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Synthesis, characterization and reactivity of binuclear palladium(I)bis(diphenylphosphino)amine complexes

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Abstract

The binuclear Pd(1) complex $[Pd_2(\mu-dppa)_2(CH_3CN)_2][BF_4]_2$ (1), where dppa is the bridging diphosphine ligand bis(diphenylphosphino) amine, was prepared by the reaction of $[Pd(dppa)_2][BF_4]_2$ and 1/2 equiv. of $[Pd_2(dba)_3]$. The acetonitrile ligands in complex 1 are readily displaced by other ligands. Substitution of one or both of the acetonitrile ligands of the dimer 1 with Cl⁻, Br⁻, l⁻, (CN)⁻ and PPh₃ is described. ³¹P NMR and mass spectral data for the complexes are reported. The single crystal X-ray structures of the binuclear complexes, $[Pd_2(\mu-dppa)_2(PPh_3)_2(THF)][BF_4]_2$. ⁴THF, $[Pd_2(\mu-dppa)_2(PPh_3)_2][BF_4]_2$. ⁴THF·H₂O and $[Pd_2(\mu-dppa)_2Cl_2]$. ³CH₃CN have been determined. Attempts to react the binuclear complex $[Pd_2(\mu-dppa)_2l_2]$ with ligands capable of bridging the Pd-Pd bond (CO, SO₂ and HgCl₂) were unsuccessful.

Keywords: Crystal structures; Palladium(1) complexes; Phosphine-amine complexes; Binuclear complexes

1. Introduction

The ligand bis(diphenylphosphino)methane (dppm) has been extensively used as a bridging ligand to stabilize bimetallic and polymetallic complexes of the platinum group metals [1]. The factors that influence whether dppm acts as a chelating, bidentate ligand to one metal center or as a bridging ligand for two metal centers are only partially understood [2]. One factor which favors formation of dppm bridged complexes is ring strain associated with the formation of a four-member ring when the ligand chelates to one metal center. Substituting the methylene group in dppm with a smaller amino group, NH, may increase the ligand's propensity to bridge two metal centers. Only a limited amount of data has been reported for the corresponding ligand bis(diphenylphosphino)amine, Ph2P(NH)PPh2 (dppa). King has published extensively on the metal-carbonyl chemistry of bis(difluorophosphinoamine) ligands [3]. Usón et al. [4] found that the 1:1 reaction of dppa with [cis- $M(C_6F_5)_2(THF)_2$ (M = Pt, Pd), gives the chelated complex [cis-M(C₆F₅)₂(dppa)]. Ring strain is evident in these complexes as the reaction with 2 equiv. of dppa yielded the complex cis-[M(C₆F₅)₂(η^1 -dppa)₂] containing monodentate dppa ligands. In continuation of our study of the dppa ligand and its derivatives [5], this paper describes the preparation, reactivity and structure of binuclear palladium(I) complexes containing bridging dppa ligands.

2. Experimental

2.1. General

All reactions were conducted under an N₂ atmosphere using vacuum line techniques, unless otherwise noted. Solvents were dried by distillation and degassed under a N₂ atmosphere. Solvents and reagents were obtained from Fischer or Aldrich chemical companies. The compounds $[Pd(CH_3CN)_4][BF_4]_2$ [6], $Pd_2(dba)_3$ [6] and dppa [7] were prepared using literature methods. The starting materials were all characterized by their IR and ³¹P and ¹H NMR spectra.

All NMR spectra were recorded on a Varian XL-200 spectrometer, except for $[Pd_2(\mu-dppa)_2(CH_3CN)X]$ (X=Br, I), 5Br and 5I, which were recorded on a Gemini 300 spectrometer. P(OMe)₃ in C₆D₆ was used as an external reference in the measurement of ³¹P NMR chemical shifts. The ³¹P NMR shifts are reported with reference to 85% H₃PO₄.

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2.2. Syntheses

2.2.1. Synthesis of $[Pd_2(\mu-dppa)_2(CH_3CN)_2][BF_4]_2(1)$

A solution of dppa (2.04 g, 5.30 mmol) in dichloromethane (60 ml) was added to a solution of [Pd(CH₃CN)₄][BF₄]₂ (1.193 g, 2.687 mmol) in CH₃CN (40 ml). The resulting yellow solution darkened slightly while stirring for 2 h at 23 °C. Pd₂(dba)₃ (1.25 g, 1.31 mmol) was added and the suspension was stirred for 12 h. After filtering, the solvent was removed under vacuum. The resulting oil was recrystallized from CH2Cl2/hexanes to give a vellow microcrystalline solid. This solid was isolated by filtration, washed with THF and diethyl ether and dried in air. The ³¹P NMR spectrum in CH₃CN shows a sharp singlet at 51.0 ppm. Yield: 1.38 g, 85%. FAB MS shows a parent ion peak at m/z = 984 with isotopic distribution consistent with the Pd₂(dppa)₂ core of the molecule. Anal. Found for $[Pd_2(\mu-dppa)_2(CH_3CN)_2][BF_4]_2$: C, 50.3; H, 4.0; N, 4.1. Calc.: C. 50.4; H. 3.9; N. 4.5%.

2.2.2. Synthesis of $[Pd_2(\mu-dppa)_2(CH_3CN)(PPh_3)][BF_4]_2$ (2)

PPh₃ (0.070 g, 0.267 mmol) was added to a CH₃CN (30 ml) solution of 1 (0.301 g, 0.243 mmol). The reaction mixture rapidly turned from yellow to orange and was further stirred for 15 min at 23 °C. Solvent evaporation under reduced pressure yielded an orange solid. The ³¹P NMR spectrum of the complex is consistent with an AA'BB'X spin system, with A as the dppa P nuclei cis to the CH₃CN ligand and B as the dppa P nuclei cis to the PPh₃ P nucleus X. The chemical shifts and coupling constants, from spectral simulation [8], are: $\delta(P_A) = 51.6$ ppm, $\delta(P_B) = 56.3$ ppm and $\delta(P_X) =$ c.0 ppm, $J(P_A - P_{A'}) = 700.0$ Hz, $J(P_B - P_{B'}) = 500.0$ Hz, $J(P_A - P_B) = 38.1 \text{ Hz}, J(P_A - P_{B_I}) = 38.1 \text{ Hz}, J(P_A - P_X) =$ 40.0 Hz, $J(P_B - P_X) = 40.6$ Hz. Yield: 0.35 g, 95%. Anal. Found for $[J'd_2(\mu-dppa)_2(CH_3CN)(PPh_3)][BF_4]_2$: C, 55.4; H, 4.2; N, 2.5; P, 11.6. Calc.: C, 55.3; H, 4.0; N, 1.9; P. 10.5%.

2.2.3. Synthesis of $[Pd_2(\mu - dppa)_2(THF)(PPh_3)][BF4]_2 \cdot 4THF (3 \cdot 4THF)$

Crystais of 3.4THF suitable for a single crystal X-ray diffraction study were grown from a THF solution of 2 by slow evaporation of solvent.

2.2.4. Synthesis of $[Pd_2(\mu - dppa)_2(PPh_3)_2][BF_4]_2(4)$

PPh₃ (0.081 g, 0.309 mmol) was added to a solution of 1 (0.192 g, 0.155 mmol) in methanol (50 ml). The resulting deep red solution was stirred for 10 min at 23 °C before the solvent was removed under reduced pressure. X-ray quality crystals $4 \cdot \text{THF} \cdot \text{H}_2\text{O}$ were grown by slow evaporation, in air, of a wet THF/CH₂Cl₂/hexanes solution of the dark orange solid. The ³¹P NMR spectrum of the complex is consistent with an AA'A"A''XX' spin system. The chemical shifts and coupling constants from spectral simulation are: $\delta(P_A) = 54.8$ ppm and $\delta(P_X) = 11.2$ ppm, $J(P_A - P_{A_f}) =$

500.0 Hz, $J(P_X - P_{X_r}) = 5.0$ Hz, $J(P_A - P_X) = 13.2$ Hz. Yield: 0.23 g, 90%. FAB MS shows a parent ion peak at m/z = 984 with isotopic distribution consistent with the $Pd_2(dppa)_2$ core of the molecule. *Anal.* Found for $[Pd_2(\mu-dppa)_2(PPh_3)_2][BF_4]_2$. THF H_2O : C, 59.6; H, 4.3; N, 1.6. Calc.: C, 59.9; H, 4.3; N, 1.7%.

