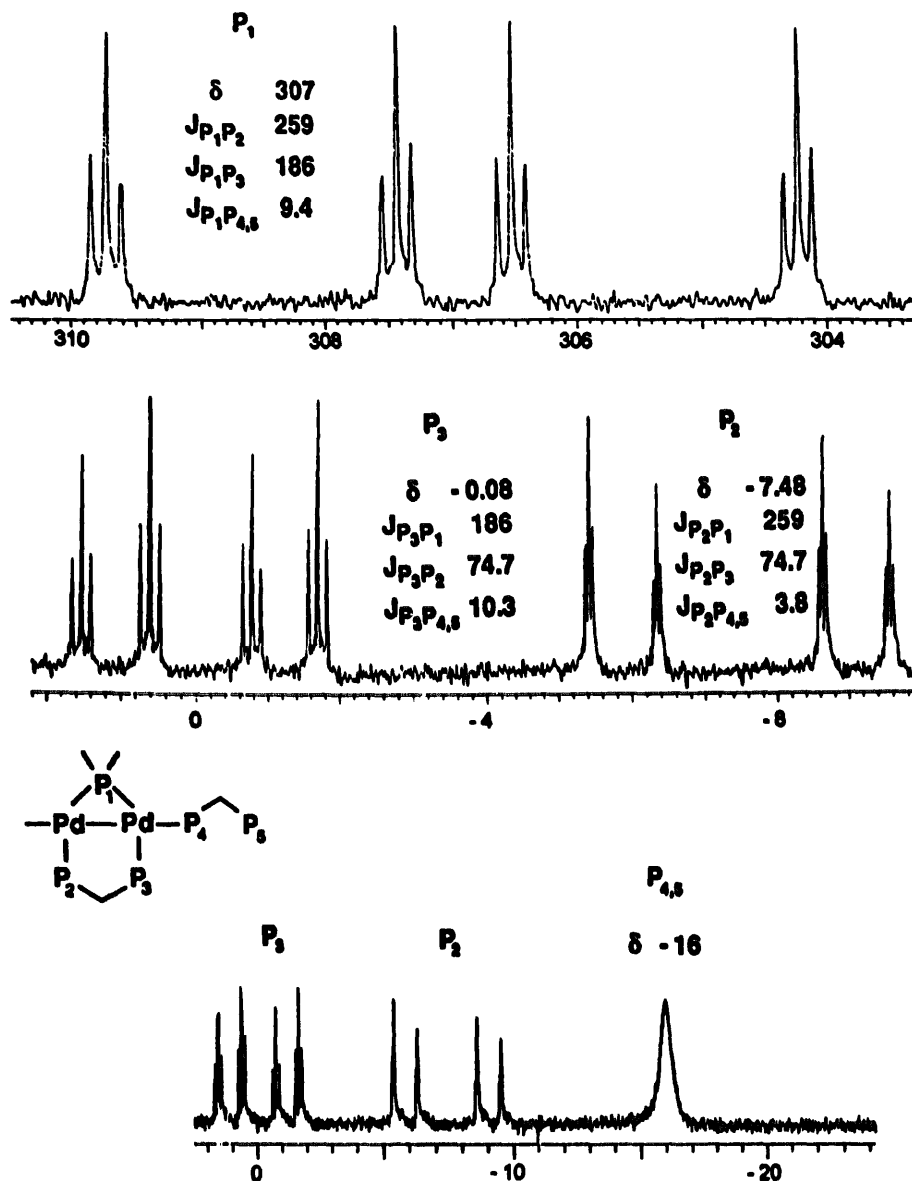
Fig. 3. $^{31}P\{^1H\}$ NMR spectra (toluene, 298 K) of complex (6).

Table 2
Selected bond distances (Å) and angles (°) for complexes (3)⁺Tf[−] and (5)⁺Tf[−]

(3) ⁺ Tf [−]		(5) ⁺ Tf [−]	
Pd1–Pd2	2.6870(9)	Pd1–Pd2	2.722(1)
Pd1–P1	2.319(2)	Pd1–P1	2.321(3)
Pd1–P3	2.261(2)	Pd1–P3	2.266(3)
Pd1–P4	2.306(2)	Pd1–P4	2.330(3)
Pd2–P2	2.316(2)	Pd2–P2	2.343(3)
Pd2–P3	2.265(2)	Pd2–P3	2.291(3)
Pd2–P5	2.320(2)	Pd2–P6	2.346(3)
Pd2–Pd1–P1	91.44(6)	Pd2–Pd1–P1	89.80(8)
Pd2–Pd1–P3	53.65(6)	Pd2–Pd1–P3	53.75(8)
Pd2–Pd1–P4	167.44(8)	Pd2–Pd1–P4	166.54(8)
P1–Pd1–P3	145.07(8)	P1–Pd1–P3	143.4(1)
P1–Pd1–P4	100.81(9)	P1–Pd1–P4	101.0(1)
P3–Pd1–P4	114.12(9)	P3–Pd1–P4	114.7(1)
Pd1–Pd2–P2	94.39(6)	Pd1–Pd2–P2	95.11(8)
Pd1–Pd2–P3	53.52(6)	Pd1–Pd2–P3	52.91(7)
Pd1–Pd2–P5	165.15(6)	Pd1–Pd2–P6	162.95(8)
P2–Pd2–P3	146.38(8)	P2–Pd2–P3	145.8(1)
P2–Pd2–P5	100.05(8)	P2–Pd2–P6	101.2(1)
P3–Pd2–P5	111.64(9)	P3–Pd2–P6	112.0(1)
Pd1–P3–Pd2	72.83(7)	Pd1–P3–Pd2	73.34(9)

