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Cyclometallated complexes of palladium(II) with the diphosphines *trans*-Ph_2 $PCH{=}CHPPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$ and $Ph_2P(CH_2)_4PPh_2$. The X-ray crystal structure of $[\{Pd[2,4\text{-}Me_2C_6H_2C(H){=}NCy]\}_2(\mu\text{-}Ph_2P(CH_2)_4PPh_2)(\mu\text{-}Cl)_2]$

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Abstract

Treatment of 2,4-$Me_2C_6H_3C(H){=}NCy$ (**a**) or 2,3-$(MeO)_2C_6H_3C(H){=}NCy$ (**b**) (Cy = cyclohexyl) with palladium(II) acetate gave the cyclometallated acetato-bridged complexes **1a** and **1b**. These were converted into the analogous halide-bridged complexes by reaction with NaX (**2a**, **2b**, X = Cl; **3a**, **3b**, X = Br; **4a**, **4b**, X = I). The halide-bridged dimers react: (a) with *trans*-$Ph_2PCH{=}CHPPh_2$ (*trans*-dppe) and $Ph_2P(CH_2)_4PPh_2$ (dppb) in a dimer/diphosphine 1:1 molar ratio to give the dinuclear phosphine-bridged complexes **5a**–**7a**, **5b**–**7b** (*trans*-dppe) and **8a**–**10a**, **8b**–**10b** (dppb); and (b) with *cis*-$Ph_2PCH{=}CHPPh_2$ (*cis*-dppe) or $Ph_2P(CH_2)_4PPh_2$ (dppb), in a dimer/diphosphine 1:2 molar ratio, and NH_4PF_6, to give the mononuclear cyclometallated species **11a**, **11b** (*cis*-dppe), or **12a** and **12b** (dppb). The structure of **8a** is described. This is the first structurally characterised dinuclear palladium(II) complex with two cyclometallated moieties bounded through a diphosphine ligand. The crystals are monoclinic, space group $P2_1/n$ with $a = 1084.1(7)$, $b = 3067.7(28)$, $c = 1181.9(10)$ pm, $\beta = 114.22(6)°$, U 3.585(5) nm^3, $Z = 2$, $R = 0.0731$ and $R_w = 0.0602$ for 3970 independent reflections.

1. Introduction

Cyclometallated complexes have been widely studied [1–4]. We have described the chemistry of cyclometallated compounds derived from ligands having one or two nitrogen-donor atoms, such as Schiff bases [5,6], phenylimidazoles [7], benzylidene hydrazones [8], and bis(*N*-benzylidene)-1,4-phenylenediamines [9]. The cyclometallated halide-bridged dimer complexes react with an extensive variety of molecular and anionic nucleophiles to give mononuclear or dinuclear species which may or may not be cyclometallated.

We have described the reactivity of cyclometallated palladium(II) dimer complexes with tertiary mono- and di-phosphines [5,6,10,11]. For dinuclear species and $Ph_2PCH_2PPh_2$ (dppm) or $Ph_2PC({=}CH_2)PPh_2$ (vdpp), the small "bite" of the diphosphine ligand brings the metal atoms sufficiently close together to allow the metals also to be bonded by an acetate or by a halide, to give dinuclear 1:1 salts. When the "bite" of the diphosphine is increased, the diphosphine only should bridge the metals, to give molecular compounds with terminal metal–halogen bonds. This happens in the case of $Ph_2PCH_2CH_2PPh_2$ [12]. X-Ray crystallographic data concerning these compounds is somewhat limited. To the best of our knowledge there is only one example for a small "bite" diphosphine [11]. In the present paper we report the first crystal structure of a cyclometallated dinuclear Schiff base complex where

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two cyclometallated palladium(II) moieties are bonded through a large "bite" diphosphine, $Ph_2P(CH_2)_4PPh_2$ (dppb). The use of *trans*-$Ph_2PCH{=}CHPPh_2$ (*trans*-dppe) and *cis*-$Ph_2PCH{=}CHPPh_2$ (*cis*-dppe) to give further dinuclear and mononuclear species is also described.

2. Results and discussion

2.1. Crystal structure of 8a

Suitable crystals of compound **8a** were obtained by slowly evaporating a chloroform solution. The molecular structure, with atom labelling, is illustrated in Fig. 1. Final fractional coordinates are listed in Table 1 while bond lengths and angles with estimated standard deviations are listed in Table 2.

