

Dinuclear cyclometallated complexes of Pd^{II} with diphosphines. X-ray crystal structure of $[1,4\text{-}\{\text{Pd}[2,4\text{-}(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{N}]\}_2\text{-C}_6\text{H}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\text{-P,P}\}_2][\text{PF}_6]_2$ ¹

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Abstract

Treatment of the cyclometallated halide-bridged complexes $[1,4\text{-}\{\text{Pd}[2,3,4\text{-}(\text{MeO})_3\text{C}_6\text{HC}(\text{H})=\text{N}(\text{X})]\}_2\text{C}_6\text{H}_4]_2$ (1a, 2a), $[1,4\text{-}\{\text{Pd}[2,4\text{-}(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{N}(\text{X})]\}_2\text{C}_6\text{H}_4]_2$ (1b, 2b), $[1,4\text{-}\{\text{Pd}[3\text{-Me-4-MeOC}_6\text{H}_2\text{C}(\text{H})=\text{N}(\text{X})]\}_2\text{C}_6\text{H}_4]_2$ (1c, 2c), $[1,4\text{-}\{\text{Pd}[4,5\text{-}(\text{OCH}_2\text{O})\text{C}_6\text{H}_2\text{C}(\text{H})=\text{N}(\text{X})]\}_2\text{C}_6\text{H}_4]_2$ (1d, 2d) (X = Cl, Br) with ditertiary diphosphines in a complex/diphosphine 1:4 molar ratio and ammonium hexafluorophosphate gave the dinuclear cyclometallated complexes $[1,4\text{-}\{\text{Pd}[2,3,4\text{-}(\text{MeO})_3\text{C}_6\text{HC}(\text{H})=\text{N}]\}_2\text{C}_6\text{H}_4(\text{L-L})_2][\text{PF}_6]_2$ [L-L = Ph₂PCH(CH₃)PPh₂, Ph₂P(CH₂)₂PPh₂, 3a, 4a], $[1,4\text{-}\{\text{Pd}[2,4\text{-}(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{N}]\}_2\text{C}_6\text{H}_4(\text{L-L})_2][\text{PF}_6]_2$ [L-L = Ph₂PCH(CH₃)PPh₂, Ph₂P(CH₂)₂PPh₂, 3b, 4b], $[1,4\text{-}\{\text{Pd}[3\text{-Me-4-MeOC}_6\text{H}_2\text{C}(\text{H})=\text{N}]\}_2\text{C}_6\text{H}_4(\text{L-L})_2][\text{PF}_6]_2$ [L-L = Ph₂PCH(CH₃)PPh₂, Ph₂P(CH₂)_nPPh₂, n = 2, 3, 3c, 4c, 5c], $[1,4\text{-}\{\text{Pd}[4,5\text{-}(\text{OCH}_2\text{O})\text{C}_6\text{H}_2\text{C}(\text{H})=\text{N}]\}_2\text{C}_6\text{H}_4(\text{L-L})_2][\text{PF}_6]_2$ [L-L = Ph₂PCH(CH₃)PPh₂, Ph₂P(CH₂)_nPPh₂, n = 2, 3, 4, 3d, 4d, 5d, 6d]. The influence of ring size on the phosphorus chemical shift is discussed. The compounds were characterized by microanalysis (C, H, N), IR and ³¹P-¹H and ¹H NMR spectroscopy. The structure of the dinuclear cyclometallated palladium(II) complex $[1,4\text{-}\{\text{Pd}[2,4\text{-}(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{N}]\}_2\text{C}_6\text{H}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\text{-PP}\}_2][\text{PF}_6]_2$ is described. There are two different crystallographic molecules per asymmetric unit.

Keywords: Palladium; Cyclometallation; X-ray structure; Dinuclear complexes; Diphosphine complexes; Schiff base

1. Introduction

Since the first cyclometallated compound was reported, the area of cyclometallation chemistry has experienced a noteworthy development and is now an important part of organometallic chemistry [1–6]. This is, in part, due to their versatile chemical behavior. Further, cyclometallated compounds have important applications, such as their use in regiospecific organic and organometallic synthesis [7,8] and in insertion reactions of alkenes [9] and alkynes [10]. One of the classical reactions of cyclometallated compounds is the cleavage of halide-bridged complexes by neutral or anionic

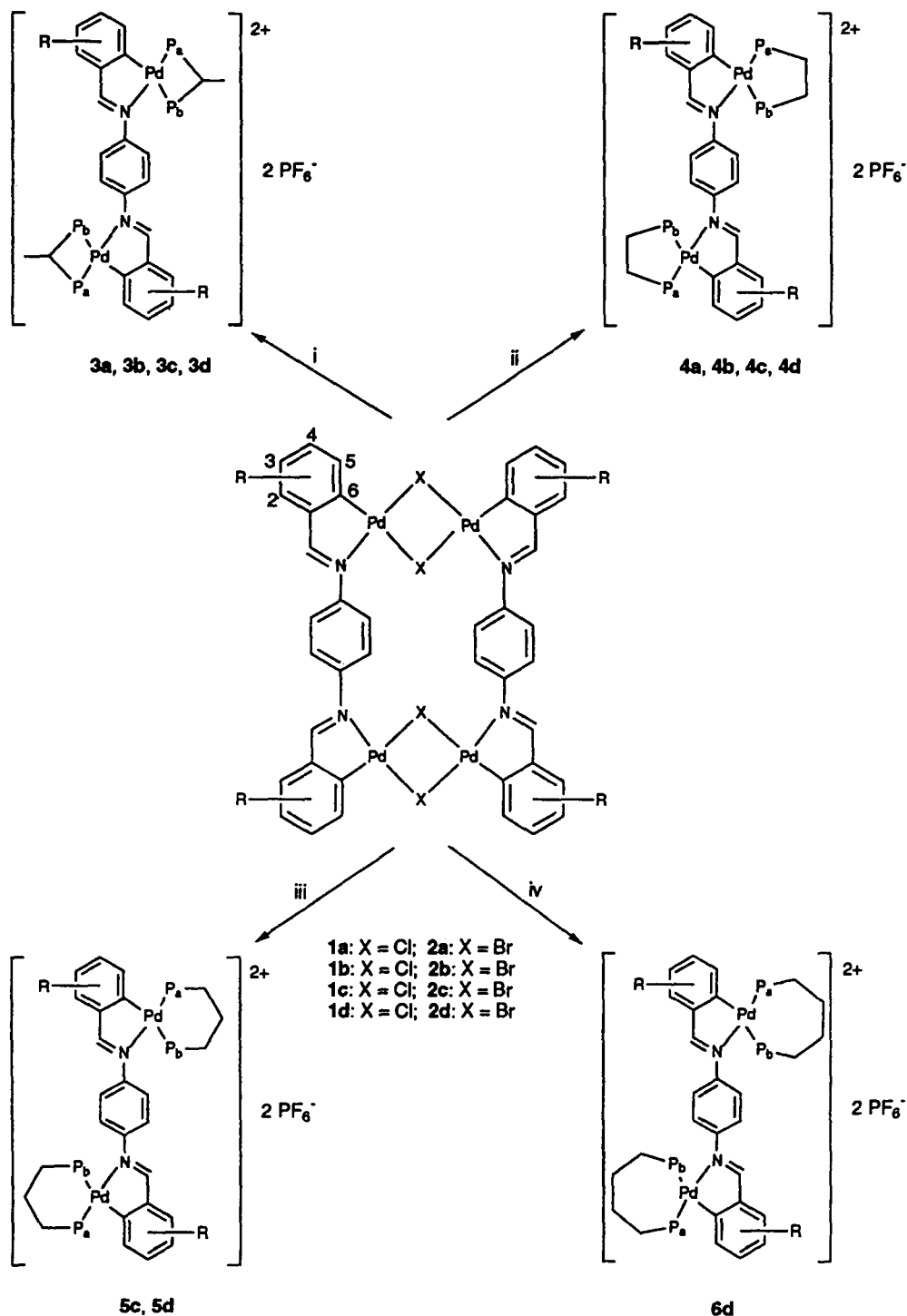
reagents. Recently, the kinetics and mechanism of these reactions have been studied [11]. We have investigated bridge-splitting reactions in complexes bearing different organic ligands such as Schiff bases [12], diimines derived from terephthalaldehydes [13] and isophthalaldehydes [14] and bis(*N*-benzylidene)-1,4-phenylenediamines [15] with, for example, tertiary monophosphines and ditertiary diphosphines. In a previous paper we have described the synthesis and characterization of tetranuclear cyclometallated Pd^{II} complexes with the diphosphines bis(diphenylphosphino)propane (dppp) or bis(diphenylphosphino)butane (dppb), to give 26- and 28-membered ring complexes respectively. The compounds show four terminal metal–halogen bonds [15]. These complexes were prepared by treatment of the corresponding tetranuclear halide-bridged compounds with the appropriate diphosphine. When the amount of