2.2.5. Synthesis of $[Pd_2(\mu-dppa)_2(CH_3CN)X]$ (X = Cl, Br, I) (5)

[NEt₄]Cl (0.0134 g, 0.0810 mmol) was added to a solution of 1 (0.100 g, 0.0808 mmol) in 1:1 CH₂Cl₂/CH₃CN (50 ml). Similar reactions were carried out using [NBu₄]Br (0.025 g, 0.08 mmol), and [NBu₄]I (0.03 g, 0.08 mmol). ³¹P NMR spectra of the reaction mixtures showed only the monosubstituted dimers, 5. The ³¹P NMR spectra of the complexes are consistent with an AA'BB' spin system with A as the dppa P nuclei cis to the CH3CN ligand. The chemical shifts and coupling constants from spectral simulation are: for **5Br**: $\delta(P_A) = 52.6$ ppm and $\delta(P_B) = 55.9$ ppm, $J(P_{A} - P_{A'}) = 892.0$ Hz, $J(P_{B} - P_{B'}) = 501.0$ Hz. $J(P_A - P_B) = 46.1$ Hz, $J(P_A - P_B) = 41.1$ Hz; for 5I: $\delta(P_A) = 49.5$ ppm and $\Im(P_B) = 53.8$ ppm, $J(P_{A} - P_{A'}) = 900.0$ Hz, $J(P_{B}-P_{B'}) = 385.0$ Hz. $J(P_A - P_B) = 46.8 \text{ Hz}, J(P_A - P_{B'}) = 39.4 \text{ Hz}.$ The spectrum of 5Cl showed a wide signal centered at approximately 55 ppm and no attempt was made to simulate it. FAB MS: 5Br MH^+ peak at m/z = 1063 with isotopic distribution corresponding to $(Pd_2(dppa)_2Br)$; 5I MH⁺ peak at m/z = 1111with isotopic distribution corresponding to $(Pd_2(dppa)_2I)$.

2.2.6. Synthesis of $[Pd_2(\mu - dppa)_2X_2]$ (X = Cl, Br, I) (6)

[NEt₄]Cl (0.0134 g, 0.0810 mmol) was added to a solution of 5 (0.099 g, 0.0808 mmol) in 1:1 CH₂Cl₂/CH₃CN (50 ml). Vacuum evaporation of the solvent resulted in an orange solid. The ³¹P NMR spectrum of **6Cl** in CH₂Cl₂ shows a sharp singlet at 55.33 ppm. Yield: 0.076 g, 90%. FAB MS: **6Cl** MH^+ peak at m/z = 1055 with isotopic distribution corresponding to (Pd₂(dppa)₂Cl₂). Anal. Found for [Pd₂(dppa)₂Cl₂] (**6Cl**): C, 54.9; H, 4.4; N, 3.0. Calc.: C, 54.7; H, 4.0; N, 2.7%.

Similar reactions were carried out using [NBu₄]Br (0.039 g, 0.20 mmol), and [NBu₄]I (0.059 g, 0.22 mmol) with yields greater than 90%. ³¹P NMR spectra show singlets at 55.35 (**6Br**), and 50.57 ppm (**6I**). FAB MS: **6Br** MH⁺ peak at m/z = 1144 with isotopic distribution corresponding to (Pd₂(dppa)₂Br₂); **6I** MH⁺ peak at m/z = 1236 with isotopic distribution corresponding to (Pd₂(dppa)₂Br₂); **6I** MH⁺ peak at m/z = 1236 with isotopic distribution corresponding to (Fd₂(dppa)₂Br₂); **6I** MH⁺ peak at m/z = 1236 with isotopic distribution corresponding to (Pd₂(dppa)₂I₂). Anal. Found for **6Br**: C, 48.8; H, 3.5; N, 2.4. Calc.: C, 50.4; H, 3.7; N, 2.5%. Anal. Found for **6I**: C, 46.1; H, 3.5; N, 2.3. Calc.: C, 46.6; H, 3.4; N, 2.2%.

2.2.7. Synthesis of [Pd2(µ-dppa)2(CN)2] (6CN)

NaCN (0.024 g, 0.48 mmol) was added to a solution of 1 (0.099 g, 0.0808 mmol) in 1:1 CH₂Cl₂/CH₃CN (50 ml). Vacuum evaporation of the solvent to dryness resulted in an orange solid, that was recrystallized from conc. CH₃CN solu-

Table 1 Data for crystal structure analyses

Compound	3·4THF	4 · THF · H₂O	6CI · 3CH3CN
Empirical formula	C86H97B2F8N2O5P3Pd2	$C_{88}H_{82}B_2F_8N_2O_2P_6Pd_2$	C54H51Cl2N5P4Pd2
Μ	1780.04	1771.80	1177.58
Crystal colour, shape	dark red blocks	orange blocks	orange blocks
Crystal system	triclinic	monoclinic	monoclinic
Space group	PĪ (No. 2)	C2/c (No. 15)	$P2_1/n$ (alternate setting No. 14)
a (Å)	13.297(4)	20.459(6)	15.313(4)
Ь(Å)	24.411(3)	16.718(7)	16.430(4)
c (Å)	13.282(2)	24.88(1)	20.867(5)
α (°)	93.49(1)		
β(°)	95.34(2)	95.95(3)	90.06(3)
γ(°)	79.16(2)		
$U(\dot{A}^3)$	4212(2)	8464(2)	5250(2)
Centering reflections, Θ range (°)	20, 14-16	25, 11-14	22, 10-14
Z	2	4	4
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	1.40	1.39	1.49
F(000)	1832	3616	2384
μ (Mo K α) (cm ⁻¹)	5.2	6.0	9.5
Indices, 20 range (°)	h = 0,14; k = 26,26; l = 14,14; 1 = 45	$h \sim 20,20; k 0,16; l 0,24; 1-42$	h - 17,17; k 0,19; l 0,24; 1-49°
No. data, unique (R)	43 11234, 10996 (0.028)	4015, 3753 (0.034)	9411, 7577 (0.028)
No. data used, criterion	$7328, I > 3\sigma(I)$	$2334, I > 3\sigma(I)$	$5747. I > 3\sigma(I)$
No. standards, frequency, decay (%)	4, 2 h, 0.7	3, 4 h, 2.2	3, 4 h, 1.7
Final $R(R_w)$	0.061 (0.063)	0.062 (0.063)	0.051 (0.057)
Number variables (observed/variables)	374 (19.6)	237 (9.8)	348 (16.5)
Largest final shift/e.s.d.	0.45 (O(4), disordered THF)	0.19 (F(3), U11)	0.388 (N(5), disordered MeCN)
Final e density map (e Å-3) (max. near)	-0.63 to 0.83 (C(215))	-0.55 to 0.62 (C(132))	-0.59 to 1.1 (Cl(2))

tions by cooling. ³¹P NMR spectrum of **6CN** in CH₂Cl₂ shows a sharp singlet at 58.93 ppm. FAB MS: **6CN** MH⁺ peak at m/z = 1036 with isotopic distribution corresponding to $(Pd_2(dppa)_2(CN)_2)$. Anal. Found for $[Pd_2(dppa)_2(CN)_2]$ (**6CN**): C, 57.1; H, 3.0; N, 5.1. Calc.: C, 57.9; H, 4.0; N, 5.4%.

2.3. Crystallography

Data for the crystal structure analyses of compounds 3.4THF, 4.THF H_2O and $6CI.3CH_3CN$ are given in Table 1. The crystals of all three complexes rapidly lose solvent upon exposure to air. A crystal of 3.4THF (size $0.19 \times 0.26 \times 0.45$ mm) was mounted in a thin-walled glass capillary with a small amount of the mother-liquor. Crystals of 4.THF H_2O and $6CI.3CH_3CN$ were mounted on glass fibres and quickly coated with epoxy resin (the size of the crystals could not be measured due to epoxy coating).