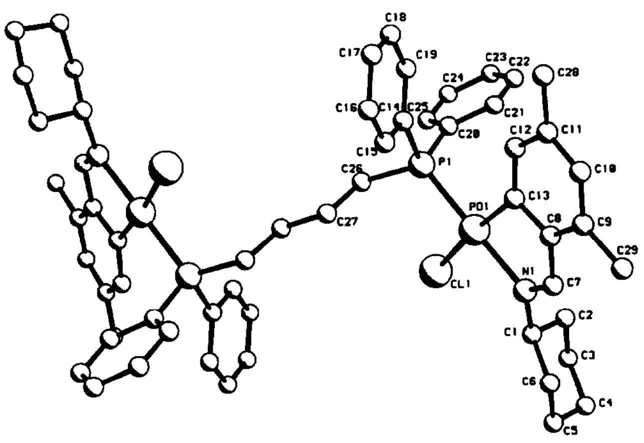
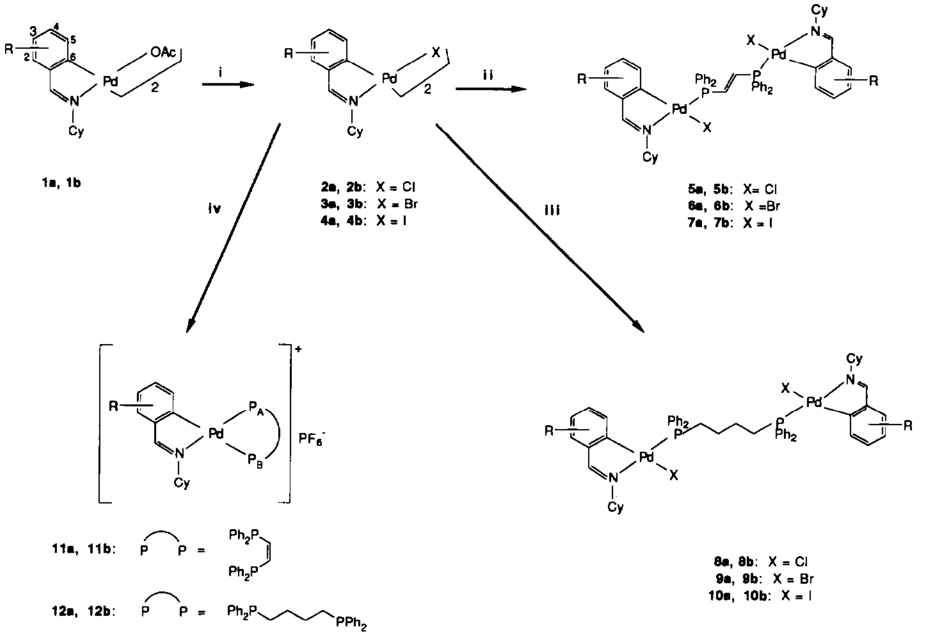


Fig. 1. Molecular structure and numbering scheme of compound **8a**.

The molecule is a centrosymmetric binuclear complex, containing two, symmetry related, square-planar palladium(II) centres as expected for Pd^{2+}, at each of which there is bound a chlorine, a bidentate *N*-(2,4-benzylidene)cyclohexylamine-C^6,*N* (C^6 *trans* to chlorine), and finally a centrosymmetric 1,4-bis(diphenylphosphino)butane which bridges the two palladium centres. The Pd(1)–C(13) bond length of 200.2(8) pm is shorter than the sum of the covalent radii (131 and 77.1 pm for palladium and for carbon, respectively [13]). This shortening, which has been observed in analogous complexes [6,9,14], is attributed to partial multiple bond character in the Pd–C(phenyl) linkage. The Pd(1)–N(1) length of 209.6(7) pm is longer than the single bond value of 201 pm calculated using the covalent radius of N(sp^2) 70 pm; palladium, 131 pm. It is also longer than the value found in other cyclometallated complexes, *ca.* 204 pm; this reflects the *trans*-influence of the phosphine. The C=N distance N(1)–C(7) of 125.6(12) pm is rather longer than the value of 123.7(3) pm observed for a related free base [15]; this is characteristic of coordinated Schiff bases where the nitrogen atom is bonded to the metal atom [16], and has been observed by us earlier [6,9]. The Pd(1)–P(1) distance of 226.2(3) pm, is similar to that value found in a related cyclometallated complex [17], but is shorter than the sum of the single bond covalent radii for Pd and P, 241 pm [13]. The relative shortness of the bond



Scheme 1. I: NaX in aqueous acetone; ii: 1 equiv. of *trans*-dppe in acetone; iii: 1 equiv. of dppb in acetone; iv: 2 equiv. of *cis*-dppe or dppb + NH_4PF_6 in acetone. **a**: R = 2,4-Me_2; **b**: R = 2,3-$(MeO)_2$.