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diphosphine in the reaction mixture was increased, dinuclear cyclometallated complexes with two chelating diphosphines were obtained. As part of our studies on polynuclear cyclometallated compounds with ditertiary diphosphines, we extended our work to smaller bite diphosphines such as 1,1-bis(diphenylphosphino)ethane (1,1-dppe) and bis(diphenylphosphino)ethane (dppe) in the hope of obtaining complexes with bridging diphos-

phine and halide ligands, in a similar fashion to related dinuclear complexes reported by us earlier [16–18]. However, the results we present here show what seems to be a strong tendency towards chelation of the diphosphines 1,1-dppe and dppe. Only compounds with these diphosphines as chelating ligands were obtained. In the present paper we also report on the influence of ring size on the chemical shift δP . We have included some



Scheme 1.

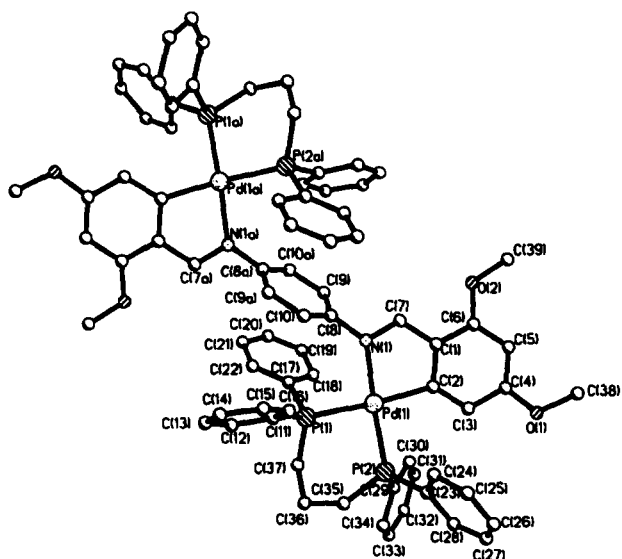


Fig. 1. The molecular structure of the Pd(1) dication of compound 5b; the PF_6^- anions are omitted.

data taken from our previous work [15] in order to establish a full correlation. Finally, we also report the crystal and molecular structure of a dinuclear cyclometallated compound with the diphosphine bis(diphenylphosphino)propane as a chelating ligand at each palladium(II). An interesting feature of this structure is the parallel arrangement of three of the phenyl rings in the compound, the central diimine phenyl ring and a further two phenyl rings, one from each diphosphine.

2. Results and discussion

2.1. Reactions with ditertiary diphosphines

The reactions of the tetranuclear complexes are summarised in Scheme 1. The compounds described were characterised by elemental analyses and IR (see Section 3) and ^{31}P - ^1H and ^1H (Table 5) NMR spectroscopy.

Treatment of the tetranuclear halide-bridged complexes 1a–1d and 2a–2d with the tertiary diphosphines $\text{Ph}_2\text{PCH}(\text{CH}_3)\text{PPh}_2$ (1,1-dppe) and $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ (dppe) in a 1:4 halide-bridged complex/diphosphine molar ratio in the presence of NH_4PF_6 gave the dinuclear cyclometallated complexes 3a–3d and 4a–4d respectively (Scheme 1). Details of the preparation are in Section 3. The final products were the same whichever halide starting material was used, as the halogen was replaced by the hexafluorophosphate ion. The complexes were 1:2 electrolytes, as shown by molar conductivity measurements in dry acetonitrile. The ^{31}P NMR spectra showed two doublets for the two inequivalent phosphorus nuclei. The resonance at lower frequency was assigned to the phosphorus nucleus *trans* to the phenyl carbon atom, in accordance with the higher *trans* influence of the latter with respect to the azomethine nitrogen atom [19]. The ^1H NMR spectra showed that the *H*(5) resonance was coupled to both phosphorus nuclei, with $^4J(\text{P}_a\text{H}) < ^4J(\text{P}_b\text{H})$, whilst the *HC=N* resonance was only coupled to the P_a nucleus. This was confirmed by selective decoupling experiments on the