2.4. Data collection and reduction

The data collections were carried out on an Enraf-Nonius CAD4 diffractometer using an incident beam graphite monochromator and Mo K α radiation [9]. Cell constants and an orientation matrix were determined and refined by using the angular settings for high angle reflections. Intensity data were recorded at variable scan speeds to optimize counting statistics. All data was collected at 23 °C using ω -2 θ scans, with a scan width of (0.8+0.35 tan θ)°. Corrections were applied for Lorentz, monochromator and crystal polarization, background radiation effects, and decay, using the Structure Determination Package [10] running on a PDP11/23 computer. An empirical absorption correction was applied [11] to the data for 3.4THF based upon the φ scans of nine reflections with θ values in the range 1.566 to 15.648°. The transmission factors ranged from 94.83 to 99.95%. The data for 4.THF·H₂O and 6C1·3CH₃CN were corrected for absorption during the refinement using the program DIFABS [11]. The mininum and maximum corrections were 0.831 and 1.096 for 4.THF·H₂O and 0.763 and 1.151 for 6C1·3CH₃CN.

2.5. Solution and refinement of the structures

The intensity statistics indicated that all three complexes had crystallized in centric space groups. Inspection of the data for systematic absences suggested the space groups reported in Table 1 and these space groups were confirmed by successful solution and refinement of the structures. The unit cell parameters for 6Cl 3CH₃CN are approximately orthorhombic however the *R* factor for averaging of equivalent reflections is 0.16 for an orthorhombic structure and 0.028 for a monoclinic structure. For the three structures, the Pd and P atoms were located by direct methods using SHELXS-86 [12]. All of the remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses and refined by full-matrix least-squares techniques on *F* using the SHELX-76 software [13]. Scattering factors for neutral, nonhydrogen atoms were taken from the literature [14]. A rigid group of D_{6h} symmetry (C-C=1.392 Å) was imposed upon the phenyl rings in the structures 3 · 4THF and 4 · THF · H₂O, and the hydrogen atoms were included in the idealized positions (C-H = 0.95 Å). The thermal parameters for the phenyl carbon atoms were refined isotropically.

In the structure of 3.4 THF, one of the THF molecules is bonded to a Pd atom, two are strongly hydrogen bonded to the amine protons of dppa ligands, and the remaining two THF molecules are in the crystal lattice as solvates. The two THF solvates and the two BF4 - ions showed disorder. None of the disorder could be described by a simple rotation or inversion of the fragments. The first BF4 - ion has two, and the second has three disorder components. They were constrained to a regular tetrahedral geometry with d(B-F) = 1.370 Å and d(F...F) = 2.237 Å. The site occupancies were fixed at 70 and 30% for the first, and 60, 20 and 20% for the second BF₄ - anion. A common isotropic thermal parameter was used for the F atoms in each anion and for the B atoms, and it was refined in the least square cycles. The closest contact between the ions is greater than the sum of the van der Waals radii of the atoms.

In the structure of 3.4THF, the two N-H protons were fixed 0.95 Å from N atoms (sp² hybridization) and their thermal parameters were also fixed (U=0.10 Å²). The methylene hydrogen atom positions were calculated and included in the idealized positions (C-H = 0.95 Å) for the three THF molecules. The bond distances and angles of the three THF molecules involved in bonding and hydrogen bonding were taken as a guide to fix an ideal geometry for the disordered THF solvates. The O-C' (C' is the carbon atom attached to the oxygen atom in THF), C'-C and C-C bond distances were fixed at 1.460, 1.491 and 1.492 Å respectively, whereas the non-bonded distances, C'...C', O...C and C'...C were fixed at 2.348, 2.371 and 2.393 Å, respectively, and the resulting model refined. The percentage of disorder components are 60, 20 and 20% for the first and 60, 30 and 10% for the second THF solvate. A common thermal parameter was used for all atoms in each of the disordered THF components and it was refined in least square cycles. An attempt was made to refine separate thermal parameters for each O, C, B and F atoms of the disordered molecules, but this was unsuccessful. Positional parameters for 3.4THF are given in Table 2. Table 3 contains selected bond lengths and bond angles and a structural diagram of the cation is presented in Fig. 1.

In the structure of $4 \cdot \text{THF} \cdot \text{H}_2\text{O}$, the BF₄ ⁻ ion is disordered about a three-fold axis of rotation running through the B-F(1) bond. A model with two configurations of the remaining three F atoms was adopted with site occupancies fixed at 85% for F(2), F(3) and F(4), and 15% for F(5), F(6) and F(7). Anisotropic thermal parameters were assigned to B, F(1) and the first configuration's atoms. The smallest anion-cation distance is 2.557 Å for H(226)-F(3).

All of the H atoms in the structure were given a common thermal parameter which was refined in least squares cycles. The N-H proton was fixed at 0.95 Å from the N atom. The

Table 2 Positional parameters and equivalent isotropic thermal coefficients for 3.4THF *

Atom	x	у	z	U or U _{cq} (Å ²)
Pd(1)	0.15585(5)	0.2816(3)	0.05917(5)	0.0315(2) ^b
Pd(2)	-0.18295(5)	0.17940(3)	-0.00528(5)	0.0351(2) b
P(1)	-0.1203(2)	0.3624(1)	0.1507(2)	0.038(1) ^b
P(2)	-0.0136(2)	0.2666(1)	-0.0343(2)	0.038(1) ^b
P(3)	-0.3194(2)	0.2880(1)	0.1144(2)	0.036(1) ^b
P(4)	-0.1284(2)	0.1935(1)	-0.1572(2)	0.039(1) ^b
P(5)	-0.2469(2)	0.1721(1)	0.1464(2)	0.036(1) ^b
0(1)	-0.1950(6)	0.0886(3)	-0.0529(6)	0.071(3) ^b
N(1)	-0.3280(6)	0.2311(3)	0.1757(6)	0.042(2) ^b
N(2)	-0.0418(5)	0.2361(3)	-0.1475(5)	0.038(2) ^b
C(11)	-0.271(1)	0.0682(6)	-0.123(1)	0.102(5)
C(12)	-0.253(1)	0.0061(7)	-0.106(1)	0.151(7)
C(13)	-0.150(1)	-0.0096(7)	-0.070(1)	0.135(6)
C(14)	-0.123(1)	0.0429(6)	-0.015(1)	0.116(5)
C(111)	-0.1085(5)	0.3518(2)	0.2861(5)	0.044(2)
C(112)	-0.1017(5)	0.2982(2)	0.3196(5)	0.053(3)
C(113)	-0.0842(5)	0.2886(2)	0.4225(5)	0.073(3)
C(114)	-0.0735(5)	0.3326(2)	0.4920(5)	0.081(4)
C(115)	-0.0804(5)	0.3862(2)	0.4585(5)	0.077(4)
C(116)	-0.0979(5)	0.3958(2)	0.3556(5)	0.065(3)
C(121)	0.0020(4)	0.3861(2)	0.1457(5)	0.039(2)
C(122)	0.0072(4)	0.4376(2)	0.1091(5)	0.056(3)
C(123)	0.1004(4)	0.4564(2)	0.1174(5)	0.069(3)
C(124)	0.1882(4)	0.4236(2)	0.1624(5)	0.076(3)
C(125)	0.1830(4)	0.3721(2)	0.1990(5)	0.073(3)
C(126)	0.0898(4)	0.3533(2)	0.1907(5)	0.056(3)
C(131)	-0.2180(5)	0.4231(3)	0.1186(4)	0.038(2)
C(132)	-0.2437(5)	0.4304(3)	0.0156(4)	0.054(3)
C(133)	-0.3166(5)	0.4760(3)	-0.0165(4)	0.068(3)
C(134)	-0.3638(5)	0.5144(3)	 ა.0544(4)	0.075(3)
C(135)	-0.3381(5)	0.5071(3)	0.1573(4)	0.081(4)
C(136)	-0.2651(5)	0.4615(3)	0.1894(4)	0.067(3)
C(211)	0.0312(4)	0.3253(3)	-0.0806(5)	0.042(2)
C(212)	-0.0362(4)	0.3575(3)	-0.1499(5)	0.054(3)
C(213)	-0.0056(4)	0.4013(3)	-0.1939(5)	0.074(3)
C(214)	0.0924(4)	0.4130(3)	-0.1686(5)	0.680(4)
C(215)	0.1598(4)	0.3808(3)	-0.0993(5)	0.074(3)
C(216)	0.1292(4)	0.3369(3)	-0.0553(5)	0.059(3)
C(221)	0.0984(5)	0.2229(3)	0.0249(4)	0.045(2)
C(222)	0.1844(5)	0.2035(3)	0.0283(4)	0.061(3)
C(223)	0.2683(5)	0.1677(3)	0.0167(4)	0.076(3)
C(224)	0.2661(5)	0.1512(3)	0.1149(4)	0.082(4)
C(225)	0.1800(5)	0.1706(3)	0.1681(4)	0.074(3)
C(220)	0.0962(5)	0.2064(3)	0.1231(4)	0.053(3)
C(311)	-0.3806(5)	0.3426(3)	0.2018(4)	0.040(2)
C(312)	-0.4551(5)	0.3872(3)	0.1650(4)	0.055(3)
C(313)	-0.4981(5)	0.4289(3)	0.2317(4)	0.072(3)
C(314)	-0.4700(5)	0.4259(3)	0.3352(4)	0.076(4)
C(315)	-0.3981(3) -0.3521(5)	0.3813(3)	0.3720(4)	0.000(3)
C(301)	-0.3331(3)	0.3396(3)	0.3033(4)	0.031(3)
C(321)	-0.4120(3)	0.2734(3)	0.0048(4)	0.042(2)
C(322)	-0.3030(3)	0.2/30(3)	0.0031(4)	0.001(3)
C(323)	-0.3770(3)	0.2022(3)	-0.0770(4)	0.08U(4)
C(324)	-0.3307(3)	0.3103(3)	-0.1394(4)	0.083(4)
C(125)	-0.40/2(3)	0.3303(3)	-0.1397(4)	0.013(3)
C(411)	-0.0578(3)	0.3217(3)	-0.0770(4)	0.030(3)
C(412)	-0.1007(4)	0 1002(3)	0.2142(3)	0.042(2)
C(413)	-0.0434(4)	0.0514(3)	-03363(5)	0.037(3)
2(413)	0.0104(4)	0.0014(0)	0.0000(0)	0.013(3)