TABLE 1. Non-hydrogen atom coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for compound **8a**

Atom [a]	x	y	z	U_{eq} [b]
Pd(1)	2310(1)	1192(1)	4678(1)	27(1)*
Cl(1)	4676(2)	1300(1)	5216(2)	45(1)*
P(1)	2301(2)	685(1)	3286(2)	29(1)*
N(1)	2263(7)	1652(2)	5972(6)	33(3)*
C(1)	3357(8)	1962(3)	6686(7)	38(4)*
C(2)	3284(11)	2341(3)	5874(8)	71(5)*
C(3)	4489(13)	2646(4)	6529(11)	104(8)*
C(4)	4572(11)	2791(3)	7763(11)	86(6)*
C(5)	4592(11)	2408(4)	8557(10)	78(6)*
C(6)	3415(10)	2103(3)	7906(8)	66(5)*
C(7)	1149(7)	1656(3)	6064(7)	37(4)*
C(8)	50(8)	11382(3)	5259(8)	43(4)*
C(9)	−1225(8)	1382(3)	5259(8)	43(4)
C(10)	−2225(8)	1141(3)	4386(8)	43(4)*
C(11)	−2015(8)	927(3)	3460(8)	43(4)
C(12)	−726(7)	934(3)	3458(7)	33(3)*
C(13)	351(7)	1149(3)	4356(7)	32(3)*
C(14)	1068(7)	246(2)	2874(7)	27(3)*
C(15)	947(8)	24(3)	3847(8)	38(4)*
C(16)	32(9)	−312(3)	2420(9)	58(5)*
C(17)	−781(10)	−427(3)	2420(9)	58(5)
C(18)	−669(10)	−212(3)	1444(9)	62(5)*
C(19)	254(8)	130(3)	1672(8)	44(4)*
C(20)	2023(8)	946(3)	1819(7)	33(3)*
C(21)	886(8)	1194(3)	1220(8)	49(4)*
C(22)	648(10)	1397(3)	137(9)	55(5)*
C(23)	1570(11)	1376(3)	−370(9)	55(5)*
C(24)	2726(10)	1145(3)	210(8)	51(4)*
C(25)	2957(9)	929(3)	1311(8)	47(4)*
C(26)	3876(8)	381(3)	3693(7)	32(4)*
C(27)	4311(8)	104(3)	4850(8)	39(4)*
C(28)	−3100(8)	665(4)	2519(9)	69(5)*
C(29)	−1500(9)	1627(4)	6243(9)	69(5)*
C(30)	4763(12)	2043(4)	3006(11)	81(6)*
C(31)	6104(12)	928(4)	8309(11)	97(7)*
Cl(2)	5764(4)	2440(1)	4024(3)	111(2)*
Cl(4)	3092(4)	2195(1)	2359(4)	125(2)*
Cl(3)	5345(4)	1946(1)	1862(4)	133(3)*
Cl(5)	6579(5)	1318(1)	9443(4)	162(3)*
Cl(6)	7485(4)	644(1)	8341(4)	142(3)*
Cl(7)	4920(6)	590(2)	8418(5)	201(4)*

[a] Atoms C(30), Cl(2)–Cl(4), and C(31), Cl(5)–Cl(7) are from two chloroform molecules per asymmetric unit. [b] For starred atoms: equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

suggests that there is effective orbital overlap between the palladium and phosphorus atoms.

The Pd(1)–Cl(1) bond length of 239.9(9) pm is very close to that observed elsewhere (236.2(3) pm [18] and 238.6(7) pm [19]), but is significantly longer than the sum of the covalent radii (230 pm), consistent with the *trans*-influence of the C(phenyl) atom. The geometry around the palladium atom is planar (r.m.s. deviation of coordination plane 0.8 pm, from which the displacement of the palladium is only 0.6 pm), and the only noteworthy angular deviation is the reduced N(1)–Pd(1)–C(13) angle of 80.9(3)° consequent upon chelation. This is reflected in the value of the Pd(1)–C(13)–C(12) angle, 132.4(7)°. The sum of angles about the palladium atom is 360°. The skeleton of the cyclometallated ring [Pd(1)–C(13)–C(8)–C(7)–N(1)] is planar (r.m.s. deviation 2.2 pm), from which the palladium