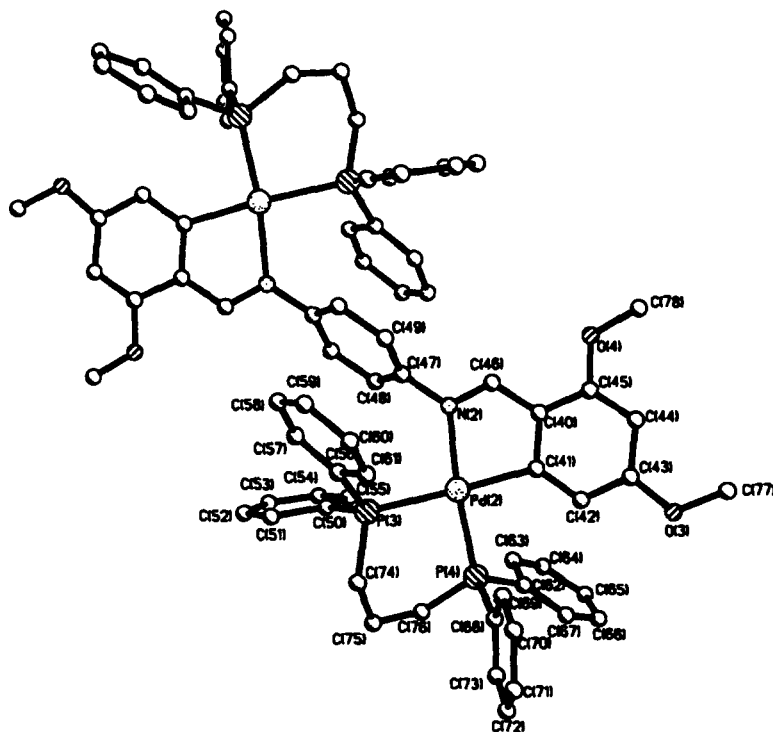


Fig. 2. The molecular structure of the Pd(2) dication of compound 5b; the PF_6^- anions are omitted.

P_a and P_b atoms. Attempts to produce tetranuclear complexes similar to those reported earlier by us [15] were unsuccessful, although complexes with bridging dppe have been described [20]. Treatment of **1c**, **1d**, **2c** or **2d** with $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ (dppp) or $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ (dppb) and $\text{NH}_4[\text{PF}_6]$ gave the dinuclear cyclometallated complexes **5c**, **5d** and **6d** (Scheme 1) which were fully characterised (Section 3 and Table 5); surprisingly, the diphosphine dppb did not give the analogous complex **6c**, i.e. with the diphosphines as chelating ligands. Even when an excess of diphosphine was used the tetranuclear complex only was formed, with the diphosphines as bridging ligands between the metal centres.

2.2. Crystal structure of $[1,4\text{-}\{\text{Pd}[2,4\text{-}(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{N}]\}_2\text{C}_6\text{H}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\text{-PP}\}_2][\text{PF}_6]_2$

Suitable crystals of the title compound were grown by slowly evaporating a chloroform solution. The molecular structures of the two dication, in different orientations, are illustrated in Figs. 1 and 2. Crystal data are given in Table 1. Fractional coordinates and isotropic thermal parameters are listed in Table 2, while selected bond lengths and bond angles with estimated standard deviations are listed in Tables 3 and 4 respectively.

The crystal structure comprises two centrosymmetric, dimetallic complex dication (half of each dication per asymmetric unit), and four hexafluorophosphate anions (two per asymmetric unit). Each four-coordinate palladium(II) is bonded to a bidentate 1,3-bis(diphenylphosphino)propane, and to one imino nitrogen and the adjacent *ortho*-carbon of a tetradentate 1,4-bis(*N,N*-[2-(carbimino)-3,5-dimethoxyphenyl])benzene which bridges a crystallographic inversion centre between the two metal centres.

The coordination geometries of the palladium atoms are tetrahedrally twisted (by 8.2 and 15.4°) from planar (r.m.s. deviations of mean P_2NC planes 0.103 and 0.184 Å). The donor atoms of the chelating Schiff base occupying *cis* sites with a somewhat reduced bond angle [$\text{C}(2)\text{-Pd}(1)\text{-N}(1)$ 81.2(4)° and $\text{C}(41)\text{-Pd}(2)\text{-N}(2)$ 80.0(3)°] consequent upon chelation. This is reflected in the value of the $\text{C}(3)\text{-C}(2)\text{-Pd}(1)$, 133.1(8)°, and $\text{C}(42)\text{-C}(41)\text{-Pd}(2)$, 130.8(8)°, angles. The sum of angles about each palladium atom is 360.54° [Pd(1)] and 361.33° [Pd(2)]. The Pd–C bond lengths [Pd(1)–C(2) 2.061(10) and Pd(2)–C(41) 2.097(9) Å] are within the expected range, about 2.081 Å based on the sum of the covalent radii for carbon and palladium, 0.771 and 1.31 Å respectively [21]. However, they are longer than those found in related complexes [12,22–24] where partial multiple-bond character of the Pd–C bond was assumed. In the present case the *trans* influence of the phosphine ligand accounts for the observed lengthening. The Pd–N bond lengths Pd(1)–N(1) [2.099(8) and Pd(2)–N(2) 2.125(7) Å], which are longer than the

Table 1

Crystal data for $[1,4\text{-}\{\text{Pd}[2,4\text{-}(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{N}]\}_2\text{C}_6\text{H}_4\{\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2\text{-P,P}\}_2][\text{PF}_6]_2$ (**5b**)

Formula	$\text{C}_{78}\text{H}_{74}\text{F}_{12}\text{N}_2\text{O}_4\text{P}_6\text{Pd}_2$
Formula weight	1730.01
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal colour	yellow
Crystal size (mm ³)	0.65 × 0.4 × 0.25
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	14.403(4)
b (Å)	15.684(4)
c (Å)	20.026(4)
α (°)	82.42(2)
β (°)	77.21(2)
γ (°)	84.55(2)
Volume (Å ³)	4363(2)
Z	2
Density (calculated) (g cm ⁻³)	1.317
Absorption coefficient (mm ⁻¹)	0.592
$F(000)$	1756
θ range for data collection	1.77 to 22.50°
Index ranges	$-1 < h < 15$, $-16 < k < 16$, $-21 < l < 21$
Reflections collected	13451
Independent reflections	11400 ($R_{\text{int}} = 0.0297$)
Absorption correction	none
Refinement method	full-matrix block least-squares on F^2
Data/restraints/parameters	11400/0/937
GOF on F^2	0.979
Final R indices [$I > 2.0\sigma(I)$]	$R_1 = 0.0795$, $wR_2 = 0.2260$
R indices (all data)	$R_1 = 0.1122$, $wR_2 = 0.2484$
Largest difference peak and hole	1.617 and $-1.227 \text{ e}\text{\AA}^{-3}$

single bond value of 2.01 Å calculated from the covalent radii of N (sp^2) 0.70 Å, palladium 1.31 Å, also reflect the *trans* influence of the phosphine ligands. The C=N distances [N(1)–C(7) 1.314(14) and N(2)–C(46) 1.250(11)] are consistent with those found in other cyclometallated complexes [24,25], and longer than the value of 1.273(3) Å of a related free Schiff base [26], which is a characteristic effect of coordination.

The distinct Pd–P bond lengths [Pd(1)–P(1) 2.352(3), Pd(1)–P(2) 2.254(3) and Pd(2)–P(3) 2.364(3), Pd(2)–P(4) 2.252(3) Å] arise from the differing *trans* influences of the phenyl carbon and nitrogen atoms of the diimine. They are shorter than the sum of the single bond radii for palladium and phosphorus, 2.41 Å [21], as has been found earlier [27].