(continued)

Table 2 (continued)

Table 2 (continued)

Atom	x	у	z	U or Uer
		-		(Å ²)
C(414)	0.0558(4)	0.0314(3)	-0.2947(5)	0.078(4)
C(415)	0.0382(4)	0.0002(3)	-0.1726(5)	0.072(3)
C(421)	-0.2253(4)	0.2184(3)	-0.2549(5)	0.000(3)
C(422)	-0.2069(4)	0.2533(3)	-0.3276(5)	0.063(3)
C(423)	-0.2822(4)	0.2703(3)	-0.4050(5)	0.085(4)
C(424)	-0.3761(4)	0.2524(3)	-0.4098(5)	0.085(4)
C(425)	-0.3945(4)	0.2175(3)	-0.3372(5)	0.085(4)
C(426)	-0.3191(4)	0.2005(3)	-0.2598(5)	0.066(3)
C(511)	-0.3277(5)	0.1195(2)	0.1403(4)	0.040(2)
C(512)	-0.4090(5)	0.1236(2)	0.0656(4)	0.053(3)
C(513)	-0.4717(5)	0.0835(2)	0.0556(4)	0.066(3)
C(514)	-0.4529(5)	0.0393(2)	0.1203(4)	0.072(3)
C(515)	-0.3715(5)	0.0352(2)	0.1950(4)	0.068(3)
C(516)	-0.3089(5)	0.0753(2)	0.2050(4)	0.053(3)
C(521)	-0.1383(3)	0.1343(3)	0.2372(4)	0.042(2)
C(522)	-0.0399(3)	0.1239(3)	0.2417(4)	0.035(3)
C(524)	-0.0237(5)	0.1007(3)	0.3237(4) 0.4217(4)	0.075(5)
C(524)	-0.12237(5)	0.1447(3)	0.4372(4)	0.001(4)
C(526)	-0.1897(5)	0.1639(3)	0.3550(4)	0.063(3)
0(2)	0.0880(7)	0.2370(4)	0.6941(6)	0.088(3) b
C(21)	0.114(1)	0.1889(6)	0.632(1)	0.096(4)
C(22)	0.180(1)	0.2020(6)	0.557(1)	0.097(4)
C(23)	0.213(1)	0.2530(7)	0.597(1)	0.118(5)
C(24)	0.163(1)	0.2701(6)	0.688(1)	0.095(4)
0(3)	0.5188(7)	0.2234(4)	0.3083(8)	0.117(4) ^b
C(31)	0.501(1)	0.1752(6)	0.346(1)	0.100(5)
C(32)	0.401(1)	0.1892(6)	0.393(1)	0.102(5)
C(33)	0.358(1)	0.2449(7)	0.368(1)	0.131(6)
C(34)	0.427(1)	0.2626(7)	0.307(1)	0.127(6)
B(1) E(1)	0.4290(6)	0.11/3(4)	0.7614(6)	0.156(9)
F(1)	0.4275(6)	0.1391(4)	0.0084(0)	0.172(3)
F(2)	0.3329(0)	0.1082(4) 0.1542(4)	0.7758(0)	0.172(3)
r(3) F(A)	0.4380(0)	0.1342(4)	0.8555(0)	0.172(3)
B(1')	0.415(2)	0.1242(8)	0.774(1)	0.156(9)
F(1')	0.406(2)	0.1017(8)	0.677(1)	0.172(3)
F(2')	0.364(2)	0.1786(8)	0.776(1)	0.172(3)
F(3')	0.372(2)	0.0943(8)	0.837(1)	0.172(3)
F(4')	0.516(2)	0.1222(8)	0.805(1)	0.172(3)
B(2)	0.3032(7)	0.5756(4)	0.3058(6)	0.091(6)
F(5)	0.2910(7)	0.6056(4)	0.2203(6)	0.128(3)
F(6)	0.2933(7)	0.5216(4)	0.2 797(6)	0.128(3)
F(7)	0.2297(7)	0.5988(4)	0.3694(6)	0.128(3)
F(8)	0.3987(7)	0.5763(4)	0.3338(0)	0.128(3)
B(2')	0.310(2)	0.573(1)	0.297(2)	0.091(0)
F(J) F(6')	0.410(2)	0.502(1)	0.275(2)	0.128(3)
F(0)	0.269(2)	0.575(1)	0.460(2)	0.128(3)
F(8')	0.267(2)	0.532(1)	0.253(2)	0.128(3)
B(2")	0.280(2)	0.577(1)	0.310(2)	0.091(6)
F(5")	0.263(2)	0.614(1)	0.234(2)	0.128(3)
F(6")	0.188(2)	0.567(1)	0.337(2)	0.128(3)
F(7")	0.339(2)	0.528(1)	0.279(2)	0.128(3)
F(8")	0.331(2)	0.600(1)	0.392(2)	0.128(3)
O(4)	0.291(3)	0.032(1)	0.402(2)	0.23(1)
C(41)	0.380(3)	-0.012(1)	0.422(2)	0.23(1)
C(42)	0.348(3)	-0.050(1)	0.493(2)	0.23(1)
C(43)	0.252(3)	-0.019(1)	0.334(2)	0.23(1)
5(44)	0.220(3)	0.030(1)	0.400(4)	0.60(1)
				(continued)