TABLE 2. Bond lengths (pm) and angles (°) [a] in compound **8a**

Pd(1)–Cl(1)	239.9(3)	Pd(1)–P(1)	226.2(3)
Pd(1)–N(1)	209.6(7)	Pd(1)–C(13)	200.2(8)
P(1)–C(14)	181.7(8)	P(1)–C(20)	181.8(9)
P(1)–C(26)	182.9(8)	N(1)–C(1)	148.3(10)
N(1)–C(7)	125.6(12)	C(1)–C(2)	148.8(13)
C(1)–C(6)	148.3(14)	C(2)–C(3)	153.5(16)
C(3)–C(4)	149.2(19)	C(4)–C(5)	149.9(16)
C(5)–C(6)	151.3(14)	C(7)–C(8)	144.3(10)
C(8)–C(9)	139.5(14)	C(8)–C(13)	141.8(13)
C(9)–C(10)	136.7(11)	C(9)–C(29)	151.3(16)
C(10)–C(11)	137.4(14)	C(11)–C(12)	139.8(13)
C(11)–C(28)	148.2(12)	C(12)–C(13)	138.1(9)
C(14)–C(15)	138.0(12)	C(14)–C(19)	137.7(10)
C(15)–C(16)	138.0(12)	C(16)–C(17)	137.9(12)
C(17)–C(18)	137.7(16)	C(18)–C(19)	139.7(14)
C(20)–C(21)	137.3(11)	C(20)–C(25)	137.4(15)
C(21)–C(22)	134.9(14)	C(22)–C(23)	136.1(18)
C(23)–C(24)	135.6(14)	C(24)–C(25)	138.8(13)
C(26)–C(27)	151.2(12)	C(27)–C(27′)	152.6(17)
C(30)–Cl(2)	174.2(11)	C(30)–Cl(4)	171.1(13)
C(30)–Cl(3)	173.6(16)	C(31)–Cl(5)	171.1(13)
C(31)–Cl(6)	171.8(15)	C(31)–Cl(7)	169.6(16)
Cl(1)–Pd(1)–P(1)	88.4(1)	Cl(1)–Pd(1)–N(1)	93.3(2)
P(1)–Pd(1)–N(1)	178.1(2)	Cl(1)–Pd(1)–C(13)	174.2(2)
P(1)–Pd(1)–C(13)	97.4(2)	N(1)–Pd(1)–C(13)	80.9(3)
Pd(1)–P(1)–C(14)	119.2(3)	Pd(1)–P(1)–C(20)	110.0(3)
C(14)–P(1)–C(20)	104.7(3)	Pd(1)–P(1)–C(26)	115.7(3)
C(14)–P(1)–C(26)	101.3(4)	C(20)–P(1)–C(26)	104.3(4)
Pd(1)–N(1)–C(1)	126.4(6)	Pd(1)–N(1)–C(7)	112.4(5)
C(1)–N(1)–C(7)	121.2(7)	N(1)–C(1)–C(2)	108.3(6)
N(1)–C(1)–C(6)	116.5(8)	C(2)–C(1)–C(6)	111.6(8)
C(1)–C(2)–C(3)	110.0(7)	C(2)–C(3)–C(4)	111.9(12)
C(3)–C(4)–C(5)	111.0(9)	C(4)–C(5)–C(6)	111.9(8)
C(1)–C(6)–C(5)	111.5(10)	N(1)–C(7)–C(8)	119.4(8)
C(7)–C(8)–C(9)	123.1(8)	C(7)–C(8)–C(13)	114.7(8)
C(9)–C(8)–C(13)	122.2(7)	C(8)–C(9)–C(10)	118.7(9)
C(8)–C(9)–C(29)	121.1(7)	C(10)–C(9)–C(29)	120.2(9)
C(9)–C(10)–C(11)	121.4(9)	C(10)–C(11)–C(12)	119.1(7)
C(10)–C(11)–C(28)	121.2(9)	C(12)–C(11)–C(28)	119.6(9)
C(11)–C(12)–C(13)	122.4(8)	Pd(1)–C(13)–C(8)	111.8(5)
Pd(1)–C(13)–C(12)	132.4(7)	C(8)–C(13)–C(12)	115.9(8)
P(1)–C(14)–C(15)	116.8(5)	P(1)–C(14)–C(19)	124.0(7)
C(15)–C(14)–C(19)	119.3(7)	C(14)–C(15)–C(16)	121.0(7)
C(15)–C(16)–C(17)	119.5(10)	C(16)–C(17)–C(18)	120.3(9)
C(17)–C(18)–C(19)	120.0(8)	C(14)–C(19)–C(18)	119.9(9)
P(1)–C(20)–C(21)	119.9(8)	P(1)–C(20)–C(25)	122.5(6)
C(21)–C(20)–C(25)	117.5(8)	C(20)–C(21)–C(22)	121.8(10)
C(21)–C(22)–C(23)	120.5(9)	C(22)–C(23)–C(24)	119.7(10)
C(23)–C(24)–C(25)	119.8(11)	C(20)–C(25)–C(24)	120.7(8)
P(1)–C(26)–C(27)	115.9(7)	C(26)–C(27)–C(27′)	110.9(10)

[a] Primed atoms are related by the symmetry operator ($1-x$, $-y$, $1-z$).

and the imino-carbon atom deviate in opposite directions by 16.1 and 14.1 pm, respectively. The cyclohexyl substituent adopts a chair conformation [r.m.s. deviation of plane C(2),C(3),C(5),C(6) 0.5 pm, displacements of C(1) and C(4) +65.1 and −63.5 pm, respectively]. The two phenyl rings are planar (r.m.s. deviations 0.3 and 1.0 pm) and mutually inclined at 71°. Torsion angles in the butane chain are −175 and (necessarily) 180°.