The six-membered rings of the substituted carbimino-phenyl are planar (r.m.s. deviations 0.007 and 0.011 Å, deviations of oxygens all less than 0.04 Å, of carbon 0.136 and 0.052 Å, and of palladium 0.094 and 0.170 Å), and approximately coplanar (4.4 and 3.8°) with the adjacent five-membered PdC₃N chelate rings (r.m.s. deviations 0.008 and 0.015 Å). The eight phenyl

Table 2
Non-hydrogen atom coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5b**

Atom	x	y	z	U_{eq}^a
Pd(1)	2386(1)	3008(1)	181(1)	38(1)
Pd(2)	8418(1)	7572(1)	4689(1)	36(1)
P(1)	2120(2)	3976(2)	1018(1)	40(1)
P(2)	3661(2)	2413(2)	597(1)	40(1)
P(3)	8972(2)	7420(2)	5727(1)	42(1)
P(4)	8119(2)	8997(2)	4763(1)	40(1)
N(1)	1291(6)	3572(5)	-304(4)	48(2)
N(2)	8748(6)	6282(5)	4454(4)	40(2)
O(1)	3356(7)	65(5)	-1113(5)	81(3)
O(2)	971(7)	2199(6)	-1783(4)	88(3)
O(3)	5926(6)	8687(5)	2996(4)	72(2)
O(4)	7339(8)	5778(6)	3036(6)	117(4)
C(1)	1766(8)	2362(7)	-921(5)	49(3)
C(2)	2441(8)	2119(6)	-501(5)	43(2)
C(3)	2942(7)	1328(7)	-588(5)	52(3)
C(4)	2803(9)	828(7)	-1090(6)	58(3)
C(5)	2146(9)	1075(7)	-1487(6)	63(3)
C(6)	1625(8)	1856(7)	-1403(5)	57(3)
C(7)	1159(9)	3128(7)	-784(6)	61(3)
C(8)	632(7)	4294(6)	-156(5)	42(2)
C(9)	-320(8)	4169(7)	160(5)	47(3)
C(10)	952(8)	5109(7)	-330(5)	50(3)
C(11)	2554(8)	5046(7)	726(5)	49(3)
C(12)	2433(9)	5676(7)	1165(6)	62(3)
C(13)	2737(11)	6504(9)	888(7)	84(4)
C(14)	3161(11)	6661(9)	232(8)	87(4)
C(15)	3300(9)	6027(9)	-195(7)	75(4)
C(16)	3032(8)	5224(7)	44(5)	53(3)
C(17)	862(7)	4054(6)	1429(4)	43(3)
C(18)	402(9)	3305(7)	1561(5)	55(3)
C(19)	-564(10)	3295(10)	1893(6)	77(4)
C(20)	-1041(10)	4033(11)	2093(7)	85(4)
C(21)	-606(9)	4785(9)	1965(6)	66(3)
C(22)	349(8)	4806(7)	1636(5)	56(3)
C(23)	4641(7)	2010(7)	-39(5)	49(3)
C(24)	4822(9)	2461(7)	-702(5)	63(3)
C(25)	5608(8)	2184(8)	-1185(6)	62(3)
C(26)	6153(10)	1465(9)	-1054(7)	78(4)
C(27)	5954(9)	995(8)	-418(7)	71(4)
C(28)	5222(8)	1256(7)	82(6)	63(3)
C(29)	3376(7)	1554(6)	1292(5)	44(2)
C(30)	2632(9)	1060(7)	1317(6)	60(3)
C(31)	2425(10)	397(9)	1856(8)	81(4)
C(32)	2952(13)	254(9)	2366(7)	85(5)
C(33)	3669(14)	739(10)	2336(7)	88(5)
C(34)	3911(9)	1401(7)	1809(5)	60(3)
C(35)	2647(7)	3580(7)	1760(5)	50(3)
C(36)	3733(8)	3581(8)	1605(6)	60(3)
C(37)	4257(8)	3201(7)	914(5)	52(3)
C(38)	3234(12)	-503(9)	-1596(9)	108(6)
C(39)	712(11)	1689(10)	-2235(7)	92(5)
C(40)	7723(8)	6740(6)	3716(5)	50(3)
C(41)	7634(7)	7570(6)	3922(5)	39(2)
C(42)	7031(7)	8188(6)	3673(5)	47(3)
C(43)	6519(8)	8017(7)	3207(5)	53(3)
C(44)	6580(9)	7192(8)	2982(6)	67(4)
C(45)	7210(9)	6587(8)	3227(7)	70(4)
C(46)	8339(8)	6106(6)	4005(6)	54(3)
C(47)	9396(8)	5622(6)	4734(5)	43(3)
C(48)	10334(7)	5803(6)	4680(5)	40(2)
C(49)	9048(8)	4844(6)	5051(5)	46(3)
C(50)	10198(8)	7444(7)	5734(5)	48(3)

Table 2 (continued)

Atom	x	y	z	U_{eq}^a
C(51)	10563(10)	7308(8)	6351(6)	68(3)
C(52)	11495(11)	7345(10)	6333(6)	83(4)
C(53)	12153(10)	7555(9)	5697(7)	77(4)
C(54)	11822(9)	7718(8)	5104(6)	62(3)
C(55)	10859(9)	7673(7)	5109(5)	54(3)
C(56)	8509(8)	6444(7)	6230(5)	48(3)
C(57)	9042(9)	5745(7)	6474(5)	59(3)
C(58)	8613(12)	4988(8)	6797(6)	69(4)
C(59)	7671(14)	4945(8)	6874(6)	79(4)
C(60)	7094(11)	5633(9)	6638(6)	78(4)
C(61)	7535(9)	6366(8)	6303(6)	62(3)
C(62)	8434(8)	9650(6)	3933(5)	44(2)
C(63)	9342(9)	9527(7)	3563(6)	59(3)
C(64)	9695(11)	10028(9)	2939(7)	82(4)
C(65)	9082(14)	10625(9)	2684(7)	92(5)
C(66)	8155(13)	10756(8)	3040(8)	87(4)
C(67)	7856(9)	10278(7)	3674(7)	68(3)
C(68)	6919(8)	9336(7)	5194(5)	50(3)
C(69)	6235(8)	8756(7)	5386(5)	54(3)
C(70)	5322(8)	8976(9)	5767(6)	67(3)
C(71)	5156(10)	9811(11)	5969(7)	83(4)
C(72)	5827(10)	10399(9)	5766(7)	82(4)
C(73)	6719(9)	10165(7)	5388(6)	69(3)
C(74)	8380(9)	8254(7)	6279(5)	57(3)
C(75)	8713(9)	9153(7)	6016(6)	64(3)
C(76)	8873(8)	9424(6)	5243(5)	48(3)
C(77)	5307(10)	8523(9)	2562(7)	86(5)
C(78)	6760(15)	5539(13)	2618(13)	202(15)
P(6)	11918(3)	7789(2)	3001(2)	70(1)
F(1)	10834(7)	7616(7)	3316(5)	139(4)
F(2)	11987(13)	7098(6)	2508(5)	187(7)
F(3)	12964(7)	8031(9)	2738(6)	153(5)
F(4)	11776(8)	8519(6)	3504(4)	123(4)
F(5)	11593(8)	8481(6)	2420(4)	121(3)
F(6)	12165(7)	7078(5)	3592(4)	99(3)
P(5)	6110(3)	12836(3)	2523(3)	94(1)
F(7)	6094(11)	11881(9)	2781(8)	219(8)
F(8)	7169(8)	12633(11)	2180(7)	188(6)
F(9)	6429(14)	13080(16)	3103(10)	291(12)
F(10)	6048(20)	13728(8)	2161(11)	300(13)
F(11)	5044(9)	12938(12)	2859(7)	208(7)
F(12)	5861(8)	12600(8)	1840(7)	152(4)