Atom	x	y	2	U or U _{eq} (Ų)
0(4')	0.252(5)	0.052(2)	0.440(5)	0.14(1)
C(41')	0.232(5)	0.001(2)	0.085(5)	0.14(1)
C(42')	0.303(5)	-0.047(2)	0.434(5)	0.14(1)
C(43')	0.344(5)	-0.024(2)	0.533(5)	0.15(1)
C(44')	0.297(5)	0.036(2)	0.541(5)	0.15(1)
O(4")	0.344(4)	-0.042(2)	0.406(5)	0.13(1)
C(41")	0.351(4)	0.012(2)	0.369(5)	0.13(1)
C(42")	0.327(4)	0.054(2)	0.453(5)	0.13(1)
C(43")	0.281(4)	0.027(2)	0.530(5)	0.13(1)
C(44")	0.278(4)	-0.032(2)	0.490(5)	0.13(1)
O(5)	0.182(3)	0.435(2)	0.576(3)	0.28(1)
C(51)	0.188(3)	0.441(2)	0.469(3)	0.28(1)
C(52)	0.300(3)	0.435(2)	0.456(3)	0.28(1)
C(53)	0.356(3)	0.407(2)	0.547(3)	0.28(1)
C(54)	0.276(3)	0.398(2)	0.613(3)	0.28(1)
O(5')	0.301(5)	0.465(2)	0.557(4)	0.19(1)
C(51')	0.194(5)	0.460(2)	0.531(4)	0.19(1)
C(52')	0.198(5)	0.402(2)	0.483(4)	0.19(1)
C(53')	0.303(5)	0.370(2)	0.512(4)	0.19(1)
C(54')	0.359(5)	0.409(2)	0.576(4)	0.19(1)
O(5")	0.290(5)	0.402	0.462(4)	0.07(1)
C(51")	0.281(5)	0.461(3)	0.496(4)	0.07(1)
C(52")	0.045(5)	0.464(3)	0.600(4)	0.07(1)
C(53")	0.265(5)	0.406(3)	0.635(4)	0.07(1)
C(54")	0.313(5)	0.369(3)	0.551(4)	0.07(1)

* Numbers in parentheses are e.s.d.s in the least significant digits.

^b Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

THF molecule also showed disorder but attempts to refine a suitable model were unsuccessful. The THF molecule was refined with anisotropic thermal parameters; its nearest contact to the cation is 2.880 Å (H(223)-C(4)).

An H_2O O atom was identified as a single peak in the difference Fourier and was refined as O(2) with anisotropic

Table 3

Selected bond distances (Å) and angles (°) for complex 3-4THF

Bond	Distance	Bond	Distance
Pd(1)-Pd(2)	2.6665(9)	Pd(1)-P(1)	2.354(2)
Pd(1)-P(2)	2.319(2)	Pd(1)-P(3)	2.334(2)
Pd(2)-P(4)	2.273(2)	Pd(2)-P(5)	2.288(2)
Pd(2)-O(1)	2.298(8)	P(5)-N(1)	1.679(8)
P(3)-N(1)	1.679(7)	P(2)-N(2)	1.679(7)
P(4)-N(2)	1.682(7)		
Atoms	Angle	Atoms	Angle
P(1)-Pd(1)-Pd(2)	167.21(7)	O(1)-Pd(2)-Pd(1)	175.5(2)
P(2)-Pd(1)-Pd(2)	86.88(6)	O(1)-Pd(2)-P(4)	9!.8(2)
P(2)-Pd(1)-P(1)	96.89(9)	O(1)-Pd(2)-P(5)	91.5(2)
P(3)-Pd(1)-Pd(2)	83.12(6)	N(2)-P(2)-Pd(1)	109.9(3)
P(3)-Pd(1)-P(1)	95.27(9)	N(1)-P(3)-Pd(1)	111.2(3)
P(3)-Pd(1)-P(2)	165.08(9)	N(2)-P(4)-Pd(2)	112.8(3)
P(4)-Pd(2)-Pd(1)	89.47(7)	N(1)-P(5)-Pd(2)	109.9(3)
P(5)-Pd(2)-Pd(1)	87.52(7)	P(5)-N(1)-P(3)	116.7(4)
P(5)-Pd(2)-P(4)	175.31(9)	P(4)-N(2)-P(2)	119.0(4)



Fig. 1. A view of dication 3 with 25% probability ellipsoids drawn for Pd, P and N. For clarity, C atoms are represented as 25% probability spheres and H atoms are omitted.

thermal parameters. Vibrations consistent with the water molecule were observed in an IR spectrum of a nujol mull of the crystals. The O atom of the H₂O molecule is 2.743 Å from F(3) and 2.761 Å from H(224). Positional parameters for 4 · THF · H₂O are given in Table 4. Table 5 shows bond lengths and bond angles. Fig. 2 is a structural diagram of the cation.

In the structure of $6Cl \cdot 3CH_3CN$, two of the acetonitrile molecules were refined with anisotropic thermal parameters. The third acetonitrile molecule containing C(51), C(52) and N(5) is disordered about an inversion center. The three atoms C(51), C(52) and N(5) were refined with isotropic thermal parameters.

The H atoms were included as riding atoms (C-H 0.95 Å and U 0.08 Å²). The closest contact between the binuclear cations (H(64)-H(52)) is greater than the sum of the van der Waals radii of the atoms. Positional parameters for **6Cl**·3CH₃CN are given in Table 6. Table 7 shows bond lengths and bond angles. Fig. 3 is a structural diagram of the molecule **6Cl**.

3. Results and discussion

3.1. Preparation of $[Pd_2(\mu-dppa)_2(CH_3CN)_2][BF_4]_2(1)$

The synthetic method of Miedaner and Dubois [6] was used to synthesize a binuclear palladium(I) complex with bridging dppa ligands and labile acetonitrile ligands. Thus reaction (1) of the $[BF_4]^-$ salt of $[Pd(CH_3CN)_4)]^{2+}$ with two dppa ligands yields the monomeric bis-chelate dication $[Pd(dppa)_2]^{2+}$.

$$[Pd(CH_3CN)_4)]^{2+} + 2dppa$$

$$\rightarrow [Pd(dppa)_2]^{2+} + 4CH_3CN \quad (1)$$

Subsequent reaction (2) of $[Pd(dppa)_2][BF_4]_2$ and 1/2 equiv. of $[Pd_2(dba)_3]$, in acetonitrile, resulted in isolation

Table 4 Positional parameters and equivalent isotropic thermal coefficients for 4 THF H₂O