The two chloroform molecules per asymmetric unit are weakly hydrogen-bonded to the coordinated chlorine [Cl(1) ··· C 249.6 and 252.5 pm, Cl(1) ··· H 260 and 258 pm] from opposite directions (H ··· H 499 pm), in a fairly symmetric and coplanar (with palladium) manner.

2.2. *Cyclometallated diphosphine compounds*

Treatment of *N*-(2,4-dimethylbenzylidene)cyclohexylamine (**a**) or of *N*-(2,3-dimethoxybenzylidene)cyclohexylamine (**b**) with palladium(II) acetate in boiling glacial acetic acid gave the corresponding cyclometallated acetato-bridged palladium(II) dimer complexes (**1a**, **1b**) as air-stable solids. These were converted into the chloro-bridged (**2a**, **2b**), bromo-bridged (**3a**, **3b**) and iodo-bridged complexes (**4a**, **4b**), respectively, as air-stable solids (see Experimental and Tables 3 and 4), by treatment of **1a** or **1b** in acetone with aqueous sodium chloride, sodium bromide or sodium iodide. They were fully characterised by elemental analysis (C, H, N) and by IR and ^{1}H NMR spectroscopy. These compounds have the characteristic properties of some analogous compounds reported by us [5,20]. Thus, coordination of the metal through the nitrogen lone pair of the C=N moiety is confirmed by the shift of the ν(C=N) frequency towards lower wavenumbers in the IR spectrum [21] and by the shift of the *H*C=N resonance towards lower frequency in the ^{1}H NMR spectrum [22]. In complexes **1a** and **1b** the separation of the asymmetric and symmetric stretching modes of the acetate groups is consistent with bridging acetate ligands [23]. The ^{1}H NMR spectra allowed unequivocal assignment of the phenyl ring protons, confirming palladation of the ligand.

Reaction of the halide-bridged complexes **2a**–**4a** or **2b**–**4b** with *trans*-$Ph_2PCH{=}CHPPh_2$ (*trans*-dppe) or with $Ph_2P(CH_2)_4PPh_2$ (dppb) in a dimer/diphosphine

TABLE 3. Microanalytical, colour, yield and IR data

	Colour	Yield (%)	Analytical data (Found (calc.) (%))			IR data (cm^{-1})		
			C	H	N	ν(C=N) [a]	$\nu(Pd{-}Cl)_b$	$\nu(Pd{-}Cl)_t$
1a [b]	Yellow	40	53.6 (53.8)	6.2 (6.1)	3.7 (3.7)	1600sh,s		
2a	White	80	51.1 (51.6)	5.7 (5.7)	3.8 (3.8)	1602m	298m 250m	
3a [c]	Yellow	85	43.4 (43.4)	4.3 (4.8)	3.0 (3.3)	1606s		
4a [c]	Yellow	90	37.6 (38.0)	4.5 (4.3)	2.9 (2.9)	1610m		
5a	White	77	60.1 (60.7)	6.0 (6.0)	2.3 (2.5)	1618m		275m
6a [c]	Pale yellow	81	54.3 (54.7)	5.1 (5.1)	2.0 (2.3)	1610m		
7a	Yellow	70	52.4 (52.1)	4.9 (4.8)	2.4 (2.2)	1610m		
8a	White	80	61.9 (61.2)	6.1 (6.0)	2.7 (2.5)	1614m		288m
9a	White	70	56.7 (56.7)	5.5 (5.6)	2.0 (2.3)	1612m		
10a	Yellow	66	52.5 (52.7)	5.2 (5.2)	1.9 (2.1)	1618m		
11a	White	90	56.8 (57.1)	4.9 (4.9)	1.6 (1.6)	1600m		
12a	Yellow	80	58.3 (57.9)	5.4 (5.4)	1.5 (1.5)	1608m		
1b [b,c]	Yellow	50	46.3 (46.3)	5.3 (5.3)	3.1 (3.4)	1598sh,m		
2b [c]	Yellow	80	47.7 (47.5)	5.6 (5.6)	3.8 (3.4)	1597m	287m 270m	
3b [c]	Yellow	70	42.5 (42.9)	5.6 (5.0)	3.2 (3.0)	1600s		
4b [c]	Yellow	85	35.6 (35.6)	4.0 (4.0)	2.8 (2.7)	1610s		
5b	White	80	54.6 (54.4)	5.5 (5.1)	2.4 (2.2)	1620m		275m
6b	White	90	53.1 (53.3)	4.9 (4.9)	2.2 (2.2)	1618m		
7b	Pale yellow	78	49.5 (49.6)	4.6 (4.6)	2.2 (2.1)	1616m		
8b	Yellow	70	58.0 (58.0)	6.1 (5.7)	2.4 (2.3)	1618m		295m
9b	Pale yellow	73	53.3 (53.9)	5.3 (5.3)	2.3 (2.2)	1618s		
10b [c]	Orange	88	51.9 (51.2)	5.8 (5.4)	2.2 (1.9)	1612m		
11b	Yellow	95	55.2 (55.1)	4.7 (4.7)	1.7 (1.6)	1609m		
12b	Yellow	80	55.8 (55.9)	5.1 (5.2)	1.4 (1.5)	1610m		