^a U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

rings on the terminal phosphines are each planar (r.m.s. deviations 0.012, 0.003; 0.014, 0.003; 0.010, 0.008 and 0.015, 0.010 Å; deviations of phosphorus atoms up to 0.17 Å) and the pairs are inclined at 49, 76, 55 and 61°. The P–C–C–P torsion angles are -46, -27 and +41, +32°. Each benzene ring is planar (r.m.s. deviations 0.009 and 0.005 Å, nitrogen deviations 0.050 and 0.009 Å) and is parallel to (7.7 and 5.4°) and sandwiched between, two symmetry related phenyl rings from which it is separated at mean distances of 3.29 and 3.27 Å. This packing arrangement optimizes opportunities for π -stacking (Fig. 3). The smaller inter-planar angles between phenyls of the diphenylphosphine groups are for those phenyls involved in the π -stacking interactions. The two crystallographically independent mole-

Table 3
Selected bond lengths (Å) with estimated standard deviations ESDs
for compound **5b**

Pd(1)–C(2)	2.061(10)	Pd(1)–N(1)	2.099(8)
Pd(1)–P(2)	2.254(3)	Pd(1)–P(1)	2.352(3)
Pd(2)–C(41)	2.097(9)	Pd(2)–N(2)	2.125(7)
Pd(2)–P(4)	2.252(3)	Pd(2)–P(3)	2.364(3)
P(1)–C(17)	1.816(11)	P(1)–C(11)	1.823(12)
P(2)–C(35)	1.827(10)	P(2)–C(23)	1.806(11)
P(2)–C(29)	1.810(11)	P(1)–C(37)	1.820(11)
P(3)–C(50)	1.773(11)	P(3)–C(56)	1.814(11)
P(3)–C(74)	1.848(10)	P(4)–C(68)	1.818(11)
P(4)–C(62)	1.823(10)	P(4)–C(76)	1.823(10)
N(1)–C(7)	1.314(14)	N(1)–C(8)	1.425(13)
N(2)–C(46)	1.250(11)	N(2)–C(47)	1.467(9)
O(1)–C(4)	1.374(14)	O(1)–C(38)	1.446(12)
O(2)–C(6)	1.366(14)	O(2)–C(39)	1.413(12)
O(3)–C(43)	1.373(10)	O(3)–C(77)	1.435(12)
O(4)–C(45)	1.358(11)	O(4)–C(78)	1.41(2)
C(1)–C(6)	1.39(2)	C(1)–C(2)	1.42(2)
C(1)–C(7)	1.44(2)	C(2)–C(3)	1.386(14)
C(3)–C(4)	1.41(2)	C(4)–C(5)	1.36(2)
C(5)–C(6)	1.38(2)	C(8)–C(10)	1.37(2)
C(8)–C(9)	1.40(2)	C(9)–C(10)#1	1.41(2)
C(10)–C(9)#1	1.41(2)	C(35)–C(36)	1.526(12)
C(36)–C(37)	1.585(14)	C(40)–C(41)	1.403(13)
C(40)–C(45)	1.41(2)	C(40)–C(46)	1.420(14)
C(41)–C(42)	1.359(13)	C(42)–C(43)	1.38(2)
C(43)–C(44)	1.41(2)	C(44)–C(45)	1.37(2)
C(47)–C(48)	1.385(14)	C(47)–C(49)	1.384(14)
C(48)–C(49)#2	1.416(14)	C(49)–C(48)#2	1.416(14)
C(74)–C(75)	1.52(2)	C(75)–C(76)	1.52(2)

Symmetry transformations used to generate equivalent atoms:
#1, $-x, -y+1, -z$; #2, $-x+2, -y+1, -z+1$.

cules adopt slightly different conformations, as can be seen from the orientations of the benzene rings with respect to the adjacent chelate planes (71 and 57°).

There are no significant intermolecular contacts.

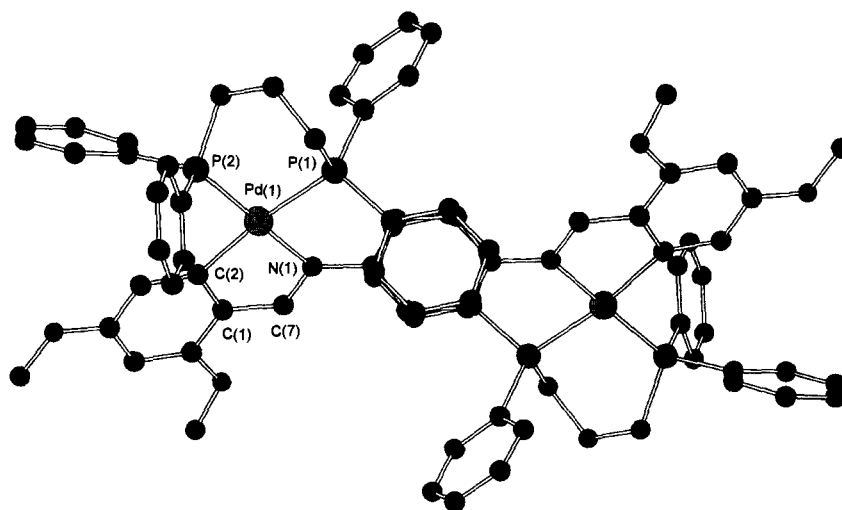


Fig. 3. The molecular structure of the Pd(1) dication of compound **5b** showing the π -stacking of the phenyl rings.