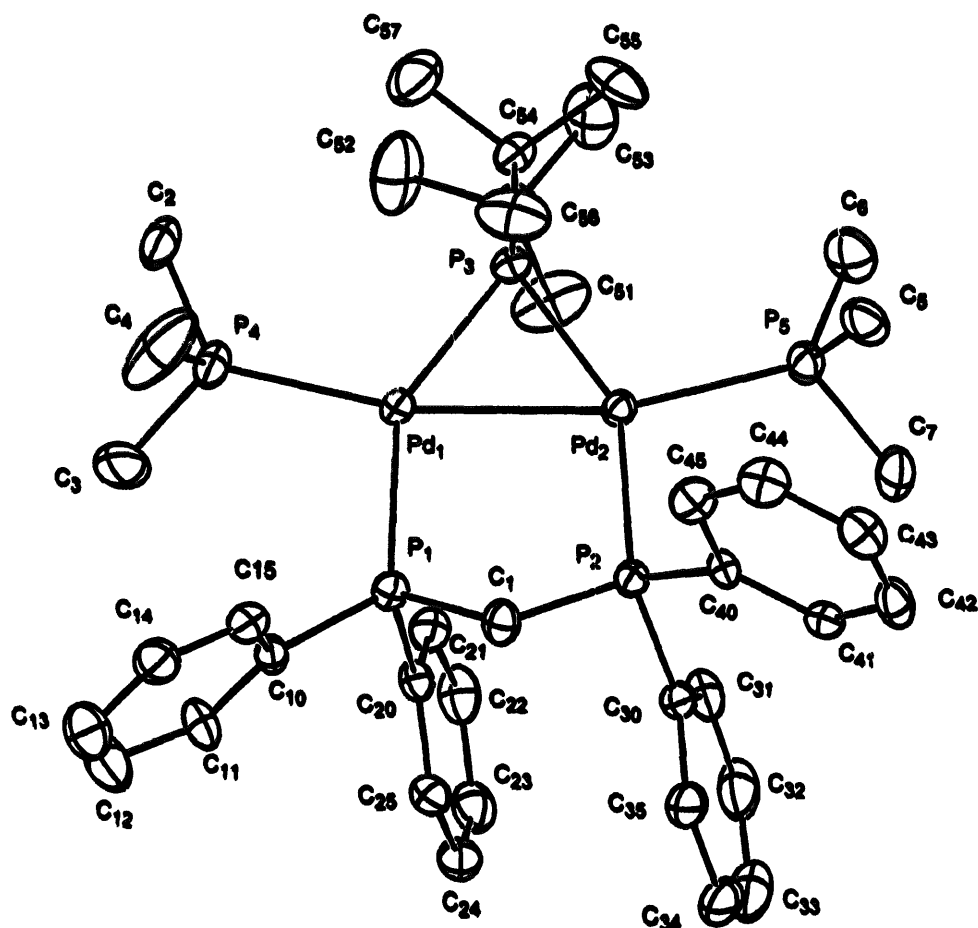


Fig. 4. ORTEP view of the molecular structure of the cation (3)⁺ with the atom numbering. Thermal ellipsoids are drawn at 30% probability.

ample having been reported with only phosphorus donor ligands.

Evidence of the existence of such intermediates is relevant, especially for its implications in the substitution reactions on cations like $(2)^+-(5)^+$ which, in the light of the above discussed results, could proceed through associative mechanisms.

A further point of interest suggested by the structure of $(5)^+$ is its possible utilization in the synthesis of new homo- or hetero-metallic complexes of higher nuclearity. A similar utilization of Pt η^1 -dppm complexes has been reported by Puddephatt and coworker [15].

Finally, we should mention that, despite the great interest in the field of ligand supported metal-metal bonded complexes, mono-phosphido mono-diphosphino bridged derivatives are relatively rare; the structures of a certain number of derivatives of the iron [16] or cobalt [17] triads and of a few members of other groups [18] have been reported.

2.4. Molecular structures of complexes $(3)^+Tf^-$ and $(5)^+Tf^-$

Single crystals of both $(3)^+Tf^-$ and $(5)^+Tf^-$ were grown by recrystallization from CH_2Cl_2/Et_2O mixtures. Relevant bond distances and angles are listed in Table 2; Figs. 4 and 5 show the ORTEP projections with the atom numbering of the cations $(3)^+$ and $(5)^+$ respectively. Both the cations contain a planar $Pd_2(\mu-P)(\mu-PP)$ core with the μ -phosphido and the μ -dppm ligands lying on opposite hemiplanes with respect to the Pd-Pd vector. The Pd-Pd distance is 2.6870(9) Å in $(3)^+$ and is slightly elongated [2.722(1) Å] in $(5)^+$, probably due to the higher steric crowding in the latter

complex. Both distances are in the range observed in single bonded Pd(I)-Pd(I) dinuclear derivatives. The relatively small Pd1-P3-Pd2 angles [72.83(7) and 73.34(9)° respectively] and the low field ^{31}P NMR resonances of the phosphido ligands are also in accord with the presence of a Pd-Pd bond.