Atom	x	у	z	U or U _{eq} (Å ²)
Pd	0.02211(6)	0.26363(7)	0.30543(5)	0.0322(6) *
P(1)	0.0487(2)	0.3007(2)	0.3994(2)	0.042(2) *
P(2)	0.1223(2)	0.2959(2)	0.2777(2)	0.039(2) *
P(3)	-0.0764(2)	0.2022(2)	0.3176(2)	0.039(2) °
N	0.1398(5)	0.2408(7)	0.2247(4)	0.040(3)
C(III)	-0.0115(6)	0.3727(7)	0.4180(4)	0.052(5)
C(112)	-0.0495(6)	0.4147(7)	0.3776(4)	0.071(6)
	-0.0942(6)	0.4/22(7)	0.3914(4)	0.086(6)
C(114)	-0.1010(6)	0.4877(7)	0.4456(4)	0.114(8)
C(115)	-0.0030(6)	0.4437(7)	0.4800(4)	0.21(2)
C(121)	-0.0185(0)	0.3662(7)	0.4722(4)	0.14(1)
C(127)	0.1203(5) 0.1307(5)	0.3338(0)	0.4239(4) 0.4053(4)	0.043(4)
C(123)	0 1853(5)	0.4790(6)	0.4033(4)	0.059(5)
C(124)	0.2338(5)	0.4462(6)	0.4609(4)	0.090(7)
C(125)	0.2271(5)	0.3681(6)	0.4795(4)	0.069(5)
C(126)	0.1720(5)	0.3230(6)	0.4609(4)	0.066(5)
C(131)	0.0498(6)	0.2164(7)	0.4455(5)	0.039(4)
C(132)	0.0238(6)	0.2182(7)	0.4951(5)	0.122(9)
C(133)	0.0298(6)	0.1515(7)	0.5290(5)	0.123(9)
C(134)	0.0618(6)	0.0831(7)	0.5132(5)	0.083(6)
C(135)	0.0878(6)	0.0812(7)	0.4636(5)	0.074(6)
C(136)	0.0818(6)	0.1479(7)	0.4297(5)	0.070(5)
C(211)	0.1945(5)	0.2687(5)	0.3229(4)	0.040(4)
C(212)	0.2437(5)	0.3228(5)	0.3412(4)	0.061(5)
C(213)	0.2995(5)	0.2962(5)	0.3733(4)	0.077(6)
C(214)	0.3059(5)	0.2155(5)	0.3870(4)	0.079(6)
C(215)	0.2567(5)	0.1614(5)	0.3688(4)	0.071(6)
C(216)	0.2009(5)	0.1880(5)	0.3367(4)	0.055(5)
C(221)	0.1340(4)	0.3989(7)	0.2002(4)	0.042(4)
C(222)	0.0872(4)	0.4330(7)	0.2724(4)	0.002(3)
C(223)	0.0507(4)	0.5500(7)	0.2020(4)	0.067(7)
C(225)	0.1997(4)	0.5049(7)	0.2373(4)	0.078(6)
C(226)	0 1902(4)	0.4238(7)	02376(4)	0.078(0)
C(311)	-0.1139(6)	0.2025(6)	0.3804(4)	0.048(4)
C(312)	-0.1527(6)	0.2670(6)	0.3931(4)	0.065(5)
C(313)	-0.1820(6)	0.2670(6)	0.4413(4)	0.109(7)
C(314)	-0.1725(6)	0.2024(6)	0.4767(4)	0.091(7)
C(315)	-0.1338(6)	0.1379(6)	0.4640(4)	0.093(7)
C(316)	-0.1044(6)	0.1379(6)	0.4159(4)	0.067(5)
C(321)	-0.0716(5)	0.0971(7)	0.3056(5)	0.047(4)
C(322)	-0.0120(5)	0.0577(7)	0.3187(5)	0.069(5)
C(323)	-0.0095(5)	-0.0257(7)	0.3172(5)	0.093(7)
C(324)	-0.0666(5)	~0.0696(7)	0.3025(5)	0.083(6)
C(325)	-0.1202(3) -0.1287(5)	-0.0301(7)	0.2894(5)	0.093(7)
R (320)	0.325(2)	0.0333(1) 0.427(2)	0.2310(3)	0.005(3)
F(1)	0.3476(7)	0.427(2)	0.124(2)	0.10(2)
F(2)	0.375(1)	0.4018(9)	0.0994(7)	0.13(1) *
F(3)	0.305(2)	0.378(2)	0.159(1)	0.21(3)*
F(4)	0.280(2)	0.442(2)	0.088(2)	0.30(5)*
F(5)	0.355(4)	0.374(6)	0.173(4)	0.10(3)
F(6)	0.266(5)	0.433(7)	0.134(5)	0.11(3)
F(7)	0.282(4)	0.438(5)	0.067(3)	0.04(2)
0	0.515(1)	0.196(2)	0.148(2)	0.23(3) *
C(1)	0.465(4)	0.151(2)	0.115(2)	0.21(4) *
C(2)	0.383(2)	0.174(2)	0.107(1)	0.15(3)*
C(3)	0.432(3)	0.223(3)	0.138(2)	0.23(5) *
C(4)	0.468(2)	0.240(2)	0.208(1)	0.22(4)
O(2)	0.2811(8)	0.237(1)	0.2031(9)	0.18(2)*

^a Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ii} tensor.

Table 5 Selected bond distances (Å) and angles (°) for complex $4 \cdot THF \cdot H_2O$

Bond	Distance	Bond	Distance
Pd-Pd'	2.812(2)	Pd-P(3)	2.309(4)
Pd-P(1)	2.426(4)	P(2)-N	1.68(1)
Pd-P(2)	2.294(4)	P(3)-N	1.71(1)
Atoms	Angle	Atoms	Angle
P(1)PdPd'	164.3(1)	P(3)-Pd-P(2)	164.4(2)
P(2)PdPd'	85.0(1)	P(3)-N-P(2)	118.8(6)
P(2)-Pd-P(1)	96.4(2)	N-P(2)-Pd	112.2(4)
P(3)-Pd-Pd'	86.1(1)	N-P(3)-Pd'	111.6(4)
P(3)-Pd-P(1)	95.7(1)		



Fig. 2. A view of dication 4 with 25% probability ellipsoids drawn for Pd, P and N. For clarity, C atoms are represented as 25% probability spheres and H atoms are omitted.

of the desired compound $[Pd_2(\mu-dppa)_2(CH_3CN)_2][BF_4]_2$ (1).

 $[Pd(dppa)_2]^{2+} + \frac{1}{2}[Pd_2(dba)_3]$

$$\rightarrow [Pd_2(\mu - dppa)_2(CH_3CN)_2]^{2+} + \frac{3}{2}dba \quad (2)$$

The air-stable, yellow solid 1 was isolated in 85% yield. A 31 P NMR spectrum of 1, recorded in a 1:1 mixture of CH₂Cl₂/CH₃CN, exhibits one sharp singlet at 51.0 ppm. FAB mass spectral data and elemental analysis of 1, given in Section 2, are consistent with the chemical formula given above.

The acetonitrile ligands in 1 are readily displaced by other two-electron donor ligands such as phosphine or halide ligands. A summary of the substitution reactions that have been studied is given in Scheme 1.

3.2. Substitution reactions of 1 with PPh₃

Reaction of 1 with 1 equiv. of PPh₃ in acetonitrile results in formation of the mono-substituted product $[Pd_2(\mu-dppa)_2(PPh_3)(CH_3CN)][BF_4]_2$ (2). Analytical and spectroscopic data for 2 are given in Section 2. Addition of a second equiv. of PPh₃ to acetonitrile solutions of 2 does not lead to further substitution. The acetonitrile ligand in 2 can be displaced by more polar donor solvents. Thus, recrystal-

Table 6							
Positional	parameters	and	equivalent	isotropic	thermal	coefficients	for
6Cl·3CH	ĊN						