2.3. Influence of ring size on the δP_a chemical shift

It has been proposed that the ^{31}P chemical shift is influenced by ring size, and correlations based on ring contribution have been established [28]. The ring contribution causes deviation in the ^{31}P chemical shift from the standard correlation for the coordination chemical shift Δ , expressed in the relationship $\Delta = A\delta + B$, (where A and B are constants and δ is the shift for the free base). The ring contribution Δ_R was defined as the difference between the coordination shift Δ of a chelated phosphine complex and the coordination shift of an equivalent phosphorus in a non-chelated analogue. In general four-membered rings give a large negative Δ_R , five-membered rings give a large positive Δ_R , and six- and seven-membered rings give large negative and small negative or positive Δ_R respectively. Since only two six-membered ring complexes (**5c**, **5d**) and one seven-membered ring complex (**6d**) are present in the compounds reported in this paper, we have included in Table 6 ^{31}P chemical shift data obtained by us earlier [15], in order to compare Δ_R with the smaller ring size compounds (Table 6). Each complex is compared to an analogous compound where the P_a phosphorus of the chelated diphosphine is a triphenylphosphine ligand. As can be seen from the data in Table 6, the four-(**3d–3d**) and five-membered (**4a–4d**) ring complexes show large negative and large positive shifts respectively. The six-membered (**5a–5d**) ring complexes show fairly large negative shifts, whereas the seven-membered (**6a**, **6b**, **6d**) ring complexes show small negative shifts.

3. Experimental details

Solvents were purified by the standard methods [29]. Chemicals were reagent grade. Elemental analyses were

carried out on a Carlo-Erba elemental analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on a Perkin-Elmer 1330 spectrophotometer. NMR spectra were obtained as CDCl₃ solutions and referenced to SiMe₄ (¹H) or 85% H₃PO₄ (³¹P–{¹H}) and were recorded on a Bruker WM-250 spectrometer. The synthesis of the halide-bridged tetranuclear complexes (**1a–1d** and **2a–2d**) and of the dinuclear complexes **5a**, **5b**, **6a**, **6b** has been described by us earlier [15,30].

*Preparation of [1,4-{Pd[2,3,4-(MeO)₃C₆HC(H)=N]}₂-C₆H₄{Ph₂PCH(CH₃)PPh₂-P,P}₂][PF₆]₂(**3a**)*

To a suspension of **1a** (0.040 g, 0.027 mmol) in acetone (around 15 cm³) Ph₂PCH(CH₃)PPh₂ (0.045 g, 0.108 mmol) was added. The mixture was stirred for 6 h at room temperature, after which ammonium hexafluorophosphate was added and the mixture was stirred for another 6 h and then filtered. The resulting solution was concentrated under reduced pressure and chromatographed on a column packed with silica gel. Elu-

Table 4
Selected bond angles (°) with estimated standard deviations (ESDs) for compound **5b**

C(2)–Pd(1)–N(1)	81.2(4)	C(2)–Pd(1)–P(2)	95.8(3)
N(1)–Pd(1)–P(2)	174.2(3)	C(2)–Pd(1)–P(1)	172.6(3)
N(1)–Pd(1)–P(1)	95.1(2)	P(2)–Pd(1)–P(1)	88.44(10)
C(41)–Pd(2)–N(2)	80.0(3)	C(41)–Pd(2)–P(4)	94.0(3)
N(2)–Pd(2)–P(4)	171.2(2)	C(41)–Pd(2)–P(3)	166.0(3)
N(2)–Pd(2)–P(3)	97.8(2)	P(4)–Pd(2)–P(3)	89.53(10)
C(17)–P(1)–C(11)	110.6(5)	C(17)–P(1)–C(35)	100.7(5)
C(11)–P(1)–C(35)	105.1(5)	C(17)–P(1)–Pd(1)	109.8(4)
C(11)–P(1)–Pd(1)	116.2(4)	C(35)–P(1)–Pd(1)	113.4(4)
C(23)–P(2)–C(29)	107.7(5)	C(23)–P(2)–C(37)	100.0(4)
C(29)–P(2)–C(37)	107.1(4)	C(23)–P(2)–Pd(1)	114.9(4)
C(29)–P(2)–Pd(1)	113.6(4)	C(37)–P(2)–Pd(1)	112.4(3)
C(50)–P(3)–C(56)	109.8(5)	C(50)–P(3)–C(74)	103.9(5)
C(56)–P(3)–C(74)	101.7(5)	C(50)–P(3)–Pd(2)	122.0(3)
C(56)–P(3)–Pd(2)	106.9(3)	C(74)–P(3)–Pd(2)	110.8(4)
C(68)–P(4)–C(62)	109.3(5)	C(68)–P(4)–C(76)	103.3(5)
C(62)–P(4)–C(76)	100.5(5)	C(68)–P(4)–Pd(2)	116.1(4)
C(62)–P(4)–Pd(2)	113.1(3)	C(76)–P(4)–Pd(2)	113.2(3)
C(7)–N(1)–C(8)	116.4(9)	C(7)–N(1)–Pd(1)	112.6(7)
C(8)–N(1)–Pd(1)	130.7(6)	C(46)–N(2)–C(47)	119.2(6)
C(46)–N(2)–Pd(2)	112.7(5)	C(47)–N(2)–Pd(2)	128.1(5)
C(4)–O(1)–C(38)	117.3(8)	C(6)–O(2)–C(39)	118.7(8)
C(43)–O(3)–C(77)	118.2(7)	C(45)–O(4)–C(78)	119.1(9)
C(6)–C(1)–C(2)	122.6(10)	C(6)–C(1)–C(7)	120.3(10)
C(2)–C(1)–C(7)	116.8(9)	C(3)–C(2)–C(1)	115.8(9)
C(3)–C(2)–Pd(1)	133.1(8)	C(1)–C(2)–Pd(1)	110.8(7)
C(2)–C(3)–C(4)	120.8(11)	C(5)–C(4)–O(1)	124.2(10)
C(5)–C(4)–C(3)	122.1(11)	O(1)–C(4)–C(3)	113.6(10)
C(4)–C(5)–C(6)	118.2(10)	O(2)–C(6)–C(1)	115.1(10)
O(2)–C(6)–C(5)	124.5(10)	C(1)–C(6)–C(5)	120.3(10)
N(1)–C(7)–C(1)	118.6(11)	C(10)–C(8)–C(9)	121.1(10)
C(10)–C(8)–N(1)	118.8(10)	C(9)–C(8)–N(1)	120.1(10)
C(8)–C(9)–C(10)#1	119.3(10)	C(8)–C(10)–C(9)#1	119.6(11)
C(36)–C(35)–P(2)	113.7(6)	C(35)–C(36)–C(37)	114.7(8)
C(36)–C(37)–P(1)	118.1(8)	C(41)–C(40)–C(45)	118.2(9)
C(41)–C(40)–C(46)	118.0(9)	C(45)–C(40)–C(46)	123.7(9)
C(42)–C(41)–C(40)	119.8(9)	C(42)–C(41)–Pd(2)	130.8(8)
C(40)–C(41)–Pd(2)	109.0(7)	C(41)–C(42)–C(43)	120.9(10)
O(3)–C(43)–C(42)	115.8(9)	O(3)–C(43)–C(44)	122.5(9)
C(42)–C(43)–C(44)	121.7(10)	C(45)–C(44)–C(43)	116.3(11)
O(4)–C(45)–C(44)	121.4(10)	O(4)–C(45)–C(40)	115.6(9)
C(44)–C(45)–C(40)	122.9(10)	N(2)–C(46)–C(40)	120.1(8)
C(48)–C(47)–C(49)	122.1(9)	C(48)–C(47)–N(2)	118.8(8)
C(49)–C(47)–N(2)	119.0(9)	C(47)–C(48)–C(49)#2	118.1(9)
C(47)–C(49)–C(48)#2	119.8(10)	C(75)–C(74)–P(3)	113.6(8)
C(76)–C(75)–C(74)	117.5(9)	C(75)–C(76)–P(4)	118.0(8)