The coordination sphere around each palladium center is completed by a terminally bonded PMe_3 [in $(3)^+$] or an η^1 -dppm [in $(5)^+$] molecule lying in the plane of the $Pd_2(\mu-P)(\mu-PP)$ core; therefore, each cation consists of two coplanar distorted square planes which share the μ -P(phosphido) and the metal-metal bond. The distortion from the regular square-planar geometry is caused principally by the presence of the small three-membered $Pd_2(\mu-P3)$ rings with Pd-Pd-P3 angles around 53° (see Table 2) which force other pseudocis angles to be larger than 90° [P3-Pd1-P4 = 114.12(9), P3-Pd2-P5 = 111.64(9), P1-Pd1-P4 = 100.81(9) and P2-Pd2-P5 = 100.05(8)° for $(3)^+$; P3-Pd1-P4 = 114.7(1), P3-Pd2-P6 = 112.0(1), P1-Pd1-P4 = 101.0(1), P2-Pd2-P6 = 101.2(1)° for $(5)^+$]. The angles Pd2-Pd1-P1 and Pd1-Pd2-P2 of both complexes are included in the rigid five-membered $Pd_2(\mu-PCP)$ rings and are in the range 89.80(8) to 95.11(8)°.

As often observed in Pd(I)-phosphido bridged complexes containing phosphine ligands the Pd-P bond lengths involving the bridging phosphide [from 2.261(2) to 2.291(3) Å] are significantly shorter than the other Pd-P bond distances [from 2.306(2) to 2.346(3) Å]. The central $Pd_2(\mu-P)(\mu-PP)$ core is nearly symmetrical in $(3)^+$ [Pd1-P3 = 2.261(2) vs. Pd2-P3 = 2.265(2) Å and Pd1-P1 = 2.319(2) vs. Pd2-P2 = 2.316(2) Å, Pd2-Pd1-P3 = 53.65(6) vs. Pd1-Pd2-P3 = 53.52(6)° and Pd2-Pd1-P1 = 91.44(6) vs. Pd1-Pd2-P2 = 94.39(6)°]

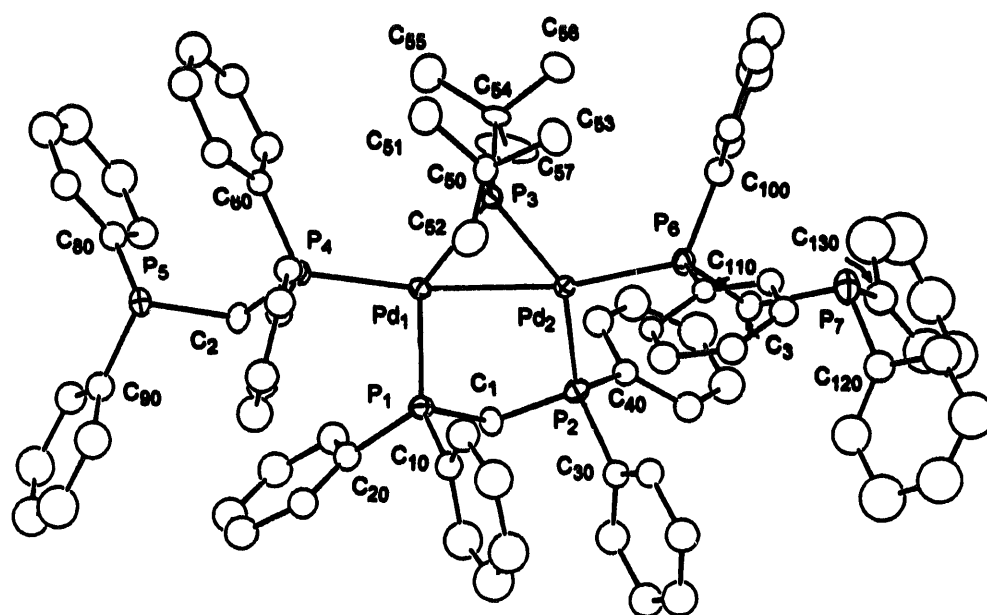


Fig. 5. ORTEP view of the molecular structure of the cation $(5)^+$ with the atomic numbering. Thermal ellipsoids are drawn at 30% probability.

while it is more distorted in (5)⁺ [Pd1–P3 = 2.266(3) vs. Pd2–P3 = 2.291(3) Å and Pd1–P1 = 2.321(3) vs. Pd2–P2 = 2.343(3) Å; Pd2–Pd1–P3 = 53.75(8) vs. Pd1–Pd2–P3 = 52.91(7)° and Pd2–Pd1–P1 = 89.80(8) vs. Pd1–Pd2–P2 = 95.11(8)°]; this effect can again be ascribed to the severe congestion in (5)⁺.

3. Experimental

3.1. General data

All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques. [Pd₂(μ-P'Bu₂)(μ-P'Bu₂H)(P'Bu₂H)₂]⁺X[−] [(1)⁺X[−]] [13b], [Pd₂(μ-P'Bu₂)(CO)(PMe₃)₃]⁺X[−] and [Pd₂(μ-P'Bu₂)(PMe₃)₄]⁺X[−] [13f] [X = BF₄[−], CF₃SO₃[−]] were prepared according to published procedures. Solvents were dried by conventional methods and distilled prior to use. IR spectra (Nujol mulls, KBr plates) were recorded on a Perkin-Elmer FT-IR 1725X spectrometer. NMR spectra were recorded on a Varian Gemini 200 BB instrument. Frequencies are referred to Me₄Si (¹H) or 85% H₃PO₄ (³¹P). Only the preparations of the BF₄[−] salts are described, the triflate salts can be prepared analogously. Owing to their higher solubility these were obtained as crystals of larger size but the yields of the isolated products were slightly lower. Solution ¹H and ³¹P NMR spectra were independent of the counterion.