[a] ν(C=N) values for **a** 1634s; *b* 1630s (cm^{-1}). [b] ν(COO) values for **1a**: ν_{as}(COO) 1570s, ν_s(COO) 1408s; **1b**: ν_{as}(COO) 1575s, ν_s(COO) 1410s (cm^{-1}). [c] Obtained as solvates: **3a**, $0.5CH_2Cl_2$; **4a**, CH_2Cl_2; **6a**, $0.5CH_2Cl_2$; **1b**, MeCOMe; **2b**, CH_2Cl_2; **3b**, CH_2Cl_2; **4b**, 2MeCOMe; **10b**, 2MeCOMe.

TABLE 4. ^{31}P-{^{1}H} [a] and ^{1}H [b] NMR data [c,d]

	δ(HC=N)	δ[H(3)]	δ[H(5)]	δ(MeO)	δ(Me)	δ(P)
a [e]	8.58s	6.97s	7.02d		2.45s 2.32s	
1a [f]	7.37s	6.52s	6.71s		2.23s 2.18s	
2a	8.00s	6.59s	7.05s		2.3s 2.26s	
3a	8.05s	6.59s	7.23s		2.37s 2.26s	
4a	8.16s	6.61s	7.48s		2.38s 2.25s	
5a [g,j]	8.32d ^4J(PH) = 7.8	6.42s	5.99d ^4J[PH(5)] = 6.2		2.38s 1.61s	32.28s
6a [g,j]	8.33d ^4J(PH) = 7.9	6.42s	5.99b		2.38s 1.61s	32.71s
7a [g,j]	8.37d ^4J(PH) = 8.1	6.42s	5.97b		2.37s 1.61s	33.30s
8a [g]	8.25d ^4J(PH) = 8.0	6.42s	5.96b		2.37s 1.64s	30.97s
9a [g]	8.32d ^4J(PH) = 8.1	6.42s	5.93d ^4J[PH(5)] = 7.6		2.37s 1.63s	31.33s
10a [g]	8.37d ^4J(PH) = 7.9	6.42s	5.87d ^4J[PH(5)] = 7.4		2.38s 1.65s	32.33s
11a [g,k]	8.54d ^4J(PH) = 8.8	6.63s	6.56t ^4J[PH(5)] = 7.2		2.44s 1.87s	57.90d (P_A) 48.02d (P_B)
12a [g,k]	8.37d ^4J(PH) = 8.1	6.51s	6.29t ^4J[PH(5)] = 7.6		2.37s 1.69s	37.45d (P_A) 12.49d (P_B)
		δ[H(4)]				
b [h]	8.66s	6.94dd ^3J[H(4)H(5)] = 7.8	7.03t	3.87s 3.86s		
1b [i]	7.63s	6.65d ^3J[H(4)H(5)] = 8.1	6.68d	3.78s 3.80s		
2b	8.11s	6.68d ^3J[H(4)H(5)] = 8.2	6.99d	3.88s 3.80s		
3b	8.17s	6.66d ^3J[H(4)H(5)] = 8.5	7.17d	3.88s 3.80s		
4b	8.26s	6.63d ^3J[H(4)H(5)] = 8.5	7.40d	3.87s 3.79s		
5b [j]	8.44d ^4J(PH) = 8.4	6.13d ^3J[H(4)H(5)] = 8.4	5.96dd ^4J[PH(5)] = 6.2	3.86s 3.60s		33.18s
6b [j]	8.47d ^4J(PH) = 8.2	6.15d ^3J[H(4)H(5)] = 8.3	5.96dd ^4J[PH(5)] = 6.3	3.85s 3.60s		33.50s
7b [j]	8.51d ^4J(PH) = 7.2	6.15d ^3J[H(4)H(5)] = 8.4	5.92d ^4J[PH(5)] = 6.6	3.84s 3.60s		28.38s
8b	8.41d ^4J(PH) = 8.4	6.18d ^3J[H(4)H(5)] = 8.4	5.96dd ^4J[PH(5)] = 6.0	3.84s 3.63s		31.06s
9b	8.43d ^4J(PH) = 8.5	6.18d ^3J[H(4)H(5)] = 8.4	5.93dd ^4J[PH(5)] = 6.1	3.81s 3.63s		33.83s
10b	8.41d ^4J(PH) = 7.1	6.18d ^3J[H(4)H(5)] = 8.4	5.90m ^4J[PH(5)] = 7.3	3.83s 3.63s		32.84s
11b [k]	8.63d ^4J(PH) = 8.0	6.53m	6.53m	3.90s 3.72s		58.99d (P_A) 49.70d (P_B)
12b [k]	8.63d ^4J(PH) = 8.6	6.25m	6.25m	3.90s 3.72s		38.46d (P_A) 14.18d (P_B)