Symmetry transformations used to generate equivalent atoms: #1, $-x, y+1, -z$; #2, $-x+2, -y+1, -z+1$.

tion with dichloromethane/ethanol (4%) afforded the desired product as a yellow solid after concentration, which was recrystallised from chloroform/*n*-hexane. Yield 82% Anal. Found: C, 52.9; H, 4.5; N, 1.6. $C_{78}H_{74}F_{12}N_2O_6P_6Pd_2$. Calc.: C, 53.2; H, 4.2; N, 1.6%. IR: $\nu(C=N)$ 1600m, sh cm^{-1} .

The following ten cyclometallated complexes were prepared similarly and isolated as solids.

$[1,4\text{-}\{\text{Pd}[2,4\text{-}(\text{MeO})_2\text{C}_6\text{H}_2\text{C}(\text{H})=\text{N}]\}_2\text{C}_6\text{H}_4\{\text{Ph}_2\text{-PCH}(\text{CH}_3)\text{PPh}_2\text{-P,P}\}_2][\text{PF}_6]_2$ (**3b**). Yield 80%. Anal. Found: C, 53.8; H, 4.0; N, 1.7, $C_{76}H_{70}F_{12}N_2O_4P_6Pd_2$. Calc.: C, 53.6; H, 4.15; N, 1.65%. IR: $\nu(C=N)$ 1602m, sh cm^{-1} .

$[1,4\text{-}\{\text{Pd}[3\text{-Me-4-MeOC}_6\text{H}_2\text{C}(\text{H})=\text{N}]\}_2\text{C}_6\text{H}_4\{\text{Ph}_2\text{-PCH}(\text{CH}_3)\text{PPh}_2\text{-P,P}\}_2][\text{PF}_6]_2$ (**3c**). Yield 62%. Anal. Found: C, 54.6; H, 4.1 N, 1.6. $C_{76}H_{70}F_{12}N_2O_2P_6Pd_2$.

Table 5
 $^{31}\text{P}\text{-}\{^1\text{H}\}$ ^a and ^1H ^b NMR data ^{c,d}

	$\delta(\text{HC}=\text{N})$	$\delta[\text{H}(6)]$	$\delta[\text{H}(5)]$	$\delta[\text{H}(3)]$	$\delta[\text{H}(2)]$	$\delta(\text{MeO})$	$\delta(\text{C}_6\text{H}_4)$	$\delta(\text{P})$ ⁱ
a	8.79s	7.92d $^3J[\text{H}(6)\text{H}(5)] = 8.8$	6.81d			3.91s 3.94s 3.99s	7.27s	
3a ^f	8.10d $^4J(\text{P}_a\text{H}) = 7.1$		5.85dd $^4J(\text{P}_a\text{H}(5)) = 8.6$ $^4J(\text{P}_b\text{H}(5)) = 9.2$			3.12s 3.77s 4.08s	6.68s	6.6d -16.4d (66.8)
4a ^c	8.21d $^4J(\text{P}_a\text{H}) = 6.4$		6.10dd $^4J(\text{P}_a\text{H}(5)) = 5.4$ $^4J(\text{P}_b\text{H}(5)) = 8.7$			3.08s 3.71s 4.10s	6.42s	66.0d 46.95d (15.5)
b	8.83s	7.13d	6.70dd $^3J[\text{H}(5)\text{H}(6)] = 8.6$ $^4J[\text{H}(5)\text{H}(3)] = 2.3$	6.47d		3.86s 3.87s	7.25s	
3b ^{c,f}	8.28d $^4J(\text{P}_a\text{H}) = 6.9$		5.86ddd $^4J(\text{P}_a\text{H}(5)) = 7.6$ $^4J(\text{P}_b\text{H}(5)) = 9.9$ $^4J[\text{H}(5)\text{H}(3)] = 2.0$	6.31d		3.37s 3.95s	6.87s	10.9d -11.6d (43.9)
4b ^c	8.24d $^4J(\text{P}_a\text{H}) = 6.7$		5.94ddd $^4J(\text{P}_a\text{H}(5)) = 5.7$ $^4J(\text{P}_b\text{H}(5)) = 8.3$ $^4J[\text{H}(5)\text{H}(3)] = 2.0$	6.31d		3.24s 3.98s	6.40s	65.4d 46.7d (15.5)
c ^g	8.41s	7.67dd $^3J[\text{H}(6)\text{H}(5)] = 8.4$ $^4J[\text{H}(6)\text{H}(2)] = 1.8$	6.90d		7.79d	3.92s 2.28s*	7.25s	
3c ^{f,g}	n.a.		6.05dd $^4J(\text{P}_a\text{H}(5)) = 8.2$ $^4J(\text{P}_b\text{H}(5)) = 9.7$		n.a.	3.07s 2.08s*	6.74s	6.9d -17.0d (34.8)
4c ^{c,g}	n.a.		6.29dd $^4J(\text{P}_a\text{H}(5)) = 6.0$ $^4J(\text{P}_b\text{H}(5)) = 10.8$		n.a.	3.06s 2.08s*	6.41s	66.4d 46.7d (15.3)
5c ^g	7.74d $^4J(\text{P}_a\text{H}) = 7.3$		6.09dd $^4J(\text{P}_a\text{H}(5)) = 6.3$ $^4J(\text{P}_b\text{H}(5)) = 9.4$		7.17s	2.93s 2.05s*	6.21s	24.8d -4.5d (36.1)
d ^h	8.40s	7.20d $^4J[\text{H}(2)\text{H}(6)] = 1.4$		6.90d	7.30dd		7.25s	
3d ^{f,h}	n.a.			6.71d	n.a.		6.89s	4.3d -17.5d (47.9)
4d ^h	n.a.			6.70d	n.a.		6.39s	51.6d 64.5d (26.4)
5d ^h	n.a.			6.43d	n.a.		6.61s	24.7d -3.7d (48.7)
6d ^{c,h}	n.a.			6.49d	n.a.		6.08s	41.7d 26.2d (14.1)