3.2. Preparation of [Pd₂(μ-P'Bu₂)(μ-dppm)(P'Bu₂-H)₂]⁺BF₄[−], (2)⁺BF₄[−]

An equimolar amount of dppm was added to a violet suspension of (1)⁺BF₄[−] (501 mg, 0.567 mmol) in DME (20 ml). After stirring over night at 60°C, the resulting yellow suspension was concentrated to ca. 10 ml and Et₂O (20 ml) was added. The yellow solid was filtered and vacuum dried (445 mg, 0.397 mmol, 70%). Anal. Found: C, 52.0; H, 6.95. C₄₉H₇₈BF₄P₅Pd₂. Calc.: C, 52.5; H, 7.01%. IR (Nujol, KBr) 3040 m (ν_{C-H}), 2330 w (ν_{P-H}), 1585 m, 1475 m (ν_{C=C}) 1050 vs, br (ν_{B-F}) cm^{−1}. ¹H NMR (CD₂Cl₂, 298 K) δ (ppm): 7.2 (m, 20 H, C₆H₅), 4.9 (dm, ¹J_{PH} = 290 Hz, 2H, PH), 4.5 (t, ²J_{PH} = 9 Hz, 2H, PC H₂P), 1.54 (d, ³J_{PH} = 13 Hz, 36H, C₄H₉), 0.95 (d, ³J_{PH} = 13.5 Hz, 18H, C₄H₉). ³¹P{¹H} (CH₂Cl₂, 298 K), δ (ppm): 340.1 (tt, ²J_{PP} = 195 Hz, ²J_{PP} = 26 Hz, μ-P'Bu₂), 24.2 (m, P'Bu₂H), −3.36 (dm, ²J_{PP} = 195 Hz, μ-dppm).

3.3. Preparation of [Pd₂(μ-P'Bu₂)(μ-dppm)(P-Me₃)₂]⁺BF₄[−], (3)⁺BF₄[−]

PMe₃ (0.12 ml, 1.16 mmol) was added to an orange solution of (2)⁺BF₄[−] (173 mg, 0.154 mmol) in DME (10 ml). The solution turned pale yellow in a few minutes and was left for 1 h at room temperature; it was then concentrated to ca. 2 ml and Et₂O (20 ml) was

Table 3
Summary of X-ray diffraction data for (3)⁺Tf[−] and (5)⁺Tf[−]

	(3) ⁺ Tf [−]	(5) ⁺ Tf [−]
Formula	C ₄₀ H ₅₈ F ₃ O ₃ P ₅ Pd ₂ S	C ₄₄ H ₆₄ F ₃ O ₃ P ₅ Pd ₂ S
<i>F</i> _w	1043.64	1660.28
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 1̄ (No. 2)
<i>a</i> (Å)	12.650(4)	17.540(9)
<i>b</i> (Å)	19.385(4)	20.25(1)
<i>c</i> (Å)	19.421(5)	11.481(3)
α (°)		96.50(4)
β (°)	102.69(3)	99.09(3)
γ (°)		77.11(5)
<i>V</i> (Å ³)	4646(3)	3913(4)
<i>Z</i>	4	2
ρ _{calc} (g cm ^{−3})	1.492	1.409
Radiation	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
μ (cm ^{−1})	10.22	6.73
<i>F</i> (000)	2128	1704
Crystal dimensions (mm ³)	0.4 × 0.3 × 0.3	0.6 × 0.6 × 0.2
<i>T</i> (°C)	−10	−10
Scan range	(3.0 < θ < 25.0°)	(3.0 < θ < 24.0°)
Scan type	ω	ω
No. of reflections measured	8815	11034
No. of unique data	5386	6734
<i>I</i> > 1.0σ(<i>I</i>)		
No. of variables refined	487	536
<i>R</i> ^a	0.075	0.096
<i>R</i> _w ^b [<i>w</i> = 1/σ ² (<i>F</i> _o)]	0.069	0.089

^a *R* = Σ|Δ*F*|/Σ|*F*_o|; ^b *R*_w = (Σ|Δ*F*|²/Σ*w*|*F*_o|²)^{1/2}; *w* = 1/σ²|*F*_o|.

Table 4
Complex (S)⁺Tf[−] positional parameters and their estimated standard deviations (in parentheses)