[a] Spectra measured at 100.6 MHz (*ca.* ± 20°C); chemical shifts (δ) in ppm (±0.1) to high frequency of 85% H_3PO_4. [b] Spectra measured at 250 MHz (*ca.* ± 20°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; t, triplet; m, multiplet; b, broad. [e] δ(H*6*) = 7.76d, ^3J[H(5)H(6)] = 7.8. [f] δ(O_2C*Me*) = 2.13s. [g] The lower δ(*Me*) value is for the C(4)-*Me* group. [h] δ(H*6*) = 7.54dd, ^3J[H(5)H(6)] = 8.1, ^4J[H(5)H(6)] = 1.5. [i] δ(O_2C*Me*) = 2.11s. [j] δ[PC(*H*)=C(*H*)P] values for: **5a**, δ6.96; **6a**, δ6.84; **7a**, δ6.82; **5b**, δ6.80; **6b**, δ6.62; **7b**, δ6.66 ppm. *N* values are *ca.* 42 Hz. [k] Coupling constants: **11a**, ^3J(PP) = 49.6; **12a**, ^5J(PP) = 48.1; **11b**, ^3J(PP) = 52.9; **12b**, ^5J(PP) = 45.7 Hz.

1/1 molar ratio gave the dinuclear species **5a**–**7a** and **5b**–**7b** and **8a**–**10a** and **8b**–**10b**, respectively (see Experimental and Tables 3 and 4). The C(4)-*Me* resonance in complexes derived from ligand **a** is shifted towards lower frequency by *ca.* 0.8 ppm in the ^{1}H NMR spectrum as compared to the parent halide-bridged dimer, due to shielding effects of the phosphine phenyl ring [24], showing that the phosphorus atom is *trans* to the nitrogen atom. Also, the *H*C=N resonance is coupled to the ^{31}P nucleus [^4J(PH) *ca.* 8 ppm]; in a *trans*-C–Pd–P geometry the *H*C=N resonance is not coupled to the ^{31}P nucleus [10] (*vide infra*). There is only one set of resonances for each cyclopalladated moiety in the ^{1}H NMR spectrum and only one singlet is observed for the two ^{31}P nuclei in the ^{31}P{^{1}H} spectrum; this indicates that the compounds are centrosymmetric, as proved for **8a** by X-ray crystal structure determination (*vide supra*).

Reaction of the halide-bridged dimer complexes **2a**–**4a** or **2b**–**4b** with *cis*-dppe or with dppb, in a dimer/diphosphine 1/2 molar ratio, and NH_4PF_6, gave mononuclear five- (**11a**, **11b**) and seven-membered-ring (**11b**, **12b**) cyclometallated species (see Experimental and Tables 3 and 4). The final products are the same whichever halide dimer is used in the reaction, as the halogen is exchanged by the hexafluorophosphate ion. For compounds derived from *trans*-dppe the apparent triplet at *ca.* 6.9–6.7 ppm is assigned to the PC*H*=C*H*P resonances (AA′XX′ spin system) with N values *ca.* 42 Hz. The ^{31}P NMR spectrum shows two doublets for the two inequivalent phosphorus nuclei. The assignment of the doublets was made on the assumption that a ligand of greater *trans*-influence shifts the ^{31}P resonance of the phosphorus nuclei *trans* to it to lower frequency [25]. This was confirmed by selective decoupling experiments of the phosphorus atoms. The *H*C=N resonance (doublet) arises from coupling to only one phosphorus nucleus [^4J(PH) *ca.* 7.5 Hz], presumably that *trans* to it. Selective irradiation reduces the H(5) resonance to a doublet [^4J(PH) *ca.* 7.5 Hz] and the *H*C=N resonance to a singlet (irradiating at P_A) or to a doublet (irradiating at P_B). The PC*H*=C*H*P proton resonances were not assigned. They are probably shifted to higher frequency due to shielding effects of the phosphine phenyl rings and hidden by the phenyl proton resonances.