Atom	x	у	Z	U or U _{eq} (Ų)
Pd(1)	0.02651(3)	0.18263(3)	0.31856(3)	0.029(1)*
Pd(2)	-0.04526(4)	0.11727(3)	0.21589(3)	0.030(1)*
P(1)	-0.1129(1)	0.1903(1)	0.35964(9)	0.031(1)*
P(2)	0.1567(1)	0.1689(1)	0.26623(9)	0.031(1)*
P(3)	-0.1571(1)	0.2082(1)	0.22715(9)	0.033(1)*
P(4)	0.0685(1)	0.0283(1)	0.21649(9)	0.030(1)*
N(1)	-0.1913(4)	0.2018(4)	0.3034(3)	0.038(2)*
N(2)	0.1631(4)	0.0768(4)	0.2316(3)	0.035(2) ^a
Cl(1)	0.0876(1)	0.2266(2)	0.4190(1)	0.051(1)*
Cl(2)	-0.1237(1)	0.0352(2)	0.1408(1)	0.056(1)*
C(111)	-0.1379(5)	0.2746(4)	0.4145(3)	0.033(2)
C(112)	-0.1211(5)	0.2671(5)	0.4795(4)	0.047(2)
C(113)	-0.1404(6)	0.3307(6)	0.5207(5)	0.057(2)
C(114)	-0.1761(6)	0.4023(7)	0.4970(5)	0.067(3)
C(115)	-0.1904(6)	0.4103(6)	0.4332(4)	0.057(2)
C(116)	-0.1706(5)	0.3483(5)	0.3910(4)	0.048(2)
C(121)	-0.1439(5)	0.1003(5)	0.4060(4)	0.037 (2)
C(122)	-0.0816(6)	0.0432(6)	0.4205(5)	0.063(3)
C(123)	-0.1060(8)	-0.0265(8)	0.4536(6)	0.087(4)
C(124)	-0.1924(7)	-0.0375(7)	0.4728(5)	0.070(3)
C(125)	-0.2515(7)	0.0182(6)	0.4603(5)	0.069(3)
C(126)	-0.2284(6)	0.0889(6)	0.4262(4)	0.057(2)
C(211)	0.2623(5)	0.1683(5)	0.3069(4)	0.037(2)
C(212)	0.2694(6)	0.1271(5)	0.3646(4)	0.051(2)
C(213)	0.3500(6)	0.1146(6)	0.3919(5)	0.061(3)
C(214)	0.4242(7)	0.1412(6)	0.3617(5)	0.064(3)
C(215)	0.4191(6)	0.1832(6)	0.3044(5)	0.061(3)
C(216)	0.3371(6)	0.1962(5)	0.2771(4)	0.050(2)
C(221)	0.1701(5)	0.2459(5)	0.2048(4)	0.040(2)
C(222)	0.1780(6)	0.2274(6)	0.1390(4)	0.056(2)
C(223)	0.1825(7)	0.2917(7)	0.0948(6)	0.073(3)
C(224)	0.1792(7)	0.3705(7)	J.1170(6)	0.079(3)
C(225)	0.1746(6)	0.3903(7)	0.1800(5)	0.065(3)
C(226)	0.1694(6)	0.3274(5)	0.2245(4)	0.052(2)
C(311)	-0.2549(5)	0.1861(5)	0.1812(4)	0.040(2)
C(312)	-0.3194(6)	0.1367(6)	0.2055(5)	0.063(3)
C(313)	-0.3931(8)	0.1166(7)	0.1671(6)	0.083 (3)
C(314)	-0.3957(7)	0.1454(7)	0.1053(5)	0.076(3)
C(315)	-0.3369(7)	0.1922(6)	0.0822(5)	0.068(3)
C(316)	-0.2637(6)	0.2149(6)	0.1183(5)	0.059(2)
C(321)	-0.1417(5)	0.3164(5)	0.2096(4)	0.038(2)
C(322)	-0.2102(6)	0.3695(6)	0.2139(4)	0.054(2)
C(323)	-0.1994(6)	0.4522(6)	0.2009(5)	0.062(3)
C(324)	-0.1198(7)	0.4805(8)	0.1850(5)	0.078(3)
C(325)	-0.0485(9)	0.4298(9)	0.1825(6)	0.102(4)
C(326)	-0.0611(7)	0.3455(7)	0.1943(5)	0.077(3)
C(411)	0.0542(5)	-0.0496(5)	0.2761(3)	0.034(2)
C(412)	0.1082(6)	-0.0567(5)	0.3282(4)	0.050(2)
C(413)	0.0912(7)	-0.1171(6)	0.3755(5)	0.070(3)
C(414)	0.0216(6)	-0.1708(6)	0.3681(5)	0.060(3)
C(415)	-0.0316(6)	-0.1629(6)	0.3154(5)	0.058(2)
C(416)	-0.0152(6)	-0.1037(5)	0.2706(4)	0.052(2)
C(421)	0.1010(5)	-0.0281(4)	0.1447(3)	0.032(2)
C(422)	0.0869(5)	0.0066(5)	0.0847(4)	0.044(2)
C(423)	0.1208(6)	-0.0309(6)	0.0303(4)	0.055(2)
C(424)	0.1682(6)	-0.1007(6)	0.0362(5)	0.063(3)
C(425)	0.1822(6)	-0.1352(7)	0.0952(5)	0.007(3)
C(426)	0.1474(5)	-0.0989(5)	0.1494(4)	0.048(2)
C(31)	-0.433(1)	0.3398(8)	0.4330(0)	0.120(7)*
				(continued)

Table 6 (continued)

Atom	x	у	z	U or U _{eq} (Å ²)
C(32)	-0.3970(6)	0.2863(8)	0.3895(7)	0.076(5) ª
N(3)	-0.3707(6)	0.2460(9)	0.3523(7)	0.121(6) *
C(41)	0.4534(9)	-0.0657(9)	0.115(1)	0.189(11)*
C(42)	0.3919(7)	-0.0168(7)	0.1482(6)	0.074(4) *
N(4)	0.3406(6)	0.0178(6)	0.1734(5)	0.094(4)*
C(51)	0.052(2)	0.676(2)	-0.039(2)	0.17(1)
C(52)	0.003(2)	0.609(2)	-0.020(2)	0.14(1)
N(5)	-0.004(4)	0.544(2)	-0.004(3)	0.28(2)

^a Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 7

Selected bond distances (Å) and angles (°) for complex 6CI·3CH₃CN

Bond	Distance	Bond	Distance
Pd(1)-Pd(2)	2.635(1)	Pd(2)Cl(2)	2.390(3)
Pd(1)-P(1)	2.305(2)	P(1)-N(1)	1.689(6)
Pd(1)-P(2)	2.285(2)	P(2)-N(2)	1.680(6)
Pd(1)-Cl(1)	2.406(2)	P(4)-N(2)	1.683(6)
Pd(2)-P(4)	2.274(2)	P(3)-N(1)	1.679(6)
Pd(2)-P(3)	2.285(2)		
Bond	Angle	Bond	Angle
Pd(2)-Pd(1)-P(1)	86.5(1)	Pd(1)-Pd(2)-Cl(2)	166.3(1)
Pd(2)-Pd(1)-P(2)	86.3(1)	P(4)-Pd(2)-Cl(2)	91.5(1)
P(1)-Pd(1)-P(2)	172.8(1)	P(3)-Pd(2)-Cl(2)	93.4(1)
Pd(2)-Pd(1)-Cl(1)	172.8(1)	Pd(1)-P(1)-N(1)	114.0(2)
P(1)-Pd(1)-Cl(1)	91.1(1)	Pd(1)-P(2)-N(2)	110.2(2)
P(2)-Pd(1)-Ci(1)	96.2(1)	Pd(2)-P(4)-N(2)	110.9(2)
Pd(1)-Pd(2)-P(4)	86.5(1)	Pd(2)-P(3)-N(1)	107.0(2)
Pd(1)-Pd(2)-P(3)	87.8(1)	P(1)-N(1)-P(3)	116.3(4)
P(4)-Pd(2)-P(3)	173.7(1)	P(2)-N(2)-P(4)	117.1(4)



Fig. 3. A view of dication 6Cl with 25% probability ellipsoids drawn for Pd, P and N. For clarity, C atoms are represented as 25% probability spheres and H atoms are omitted.

lization of the orange solid 2 in THF yielded crystals of $[Pd_2(\mu-dppa)_2(PPh_3)(THF)][BF_4]_2 \cdot 4THF$ (3 · 4THF). The structure of 3, as illustrated in Scheme 1, has been confirmed by single crystal X-ray diffraction. Substitution of the



Scheme 1. For the X⁻ reactions, where X⁻ = Cl⁻, Br⁻, l⁻ or CN⁻, the solvent was a 1:1 mixture of CH₂Cl₂/MeCN. For the other reactions the solvent is shown in square brackets. In all cases, the cations have $[BF_4]^-$ counter ions.

acetonitrile ligand in 2 by PPh₃, producing the bis-phosphine substituted product, $[Pd_2(\mu-dppa)_2(PPh_3)_2][BF_4]_2$ (4), does occur in these more polar solvents. The reaction of 1 with 2 equiv. of PPh₃ or the reaction of 2 with 1 equiv. of PPh₃, in methanol, gives compound 4 in high yields. FAB mass spectral data and elemental analysis of 4 are reported in Section 2. Crystals of 4 · THF · H₂O were grown by slow evaporation, in air, of a wet THF/CH₂Cl₂/hexanes solution and the structure of 4 was confirmed by single crystal X-ray diffraction. Recrystallization of 4 from acetonitrile solutions regenerates the mono-phosphine-substituted dimer 2 and 1 equiv. of PPh₃.

The ³¹P NMR spectroscopic data for the compounds 2 and 4, recorded in a 1:1 mixture of CH₂Cl₂/CH₃CN are presented in Section 2. Dissolving compound 3 in a 1:1 mixture of CH₂Cl₂/CH₃CN results in an identical NMR spectrum to that recorded for 2. ³¹P NMR spectra for 2 and 4 display second order effects and the results of spectral simulation are given in Section 2. The ³¹P NMR spectrum of 2 was simulated as an AA'BB'X system. The AA'A''A'''XX' spectrum of 4 has significantly larger line widths than that of 2 at room temperature. The iterated values for the two and three bond P–P coupling constants are of the same order of magnitude as those reported for similar complexes [15,16].

The substitution reactions are consistent with the results reported by Blau and Espenson for the complexes $[Pt_2(\mu-dppm)_2L_2]^{n+}$, where L is a terminal halide (n=0) or PPh₃ ligand (n=2) [16]. Substitution reactions of these sterically congested complexes required the formation of coordinatively unsaturated binuclear η^1 -dppm intermediates. Changes in solvent were reported to greatly alter the course of the reactions.

