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Complexes of Hybrid Ligands. Synthesis of Mixed-ligand, Phosphino–Alkoxide Complexes of Pd^{2+}: the Crystal and Molecular Structure of the Complex $Ph_2\overline{PCH_2C(CF_3)_2O}PdCl(PPh_2Me)$

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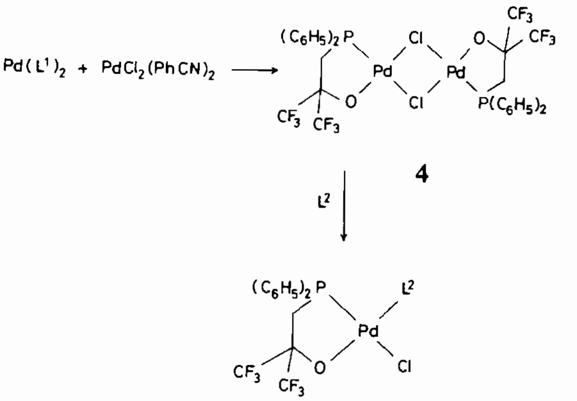
Abstract

The hybrid, bidentate, diarylphosphino–alkoxide ligand $PPh_2CH_2C(CF_3)_2O^-$, L^1, gives the Pd^{2+} bis-complex $Pd(L^1)_2$, from which the chloride-bridged dinuclear complex $[(L^1)Pd(\mu\text{-}Cl)_2Pd(L^1)]$ is made by reaction with $PdCl_2(PhCN)_2$. Cleavage of the dinuclear complex with monodentate ligands L^2 then gives $Pd(L^1)Cl(L^2)$ ($L^2 = PPh_3$, PPh_2Me, $PPhMe_2$, PMe_3, SMe_2, or pyridine); NMR data show that PR_3 is *cis* to the phosphine site in L^1 in these complexes, but SMe_2 or pyridine are probably *trans*.

A complete crystal and molecular structural determination has been made for *cis*-$Pd(L^1)Cl(PPh_2Me)$. Crystals are monoclinic, space group $P2_1/c$, $a = 10.821(1)$, $b = 14.600(1)$, $c = 18.674(2)$ Å, $\beta = 101.25(1)°$, $V = 2893$ Å^3, $Z = 4$. Least-squares refinement on F of 361 variables using 3977 observations converged at a conventional agreement factor $R = 0.025$. The complex is square-planar, with the two phosphines *cis*; the 5-membered chelate ring is in a dissymmetric envelope conformation. The Pd–P bonds differ in length, with that to the unidentate phosphine, 2.259(1) Å, being significantly longer than that to the phosphine on the chelating ligand, 2.231(1) Å.

Introduction

We have previously reported the synthesis of the hybrid diarylphosphino fluoro-alcohol $PPh_2CH_2C(CF_3)_2OH$, HL^1, and its use (in the ionized form) to give neutral, square-planar, complexes $Ni(L^1)_2$ (**1**), $Pd(L^1)_2$ (**2**), and $Pt(L^1)_2$ (**3**) [1]. The hybrid ligand forms five-membered chelate rings, coordinated through phosphine and alkoxide donors, and the conformation is *cis*** for **2** and **3**, while the nickel complex **1** is *trans* in the solid state, but a *cis–trans* mixture in solution. It was clearly of interest to extend the use of this ligand, and in this paper we report a study on a series of Pd^{2+} complexes synthesised by the formation of a dinuclear, chloride-bridged, compound **4** and its cleavage with monodentate ligands:



4

5–10

where $L^2 = PPh_3$ (**5**), PPh_2Me (**6**), $PPhMe_2$ (**7**), PMe_3 (**8**), SMe_2 (**9**), or C_5H_5N (**10**); for **9** and **10**, L^2 appears to be *trans* to phosphino, rather than alkoxide. In view of the small amount of specific structural data available on alkoxides of palladium, we have determined the structure of the PPh_2Me complex, **6**, while NMR data on the series are used to supplement our study of the *trans* influence of the fluorinated alkoxide ligand [2].

Experimental

General techniques and the synthesis of the phosphino-alcohol HL^1 and the bis-complex $Pd(L^1)_2$, **2**, have been described previously [1].

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**Throughout this paper, we use the terms *cis* and *trans* with respect to the orientation of the two phosphine donors, or the phosphine in L^1 and the incoming ligand L^2.

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Preparation of Bridged Complex 4

Bis complex 2 (1.00 g) was dissolved in $CHCl_3$ containing 10% acetone (50 ml) and heated to reflux, then $PdCl_2(PhCN)_2$ (0.46 g) in $CHCl_3$ (25 ml) added dropwise. After refluxing a further 1 h, the solution was concentrated to ~20 ml volume by rotary evaporation and added to 40/60 pet ether (~200 ml). The orange precipitate of $[PdCl(L^1)]_2$, **4**, was removed by filtration and washed with pet ether; yield 91%.

Cleavage Reactions of 4

In each case, a product of analytical purity was obtained in the initial cleavage reaction. With the exception of **6**, where data crystals were prepared, recrystallization was not attempted because of the possibility of inducing disproportionation reactions of the products.

(i) Using PPh_3: Complex **4** (0.10 g) was dissolved in 1/1 ethanol/acetone and PPh_3 (0.062 g, 20% molar excess) in ethanol added with stirring. After removal of solvent by rotary evaporation, the remaining yellow solid was washed with ether to give $Pd(L^1)Cl(PPh_3)$, **5**.