^a In CDCl_3 . Measured at 100.6 MHz (ca. $\pm 20^\circ\text{C}$); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H_3PO_4 . ^b In CDCl_3 , unless otherwise stated. Measured at 250 MHz (ca. $\pm 20^\circ\text{C}$); chemical shifts (δ) in ppm (± 0.01) to high frequency of SiMe_4 . ^c Coupling constants in Hz. ^d s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublets of doublets; n.a., not assigned, occluded by the phosphine resonances. ^e In acetone- d_6 . ^f Data for the 1,1-dppe ligand: **3a**, δ 4.48 (1H, m, CH), δ 1.23 (3H, m, CHMe); **3b**, δ 4.95 (1H, m, CH), δ 1.29 (3H, s, CHMe); **3c**, δ 4.46 (1H, m, CH), δ 1.13 (3H, m, CHMe); **3d**, δ 4.77 (1H, m, CH), δ 1.21 (3H, s, CHMe). ^g Values marked with * are for the 3-Me group. ^h $\delta(\text{OCH}_2\text{O})$: **d**, 6.05s; **3d**, 5.18d, 5.13d $^2J(\text{HH}) = 2.3$; **4d**, 4.96s; **5d**, 4.86s; **6d**, 4.62s. ⁱ $^1J(\text{PP})$ values in parentheses.

Table 6
31P parameters

	P ^a	P _a	Δ _R
3a	41.6	6.6	-35.0
4a	41.6	66.0	+24.4
5a	41.6	24.0	-17.6
6a	41.6	30.1	-11.5
3b	41.7	10.9	-30.8
4b	41.7	65.4	+23.7
5b	41.7	13.2	-28.5
6b	41.7	28.1	-13.6
3c	45.4	6.9	-38.5
4c	45.4	66.4	+21.0
5c	45.4	24.8	-20.6
6c	45.4	—	—
3d	36.4	4.3	-32.1
4d	36.4	51.6	+15.2
5d	36.4	24.7	-11.7
6d	36.4	41.7	-5.3

^a Equivalent phosphorus (PPh₃) in a non-chelated analogue (Refs. [15] and [30]).

Calc.: C, 54.7; H, 4.2; N, 1.7%. IR: ν(C=N) 1602m, sh cm⁻¹.

[1,4-{Pd[4,5-(OCH₂O)C₆H₂C(H)=N]}₂C₆H₄{Ph₂-PCH(CH₃)PPh₂-P,P]}₂][PF₆]₂ (3d). Yield 62%. Anal. Found: C, 53.0; H, 3.6; N, 1.6. C₇₄H₆₂F₁₂N₂O₄P₆Pd₂. Calc.: C, 53.2; H, 3.7; N, 1.7%. IR: ν(C=N) 1605m cm⁻¹.

[1,4-{Pd[2,3,4-(MeO)₃C₆HC(H)=N]}₂C₆H₄{Ph₂-P(CH₂)₂PPh₂-P,P]}₂][PF₆]₂ (4a). Yield 89%. Anal. Found: C, 53.4; H, 4.0; N, 1.7. C₇₈H₇₄F₁₂N₂O₆P₆Pd₂. Calc.: C, 53.2; H, 4.2; N, 1.6%. IR: ν(C=N) 1600m, sh cm⁻¹.

[1,4-{Pd[2,4-(MeO)₂C₆H₂C(H)=N]}₂C₆H₄{Ph₂-P(CH₂)₂PPh₂-PP]}₂][PF₆]₂ (4b). Yield 84%. Anal. Found: C, 53.7; H, 4.0; N, 1.6. C₇₆H₇₀F₁₂N₂O₄P₆Pd₂. Calc.: C, 53.6; H, 4.15; N, 1.65%. IR: ν(C=N) 1598m cm⁻¹.

[1,4-{Pd[3-Me-4-MeOC₆H₂C(H)=N]}₂C₆H₄{Ph₂-P(CH₂)₂PPh₂-P,P]}₂][PF₆]₂ (4c). Yield 85%. Anal. Found: C, 54.7; H, 4.2; N, 1.7. C₇₆H₇₀F₁₂N₂O₂P₆Pd₂. Calc.: C, 54.5; H, 4.0; N, 1.7%. IR: ν(C=N) 1601m, sh cm⁻¹.

[1,4-{Pd[4,5-(OCH₂O)C₆H₂C(H)=N]}₂C₆H₄{Ph₂-P(CH₂)₂PPh₂-P,P]}₂][PF₆]₂ (4d). Yield 81%. Anal. Found: C, 53.2; H, 3.7; N, 1.7. C₇₄H₆₂F₁₂N₂O₄P₆Pd₂. Calc.: C, 53.1; H, 3.7; N, 1.7%. IR: ν(C=N) 1607m cm⁻¹.

[1,4-{Pd[3-Me-4-MeOC₆H₂C(H)=N]}₂C₆H₄{Ph₂-P(CH₂)₃PPh₂-PP]}₂][PF₆]₂ (5c). Yield 76%. Anal. Found: C, 54.9; H, 4.5; N, 1.5. C₇₈H₇₄F₁₂N₂O₂P₆Pd₂. Calc.: C, 55.2; H, 4.4; N, 1.65%. IR: ν(C=N) 1607m, sh cm⁻¹.

[1,4-{Pd[4,5-(OCH₂O)C₆H₂C(H)=N]}₂C₆H₄{Ph₂-P(CH₂)₃PPh₂-P,P]}₂][PF₆]₂ (5d). Yield 78%. Anal. Found: C, 53.8; H, 4.0; N, 1.6. C₇₆H₆₆F₁₂N₂O₄P₆Pd₂.

Calc.: C, 53.8; H, 3.9; N, 1.65%. IR: ν(C=N) 1611m cm⁻¹.

[1,4-{Pd[4,5-(OCH₂O)C₆H₂C(H)=N]}₂C₆H₄{Ph₂-P(CH₂)₄PPh₂-P,P]}₂][PF₆]₂ (6d). Yield 80%. Anal. Found: C, 54.2; H, 4.0; N, 1.5. C₇₈H₇₀F₁₂N₂O₄P₆Pd₂. Calc.: C, 54.3; H, 4.1; N, 1.6%. IR: ν(C=N) 1604m cm⁻¹.

3.1. Single-crystal X-ray diffraction analysis

Three-dimensional, room temperature X-ray data were collected in the range 3.5 < 2θ < 45° on a Siemens P4 diffractometer by the omega scan method. The 7497 independent reflections (13455 measured) for which |F|/σ(|F|) > 4.0 were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods and refined by full-matrix blocked least squares on F². Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R₁ = 0.0795, wR₂ = 0.2260 for 7497 reflections (R₁ = 0.1122, wR₂ = 0.2484 for all 11400 unique data, 937 parameters, mean and maximum δ/σ 0.000, 0.000), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density -1.23 and 1.62 Å⁻³. A weighting scheme w = 1/[σ²(F_o²) + (0.1775P)² + 0.0P] where P = (F_o² + 2F_c²)/3 was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL93 [31] as implemented on the Viglen 486dx computer.

Full lists of atomic coordinates, thermal parameters and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

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