3.3. Description of the crystal structures of $3 \cdot 4THF$ and $4 \cdot THF \cdot H_2O$

Crystal data for the compounds $3 \cdot 4$ THF and $4 \cdot$ THF \cdot H₂O are given in Table 1. Tables 2 and 3 present the positional and geometrical parameters for $3 \cdot 4$ THF, respectively. The corresponding values for $4 \cdot$ THF \cdot H₂O are given in Tables 4 and 5. Structural diagrams showing the dications of 3 and 4

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are presented in Figs. 1 and 2. The fragile nature of the crystals and the disorder associated with the solvent molecules hampered the structural determinations.

In both dications, distorted square-planar coordination geometries are observed about the Pd centers. For example, in 3 the P(1)-Pd(1)-P(dppa) angles, between the P(1) atom of the terminal PPh₃ ligand and the P atoms of the bridging dppa ligands, are 96.89(9) and 95.27(9)°. The remaining two *cis* angles subtended at Pd(1) are 86.88(6) and 83.12(6)°. The bridging dppa ligands are clearly bent away from the terminal PPh₃ ligand, however the planarity at the Pd center is maintained. The planarity at the Pd center is evident in the sum of the four *cis* angles, which is 362.16(9)°. The Pd(1) atom sits furthest, at 0.112(1) Å, from a least squares plane defined by Pd(1) and the three P atoms bonded to it. The Pd(2) atom, which is bound to the THF O(1) atom shows much less distortion from a squareplanar coordination geometry.

The dication of 4 contains similar distortions about Pd to those discussed for Pd(1) in 3. A crystallographically imposed center of inversion bisects the Pd-Pd bond in 4. The four *cis* angles subtended at the Pd center are 96.4(2), 95.7(1), 85.0(1) and 86.1(1)°, where the former two involve the terminal PPh₃ P atom and the latter two the Pd' atom. Again, the size of the PPh₃ ligand is evident. The sum of the four *cis* angles at Pd is $363.2(2)^\circ$. The largest deviation from a least-squares plane defined by Pd, Pd', P(1), P(2) and P(3) is 0.307(4) Å (P(1)).

In the dication 3 the dihedral angle between the two distorted square-planes centered at the Pd atoms is $44.4(2)^{\circ}$ while the corresponding value in 4 is $17.4(2)^{\circ}$. Dihedral angles of approximately 45° are observed for binuclear complexes containing dppm ligands with small terminal ligands [17,18]. The dihedral angle between the square planes in $[Pd_2(\mu-dppm)_2(CO_2CF_3)_2]$ is 44.5° [19] and that in $[Pd_2(\mu-dppm)_2Br_2]$ is 39° [19]. This 45° twist minimizes antibonding interactions between the filled metal d-orbitals [20]. Thus, the dihedral angle in 3 is typical of these complexes and the small angle in 4 is ascribed to crowding at the Pd centres due to the PPh₃ ligands.

The Pd-Pd bond length in 3 of 2.6665(9) Å is comparable to those observed in other Pd(I) binuclear complexes [20-22]. The Pd-Pd bond length is considerably longer in 4 (2.812(2) Å). This lengthening may be another indication of the strain caused by the large PPh₃ ligands. This congestion associated with the PPh₃ ligands affects the Pd-P(dppa) bond distances. In 3, the Pd(2)-P(4) and Pd(2)-P(5) distances, where Pd(2) is bonded to the THF ligand, are just significantly different at 2.273(2) and 2.288(2) Å, respectively. The Pd-P(dppa) distances measured for the PPh₃ substituted Pd(1), in 3, are significantly longer at 2.319(2) and 2.334(2) Å as are those found in 4, at 2.294(4) and 2.309(4) Å. The Pd-P(PPh₃) bond lengths are 2.354(2) and 2.426(4) Å for 3 and 4, respectively.

The P-N bond lengths of the bridging dppa ligands in 3 and 4 are statistically equivalent and average to 1.684(9) Å. The P–N–P bond angles are 116.7(4) and $119.0(4)^{\circ}$ in 3 and $118.8(6)^{\circ}$ in 4. These values compare favorably with those found in other dppa complexes [5,23,24].

All remaining bond distances and angles in the salts 3 and 4 are normal [25].

3.4. Substitution reactions of 1 with halide ligands

The reaction of 1 with 1 equiv. of halide ions, in CH₂Cl₂/ CH₃CN solutions, yields the monosubstituted salts [Pd₂(μ -dppa)₂(CH₃CN)X][BF₄] (5), where X = Cl, Br or I. Addition of a second equiv. of halide ion produces the neutral binuclear compounds [Pd₂(μ -dppa)₂X₂] (6). Analytical and spectroscopic data for the compounds 5 and 6 are given in Section 2. The salt 1 can be regenerated from the molecules 6 by halide abstraction with 2 equiv. of Ag[BF₄].

The reaction of 1 with 2 equiv. of cyanide ions, in CH₂Cl₂/ CH₃CN solution, yields the neutral binuclear compound $[Pd_2(\mu-dppa)_2(CN)_2]$ (6CN). Data for the compound are given in Section 2.

The ³¹P NMR spectra of halide derivatives of **6** all contain singlet resonances, resulting from equivalent Penvironments. The mono-substituted dimers exhibit patterns best described as second order AA'BB' systems. The spectrum of **5CI** contained a wide signal centered at approximately 55 ppm and no attempt was made to simulate it. The spectrum of **5Br** was best simulated using a line width of 7 Hz. The iterated values of the coupling constants are within normal ranges. The coupling constants $J(P_A - P_B)$ and $J(P_A - P_B)$, for **2**, **4**, **5Br** and **5I** increase as crowding at the metal center decreases.

3.5. Description of the crystal structure of 6Cl · 3CH₃CN

Crystal data for the compound are given in Table 1. Tables 6 and 7 present the positional and geometrical parameters. A structural diagram showing the molecule 6Cl is presented in Fig. 3. The structure solution and refinement of 6Cl · 3CH₃CN was less problematic than those of 3 · 4THF and 4 · THF · H₂O.

The square-planar Pd(I) coordination spheres in **6Cl** are generally less distorted than the geometries observed in **3** and 4. The *cis* angles subtended at Pd range from 86.3(1) to 96.2(1)°, summing to 360.1(1)°, for Pd(1) and from 86.5(1) to 93.4(1)°, summing to 359.2(1)°, for Pd(2). The atom Cl(1) is 0.090(2) Å from a least squares plane defined by Pd(1) and the four atoms in its coordination sphere. The corresponding value for Pd(2) is 0.155(2) Å for Cl(2).

The Pd(1)-Pd(2) bond distance is 2.635(1) Å which is slightly shorter than that observed in 3 however the distance is comparable to values observed in other Pd(1) binuclear complexes [20-22]. The Pd(1)-P distances differ by 7σ while the Pd(2)-P distances are statistically equivalent. No chemical significance is attributed to this difference and the average value for the Pd-P bond length is 2.287(4) Å. The average Pd-P distance is indistinguishable from that found for the THF substituted Pd(2) in 3, 2.281(3) Å. The Pd-CI distances are normal and their average is 2.398(3) Å [5]. In **6CI** the dihedral angle between the two distorted squareplanes centered at the Pd atoms is $42.2(2)^\circ$.

The P–N bond lengths for the bridging dppa ligands in 6Cl are statistically equivalent and average to 1.68(1) Å which is statistically equivalent to the average found in 3 and 4. The P–N–P bond angles, 116.3(4) and $117.1(4)^\circ$, also are comparable with those found in 3 and 4.

All remaining bond distances and angles in 6Cl are normal [25].

3.6. Reactions of the binuclear complexes with small molecules

Binuclear complexes of dppm are known to add small molecules across the Pd–Pd bond [1]. Attempts to react the binuclear complex **6I** with ligands that may bridge the Pd–Pd bond were unsuccessful. The binuclear complex did not react with CO, SO₂ or HgCl₂ at room temperature or under reflux conditions in THF. Reactions of **1**, **4** and **6CN** with X₂, where X=I or Cl, gave the monomeric dppa chelate products PdX₂(dppa) which were identified by their ³¹P NMR, IR and mass spectra [5].

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