3. Experimental details

The general procedures and apparatus used were the same as described previously [9]. The preparations of the Schiff base ligands and of the acetato- (**1a**, **1b**), chloro- (**2a**, **2b**), bromo- (**3a**, **3b**) and iodo-bridged (**4a**, **4b**) complexes were performed as reported for similar compounds [5,11]. The diphosphines *trans*-dppe and *cis*-dppe were prepared following the literature procedure [26] using the appropriate dichloride, *trans*-ClCH=CHCl or *cis*-ClCH=CHCl; dppb was purchased from Aldrich Chemie.

3.1. Preparation of $[\{\overline{Pd[2,4\text{-}Me_2C_6H_2C(H)=N}Cy]\}_2(\mu\text{-}trans\text{-}Ph_2PCH=CHPPh_2)(Cl)_2]$ (5a)

trans-$Ph_2PCH=CHPPh_2$ (0.028 g, 0.07 mmol) was added to a suspension of the chloro-bridged dimer **2a** (0.05 g, 0.07 mmol) in acetone (*ca.* 5 cm^3). The mixture became clear upon stirring. After 2 h the product precipitated out, was filtered off and dried *in vacuo*. Recrystallisation from dichloromethane/hexane gave the desired product as a white solid.

Complexes **6a**–**10a** and **5b**–**10b** were prepared similarly. Compounds **1b**, **4b** and **10b** were recrystallised from acetone/n-hexane.

3.2. Preparation of $[\{\overline{Pd[2,4\text{-}Me_2C_6H_2C(H)=N}Cy]\}(cis\text{-}Ph_2PCH=CHPPh_2)]PF_6$ (11a)

cis-$Ph_2PCH=CHPPh_2$ (0.028 g, 0.07 mmol) was added to a suspension of the chloro-bridged dimer **2a** (0.025 g, 0.035 mmol) in acetone (*ca.* 5 cm^3). The resulting mixture was stirred for 1 h at room temperature after which NH_4PF_6 (0.011 g, 0.07 mmol) was added. The complex was then precipitated out by addition of water, filtered off, and dried *in vacuo*. Recrystallisation from dichloromethane/hexane gave the final compound as a white solid. Compounds **12a**, **11b** and **12b** were prepared similarly.

3.3. Single-crystal X-ray diffraction analysis

Three-dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 4-circle diffractometer by the ω–2θ scan method. The 3970 independent reflections (of 6907 measured) for which $|F|/\sigma(F) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of 10 azimuthal scans (minimum and maximum transmission coefficients 0.654 and 0.686). The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least squares methods. Hydrogen atoms were included in calculated positions and refined in riding mode with isotropic thermal parameters related to those of the supporting atom. Refinement converged at a final *R* 0.0731 (R_w 0.0602, 370 parameters, mean and maximum shift/e.s.d. 0.019 and 0.079 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron density synthesis showed peaks of −83 and +79 e Å^{-3}. Complex scattering factors were taken from ref. 27 and from the program package SHELXTL [28], as implemented on the Data General DG30 computer, which was used for structure solution and refinement. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.00030(F)^2]$ was used in the latter stages of the refinement. Table 1 lists atomic positional parameters with estimated standard deviations.

3.3.1. Crystal data

p[{Pd[2,4-$Me_2C_6H_2C(H)$=NCy]}$_2$(Cl)$_2$(μ-$Ph_2P(CH_2)_4PPh_2$)] · $4CHCl_3$, $C_{62}H_{72}Cl_{14}N_2P_2Pd_2$; M = 1616.35 (includes solvent molecules); crystallises from chloroform as yellow, elongated blocks; crystal dimensions 0.45 × 0.20 × 0.15 mm. Monoclinic, $a = 1084.1(7)$, $b = 3067.7(28)$, $c = 1181.9(10)$ pm, $\beta = 114.22(6)°$, $U = 3.585(5)$ nm^3; $D_c = 1.497$ g cm^{-3}, $Z = 2$. Space group $P2_1/n$, graphite-monochromated (Mo Kα) radiation, $\lambda = 71.069$ pm, μ(Mo Kα) = 11.03 cm^{-1}, $F(000) = 1635.89$ cm^{-1}.

Tables of structure factors, hydrogen-atom coordinates, etc., are available from the authors.

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