Atom	x	y	z	U _{eq}
Pd1	0.62375(6)	0.19786(5)	0.3862(1)	0.0257(3)
Pd2	0.46682(6)	0.24163(5)	0.3137(1)	0.0258(3)
S	0.7471(4)	0.3304(3)	0.1876(5)	0.101(2)
P1	0.6221(2)	0.2934(2)	0.5187(3)	0.034(1)
P2	0.4622(2)	0.3538(2)	0.3945(4)	0.033(1)
P3	0.5460(2)	0.1416(2)	0.2530(3)	0.030(1)
P4	0.7505(2)	0.1354(2)	0.4414(4)	0.033(1)
P5	0.9269(2)	0.1301(2)	0.5272(4)	0.041(1)
P6	0.3329(2)	0.2446(2)	0.2449(3)	0.033(1)
P7	0.1643(2)	0.3381(2)	0.1672(4)	0.052(1)
F1	0.727(1)	0.2571(8)	0.002(1)	0.344(7)
F2	0.835(1)	0.289(1)	0.034(2)	0.26(1)
F3	0.736(2)	0.347(1)	−0.019(2)	0.31(1)
O1	0.6670(9)	0.356(1)	0.185(2)	0.23(1)
O2	0.767(2)	0.2695(9)	0.240(1)	0.29(1)
O3	0.796(1)	0.373(1)	0.222(2)	0.309(9)
C1	0.5619(8)	0.3692(6)	0.449(1)	0.036(4)
C2	0.8268(8)	0.1844(6)	0.483(1)	0.037(4)
C3	0.2721(7)	0.3294(6)	0.229(1)	0.038(4)
C4	0.763(2)	0.292(1)	0.055(3)	0.17(1) *
C10	0.5722(8)	0.2878(7)	0.642(1)	0.041(4) *
C11	0.5445(9)	0.2308(8)	0.646(1)	0.062(5) *
C12	0.496(1)	0.2290(9)	0.736(2)	0.082(6) *
C13	0.479(1)	0.288(1)	0.814(2)	0.093(7) *
C14	0.507(1)	0.343(1)	0.808(2)	0.095(7) *
C15	0.555(1)	0.3455(9)	0.724(2)	0.083(6) *
C20	0.7091(8)	0.3292(7)	0.584(1)	0.041(4) *
C21	0.7416(9)	0.3612(8)	0.510(1)	0.056(5) *
C22	0.810(1)	0.3860(8)	0.551(2)	0.065(5) *
C23	0.847(1)	0.3733(8)	0.663(2)	0.065(5) *
C24	0.8171(9)	0.3403(8)	0.739(1)	0.063(5) *
C25	0.7457(9)	0.3181(7)	0.698(1)	0.051(4) *
C30	0.4056(8)	0.3927(7)	0.514(1)	0.039(4) *
C31	0.4142(9)	0.4551(8)	0.570(1)	0.065(5) *
C32	0.368(1)	0.4864(8)	0.660(2)	0.067(5) *
C33	0.317(1)	0.4499(9)	0.696(2)	0.072(6) *
C34	0.3096(9)	0.3889(8)	0.638(2)	0.064(5) *
C35	0.3547(8)	0.3591(7)	0.549(1)	0.044(4) *
C40	0.4291(8)	0.4138(6)	0.279(1)	0.036(4) *
C41	0.3623(8)	0.4653(7)	0.282(1)	0.048(4) *
C42	0.337(1)	0.5068(9)	0.182(2)	0.072(6) *
C43	0.382(1)	0.4933(9)	0.090(2)	0.083(6) *
C44	0.450(1)	0.4477(8)	0.093(2)	0.070(6) *
C45	0.4721(9)	0.4054(7)	0.185(1)	0.051(4) *
C50	0.5321(8)	0.0590(7)	0.296(1)	0.044(5)
C51	0.597(1)	0.0002(8)	0.264(2)	0.066(6)
C52	0.5347(9)	0.0681(7)	0.431(1)	0.058(5)
C53	0.4525(9)	0.0428(7)	0.242(1)	0.058(5)
C54	0.5597(8)	0.1364(7)	0.092(1)	0.042(5)
C55	0.636(1)	0.091(1)	0.066(2)	0.109(9)
C56	0.492(1)	0.1155(9)	0.010(1)	0.070(6)
C57	0.563(1)	0.2071(8)	0.071(1)	0.103(7)
C60	0.8002(7)	0.0695(6)	0.336(1)	0.033(4) *
C61	0.8363(8)	0.0041(7)	0.359(1)	0.046(4) *
C62	0.8768(9)	−0.0370(8)	0.269(1)	0.060(5) *
C63	0.884(1)	−0.0129(8)	0.169(2)	0.067(5) *
C64	0.8528(9)	0.0524(8)	0.150(1)	0.058(5) *
C65	0.8095(9)	0.0961(7)	0.231(1)	0.049(4) *
C70	0.7501(8)	0.0959(7)	0.576(1)	0.039(4) *
C71	0.7291(8)	0.0297(7)	0.564(1)	0.043(4) *
C72	0.7207(9)	0.0025(7)	0.667(1)	0.050(4) *
C73	0.7341(9)	0.0390(8)	0.779(1)	0.061(5) *

added under vigorous stirring. A yellow solid precipitated, the suspension was kept over night at -30°C and filtered; the solid was vacuum dried yielding 136 mg (0.139 mmol, 90%) of $(3)^{+}\text{BF}_4^{-}$. Anal. Found: C, 47.3; H, 5.91. $\text{C}_{39}\text{H}_{58}\text{BF}_4\text{P}_5\text{Pd}_2$. Calc.: C, 47.7; H, 5.95%. IR (Nujol, KBr) 3040 m ($\nu_{\text{C-H}}$), 1573 m, 1445 m ($\nu_{\text{C=C}}$) 1062 vs, br ($\nu_{\text{B-F}}$) cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ (CH_2Cl_2 , 298 K), δ (ppm): 342.8 (tt, $^2J_{\text{PP}} = 199.5$ Hz, $^2J_{\text{PP}} = 26$ Hz, $\mu\text{-P}^i\text{Bu}_2$), 2.98 (dm, $^2J_{\text{PP}} = 199.5$ Hz, $\mu\text{-dppm}$), -33.3 (m, PMe_3).

3.4. Preparation of $[\text{Pd}_2(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-dppm})(\text{PEt}_3)_2]^+\text{BF}_4^{-}$ (4) $^+\text{BF}_4^{-}$

PEt_3 (0.16 ml, 1.08 mmol) was added to an orange solution of $(2)^{+}\text{BF}_4^{-}$ (151 mg, 0.135 mmol) in DME (10 ml). The solution turned pale yellow in a few minutes and was left for 1 h at room temperature; it was then concentrated to ca. 2 ml and Et_2O (20 ml) was

added under vigorous stirring. A yellow solid precipitated, the suspension was kept over night at -30°C and filtered; the solid was vacuum dried yielding 114 mg (0.107 mmol, 79.5%) of $(4)^{+}\text{BF}_4^{-}$. Anal. Found: C, 50.2; H, 6.57. $\text{C}_{45}\text{H}_{70}\text{BF}_4\text{P}_5\text{Pd}_2$. Calc.: C, 50.7; H, 6.62%. IR (Nujol, KBr) 3040 m ($\nu_{\text{C-H}}$), 1587 m, 1445 m ($\nu_{\text{C=C}}$) 1060 vs, br ($\nu_{\text{B-F}}$) cm^{-1} . NMR (CD_2Cl_2 , 298 K). $^{31}\text{P}\{^1\text{H}\}$ δ : 338.2 (tm, $^2J_{\text{PP}}$ ca. 190 Hz, $\mu\text{-P}^i\text{Bu}_2$), -2.4 (dm, $^2J_{\text{PP}}$ ca. 190 Hz, $\mu\text{-dppm}$), -3.8 ppm (m, PEt_3); ^1H : δ 7.2 (m, 20H, C_6H_5), 4.6 (broad t, 2H, PCCH_2P), 1.5 (d, $^3J_{\text{PH}} = 14$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$), 1.25 (m, 4H, PCCH_2CH_3), 0.8 (t, $^3J_{\text{HH}} = 7$ Hz, 6H, PCH_2CH_3).

3.5. Preparation of $[\text{Pd}_2(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-dppm})(\eta^1\text{-dppm})_2]^+\text{BF}_4^{-}$ (5) $^+\text{BF}_4^{-}$

Dppm (300 mg, 0.78 mmol) was added to a violet suspension of $(1)^{+}\text{BF}_4^{-}$ (223 mg, 0.252 mmol) in DME

Table 4 (continued)

Atom	x	y	z	U_{eq}
C74	0.753(1)	0.0992(9)	0.785(2)	0.073(6) *
C75	0.7623(9)	0.1278(8)	0.686(1)	0.057(5) *
C80	0.9755(8)	0.1259(7)	0.396(1)	0.044(4) *
C81	1.0267(8)	0.0657(7)	0.367(1)	0.048(4) *
C82	1.062(1)	0.0569(8)	0.267(2)	0.066(5) *
C83	1.048(1)	0.1061(9)	0.193(2)	0.083(6) *
C84	0.999(1)	0.1714(8)	0.220(2)	0.071(6) *
C85	0.9603(9)	0.1796(7)	0.323(1)	0.053(5) *
C90	0.9714(8)	0.1886(7)	0.638(1)	0.046(4) *
C91	1.0182(9)	0.2314(8)	0.613(1)	0.056(5) *
C92	1.056(1)	0.2713(9)	0.709(2)	0.085(6) *
C93	1.045(1)	0.2647(9)	0.820(2)	0.083(6) *
C94	1.002(1)	0.223(1)	0.847(2)	0.100(7) *
C95	0.964(1)	0.1821(9)	0.756(2)	0.077(6) *
C100	0.3031(8)	0.2057(7)	0.098(1)	0.042(4) *
C101	0.3092(9)	0.2359(7)	0.000(1)	0.051(4) *
C102	0.288(1)	0.2071(9)	$-0.113(2)$	0.073(6) *
C103	0.266(1)	0.1476(9)	$-0.126(2)$	0.077(6) *
C104	0.2590(9)	0.1146(8)	$-0.035(1)$	0.063(5) *
C105	0.2794(8)	0.1415(7)	0.086(1)	0.043(4) *
C110	0.2883(7)	0.2072(6)	0.348(1)	0.031(4) *
C111	0.2105(8)	0.2006(7)	0.331(1)	0.039(4) *
C112	0.1790(8)	0.1787(7)	0.418(1)	0.047(4) *
C113	0.2244(9)	0.1621(7)	0.523(1)	0.052(5) *
C114	0.3041(9)	0.1664(8)	0.543(1)	0.055(5) *
C115	0.3348(7)	0.1901(6)	0.455(1)	0.031(4) *
C120	0.1144(9)	0.3671(7)	0.296(1)	0.054(5) *
C121	0.040(1)	0.3517(9)	0.283(2)	0.084(6) *
C122	$-0.004(1)$	0.374(1)	0.380(2)	0.119(8) *
C123	0.026(1)	0.404(1)	0.480(2)	0.117(8) *
C124	0.096(1)	0.427(1)	0.495(2)	0.122(9) *
C125	0.142(1)	0.4039(9)	0.396(2)	0.084(6) *
C130	0.1483(9)	0.4172(8)	0.092(1)	0.061(5) *
C131	0.172(1)	0.407(1)	$-0.017(2)$	0.129(9) *
C132	0.157(2)	0.463(1)	$-0.091(2)$	0.16(1) *
C133	0.125(1)	0.526(1)	$-0.039(2)$	0.121(9) *
C134	0.088(1)	0.539(1)	0.056(2)	0.122(9) *
C135	0.101(1)	0.477(1)	0.126(2)	0.112(8) *

* Atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as one third of the trace of the orthogonalized U tensor.

(20 ml). After stirring over night at 70°C, the yellow suspension was concentrated to ca. 10 ml and Et₂O (15 ml) was added; the yellow solid was filtered and vacuum dried yielding 342 mg (0.214 mmol, 85%) of

(5)⁺BF₄[−]. Anal. Found: C, 61.8; H, 5.31 C₈₃H₈₄BF₄P₇·Pd₂. Calc.: C, 62.4; H, 5.36%. IR (Nujol, KBr) 3040 m ($\nu_{\text{C-H}}$), 1470 m, 1440 m ($\nu_{\text{C=C}}$), 1068 vs, br ($\nu_{\text{B-F}}$) cm^{−1}. NMR (CD₂Cl₂, 298 K). ³¹P{¹H} δ (ppm): 337.4

Table 5

Complex (3)⁺Tf[−] positional parameters and their estimated standard deviations (in parentheses)

Atom	x	y	z	U _{eq}
Pd1	0.12099(6)	0.23761(4)	0.24873(4)	0.0314(2)
Pd2	0.09049(6)	0.28378(4)	0.37338(4)	0.0295(2)
S	0.5267(3)	0.3451(3)	0.2924(2)	0.106(2)
P1	0.1022(2)	0.3480(1)	0.2017(1)	0.0322(7)
P2	0.1085(2)	0.3990(1)	0.3464(1)	0.0303(7)
P3	0.1177(2)	0.1728(1)	0.3451(1)	0.0335(7)
P4	0.1594(3)	0.1762(2)	0.1555(2)	0.0563(9)
P5	0.0711(2)	0.2939(1)	0.4890(1)	0.0408(7)
F1	0.6014(9)	0.2686(9)	0.3911(6)	0.245(7)
F2	0.7102(8)	0.2886(6)	0.3349(6)	0.171(5)
F3	0.574(2)	0.2285(7)	0.285(1)	0.39(1)
O1	0.4220(7)	0.3271(6)	0.3001(5)	0.105(3)
O2	0.5428(8)	0.3533(9)	0.2272(6)	0.182(6)
O3	0.578(1)	0.4012(8)	0.340(1)	0.275(9)
C1	0.1670(7)	0.4098(5)	0.2688(5)	0.038(3)
C2	0.146(1)	0.0828(6)	0.1499(6)	0.064(4)
C3	0.081(2)	0.2004(7)	0.0683(7)	0.141(8)
C4	0.300(1)	0.1883(8)	0.1499(8)	0.141(5)
C5	0.1967(9)	0.3127(6)	0.5522(5)	0.055(3)
C6	0.0174(9)	0.2228(6)	0.5313(6)	0.066(4)
C7	−0.0173(9)	0.3645(6)	0.5042(5)	0.061(4)
C8	0.604(1)	0.270(1)	0.3336(8)	0.158(8)
C10	0.1594(7)	0.3745(5)	0.1272(4)	0.031(3)
C11	0.0979(8)	0.3869(6)	0.0616(5)	0.046(3)
C12	0.148(1)	0.4001(7)	0.0056(6)	0.075(4)
C13	0.260(1)	0.4041(7)	0.0173(6)	0.074(4)
C14	0.3207(9)	0.3915(5)	0.0827(6)	0.052(3)
C15	0.2714(8)	0.3764(5)	0.1370(5)	0.043(3)
C20	−0.0388(7)	0.3763(5)	0.1762(4)	0.033(3)
C21	−0.1199(8)	0.3276(5)	0.1822(5)	0.047(3)
C22	−0.2272(8)	0.3489(6)	0.1693(5)	0.051(3)
C23	−0.2552(8)	0.4146(6)	0.1499(5)	0.052(3)
C24	−0.1772(8)	0.4620(6)	0.1428(5)	0.049(3)
C25	−0.0696(8)	0.4427(5)	0.1555(5)	0.039(3)
C30	−0.0038(8)	0.4591(5)	0.3305(5)	0.036(3)
C31	−0.1080(8)	0.4364(6)	0.3310(5)	0.045(3)
C32	−0.1923(9)	0.4818(7)	0.3178(6)	0.066(4)
C33	−0.1768(9)	0.5500(7)	0.3063(6)	0.071(4)
C34	−0.076(1)	0.5744(6)	0.3026(6)	0.067(4)
C35	0.0116(9)	0.5289(5)	0.3156(5)	0.049(3)
C40	0.2093(7)	0.4391(5)	0.4170(4)	0.031(2)
C41	0.1831(8)	0.4890(5)	0.4612(5)	0.038(3)
C42	0.2614(9)	0.5140(5)	0.5183(5)	0.048(3)
C43	0.3658(8)	0.4880(6)	0.5300(5)	0.050(3)
C44	0.3919(8)	0.4389(6)	0.4865(6)	0.052(3)
C45	0.3160(8)	0.4148(5)	0.4300(5)	0.045(3)
C50	0.0035(8)	0.1088(5)	0.3403(6)	0.048(3)
C51	−0.099(1)	0.1525(7)	0.3276(9)	0.095(6)
C52	−0.003(1)	0.0584(7)	0.2805(7)	0.098(5)
C53	0.002(1)	0.0701(7)	0.4070(6)	0.079(4)
C54	0.2523(8)	0.1366(5)	0.3917(5)	0.045(3)
C55	0.259(1)	0.1185(7)	0.4683(6)	0.072(4)
C56	0.3330(9)	0.1941(7)	0.3899(7)	0.081(5)
C57	0.284(1)	0.0733(7)	0.3547(7)	0.076(4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as one third of the trace of the orthogonalized *U* tensor.

(t quint, $^2J_{\text{PP}} = 195$ Hz, $\mu\text{-P}^i\text{Bu}_2$), 2.34 (dm, $^2J_{\text{PP}} = 195$ Hz, $\mu\text{-dppm}$), -11.5 (br s, $\eta^1\text{-dppm}$); ^1H δ (ppm): 7.3 (m, 60H, C_6H_5), 4.25 (br t, 2H, PCH_2P), 2.5 (br s, 4H, PCH_2P), 0.92 (d, $^3J_{\text{PH}} = 13$ Hz, 18H, C_4H_9). The same complex was obtained in 83% yield by reacting $(2)^+\text{BF}_4^-$ (100 mg, 0.0892 mmol) with two equivalents of dppm in DME (10 ml); the isolation of the yellow solid and its IR and NMR spectra were identical with those of the samples prepared by the former procedure.

3.6. Reaction of $(5)^+\text{BF}_4^-$ with $[\text{Pd}_2(\mu\text{-P}^i\text{Bu}_2)(\text{CO})(\text{PMe})_3]\text{BF}_4$

$[\text{Pd}_2(\mu\text{-P}^i\text{Bu}_2)(\text{CO})(\text{PMe})_3]\text{BF}_4$ (240 mg, 0.342 mmol) and $(5)^+\text{BF}_4^-$ (270 mg, 0.170 mmol) were dissolved in CH_2Cl_2 (15 ml). The orange solution turned yellow in a few minutes and was kept at room temperature for 0.5 h. Most of the solvent was evaporated and Et_2O (30 ml) was added. The yellow solid was filtered and vacuum dried (147 mg, 88.1%). IR and NMR spectra were identical with those of an authentic sample of $(3)^+\text{BF}_4^-$.

3.7. Preparation of $[\text{Pd}_2(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-dppm})(\eta^1\text{-dppm})(\text{SPh})](6)$

A solution of PhSNa (0.118 mmol) in acetone (1 ml) was added to a yellow solution of $(5)^+\text{BF}_4^-$ (155 mg, 0.097 mmol) in toluene (15 ml). The color of the solution turned instantaneously red and NaBF_4 precipitated and was filtered off. The filtrate was concentrated to ca. 3 ml and *n*-hexane (20 ml) was slowly added with vigorous stirring. The red solid which precipitated was filtered and vacuum dried (134 mg, 0.108 mmol, 92%). Anal. Found: C, 62.1; H, 5.43. $\text{C}_{64}\text{H}_{67}\text{P}_3\text{Pd}_2\text{S}$. Calc.: C, 62.2; H, 5.46%. IR (Nujol, KBr) 3040 m ($\nu_{\text{C-H}}$), 1578 m, 1474 m, 1440 m ($\nu_{\text{C=C}}$) cm^{-1} . ^1H NMR (C_6D_6 , 298 K) δ (ppm): 7.2 (m, 45H, C_6H_5), 4.2 (t, $^2J_{\text{PH}} = 8$ Hz, 2H, PCH_2P), 2.6 (t, $^2J_{\text{PH}} = 3$ Hz, 2H, PCH_2P), 1.32 (d, $^3J_{\text{PH}} = 13$ Hz, 18H, C_4H_9). $^{31}\text{P}\{^1\text{H}\}$ (toluene, 298 K) δ (ppm): 307 [ddt, $^2J_{\text{PP}} = 186$, $^2J_{\text{PP}} = 259$, $(^2J_{\text{PP}} + ^4J_{\text{PP}})/2 = 9.4$ Hz, $\mu\text{-P}^i\text{Bu}_2$], -0.08 [ddt, $^2J_{\text{PP}} = 186$, $^2J_{\text{PP}} = 74.7$, $(^2J_{\text{PP}} + ^4J_{\text{PP}})/2 = 10.3$ Hz, $\mu\text{-dppm}$; P *cis* to $\eta^1\text{-dppm}$], -7.48 [ddt, $^2J_{\text{PP}} = 259$, $^2J_{\text{PP}} = 74.7$, $(^3J_{\text{PP}} + ^3J_{\text{PP}})/2 = 3.8$ Hz, $\mu\text{-dppm}$; P *cis* to SPh], -16 (broad s, $\eta^1\text{-dppm}$).

3.8. Molecular structure determinations

Crystals suitable for X-ray diffraction of $(3)^+\text{Tf}^-$ and $(5)^+\text{Tf}^-$ were obtained as described previously. Crystal data, data collection parameters and convergence results are presented in Table 3. Data were collected at -10°C on an Enraf-Nonius CAD4 diffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation; 8815 reflections ($3.0 < \theta < 25.0^\circ$) were measured

for $(3)^+\text{Tf}^-$, 5386 unique with $I > 1.0\sigma(I)$ were used for further computations. A slight, approximately linear loss of diffraction intensity (3%) was corrected according to the intensity of three periodically monitored check reflections. No absorption correction was required as the rod shaped crystal was mounted with its long axis parallel to the supporting glass fiber. For $(5)^+\text{Tf}^-$ 11034 reflections ($3.0 < \theta < 24.0^\circ$) were measured, 6734 unique with $I > 1.0\sigma(I)$ were used for further computations. The shape of the crystal was that of a platelet with approximate dimensions $0.6 \times 0.6 \times 0.2$ mm³ and required an empirical absorption correction which was carried out with the help of the program DIFABS [19]. The minimum and maximum corrections applied amounted to 0.723 and 1.098 respectively. Structure solutions for both compounds were by conventional heavy atom methods followed by Fourier difference syntheses. Full-matrix least-squares refinements were carried out with isotropic thermal parameters for the phenyl carbon atoms in $(5)^+\text{Tf}^-$, anisotropic displacement parameters for all non-hydrogen atoms in both compounds and riding hydrogen atoms with isotropic thermal parameters of $\text{B(H)} = 1.3\text{B(C)}$ and $\text{C-H} = 0.98$ Å. The maximum residual electron density in final difference Fourier syntheses was $1.6 \text{ e}\text{\AA}^{-3}$ for $(3)^+\text{Tf}^-$ and $1.0 \text{ e}\text{\AA}^{-3}$ for $(5)^+\text{Tf}^-$ with the local maxima close to the sulfur atoms in the anions in both cases. Atomic coordinates are given in Tables 4 and 5. Calculations were performed using the SDP system of programs [20].

4. Supplementary material available

Additional material available from the Cambridge Crystallographic Data Centre comprises tables of complete positional and thermal parameters, general displacement parameter expressions, complete bond distances and angles, and figures with the atom numbering scheme for the structures $(3)^+\text{Tf}^-$ and $(5)^+\text{Tf}^-$.

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