(ii) Using PPh_2Me or $PPhMe_2$: Complex **4** (0.50 g) was dissolved in $CHCl_3$ (50 ml) and the phosphine (20% excess) added by syringe with stirring. Removal of solvent gave an oil, which was taken up in the minimum quantity of CH_2Cl_2 and hexane added to precipitate the yellow solid products $Pd(L^1)Cl(PPh_2Me)$, **6**, and $Pd(L^1)Cl(PPhMe_2)$, **7**, washed with ether.

(iii) Using PMe_3: Complex **4** (0.125 g) and $AgI(PMe_3)$ (0.90 g, 20% excess) were placed in separate arms of a evacuated manifold and dry ethanol condensed onto the former. The $AgI(PMe_3)$ was heated to ~240 °C with cooling of the other arm to 77 K, then the solution allowed to warm up with stirring. Workup as before gave yellow $Pd(L^1)Cl(PMe_3)$, **8**.

(iv) Using SMe_2: Complex **4** (0.135 g) was dissolved in acetone (30 ml) and SMe_2 (0.50 ml) syringed in with stirring. Removal of solvent gave a yellow oil which was taken up in $CHCl_3$ and hexane added to precipitate orange $Pd(L^1)Cl(SMe_2)$, **9**.

(v) Using Pyridine: Complex **4** (0.125 g) was dissolved in $CHCl_3$ (20 ml) and pyridine (24 μl, 20% excess) syringed in with stirring. Workup as for **9** gave light yellow $Pd(L^1)Cl(C_5H_5N)$, **10**.

Characterization

Analytical data on new compounds are available, see 'Supplementary Material'. The mass spectrum of each compound showed a peak corresponding to the molecular ion, with the exception of the SMe_2 complex **9**, where disproportionation to give bis-complex **2** and $PdCl_2(SMe_2)_2$ predominated. Other mononuclear complexes **5**–**10** showed peaks corresponding to the loss of Cl^-, C_6H_5, or ligand L^2, together with some disproportionation. The dinuclear complex **4** gave a strong peak corresponding to the loss of F^- from a CF_3 group, rather than loss of bridging Cl^-. Infrared spectra were in all cases consistent with the proposed structures, with strong absorptions at 1160–1190 cm^{-1} associated with the C–F stretching mode of the ligand. In the dinuclear complex **4**, absorptions at 314 and 253 cm^{-1} were assigned to bridging chloride–metal vibrations [3].

Structural Determination

Collection and Reduction of X-ray Data

Yellow, prismatic crystals of $Pd(L^1)Cl(PPh_2Me)$, **6**, were grown by slow evaporation from solution in acetone.

A photographic analysis gave preliminary cell constants and showed Laue symmetry $2/m$, with systematic absences $h0l$ for l odd, and $0k0$ for k odd. The space group is thus $P2_1/c$, C_{2h}^5, No. 14 [4a]. The crystal density was determined by the flotation method in a mixture of cyclohexane and 1,2-dibromoethane. A crystal of approximate dimensions 0.17 × 0.25 × 0.32 mm was chosen, and the eight crystal faces identified by optical goniometry. It was mounted in a random orientation on an Enraf-Nonius CAD4F diffractometer, and an orientation matrix and cell determined [5a]. Omega scans of reflections 300, 020 and 002 had an average width at half-height of 0.15°, a satisfactory value [6]. Intensity data were recorded at variable scan speeds chosen to optimize counting statistics. Background estimates were made by extending the scans by 25% at each side. Four standard reflections were monitored every 3 h during the 124.4 h required for collection of the 5930 observations; the average decay was 0.5%, so no correction was deemed necessary. Corrections were applied for Lorentz, monochromator and crystal polarization, and background effects using the Structure Determination Package [5b] running on a Digital PDP 11/23+ computer. Standard deviations were based upon counting statistics, and a starting value chosen for p of 0.04 [7]. Of the data collected, 200 were standards. There were 1290 symmetry equivalent reflections; averaging gave $R = 0.018$ on F_o. An absorption correction was then applied to the unaveraged data using the Gaussian method [8], and the corrected data averaged ($R = 0.017$ on F_o), yielding 5085 unique data, of which 3977 with $F_o > 3\sigma(F_o)$ were used for the solution and refinement of the structure. Crystal data and details of data collection are given in Table I.

Solution and Refinement of the Structure

The structure was solved using the heavy atom method and refined by full-matrix least-squares

TABLE I. Crystal Data and Experimental Conditions

Compound	$C_{29}H_{25}ClF_6OP_2Pd$
Formular weight	707.31
Space group	monoclinic $P2_1/c$ No. 14
Unit cell dimensions	a = 10.821(1), b = 14.600(1), c = 18.674(2) A, β = 101.25(1)°
Cell volume (A^3)	2893(1)
Temperature (°C)	19 ± 1
Z, F(000) electrons	4, 1416
Density (g cm^{-3}) (obs.)	1.612(8)
(calc.)	1.62
Crystal faces	{100} {011} and {001}
Crystal volume (mm^3)	0.00954
Radiation, wavelength (A)	Mo Kα, λ = 0.71073
Absorption coefficient (cm^{-1})	8.94
Gaussian grid	16 × 12 × 8
Transmission factors (max.)	0.913
(min.)	0.817
Detector aperture (mm)	
(vert.)	4.0
(horiz.)	5.0 + 0.35 tan θ
Crystal-detector distance (mm)	205
Take-off angle (deg)	2.5
Scan mode	$\theta - 2\theta$ at 0.76 to 2.75 deg min^{-1}
Scan width (deg)	0.70 + 0.35 tan θ
Data collected	$1 < 2\theta < 50$, $0 \leqslant h \leqslant 12$, $-17 \leqslant k \leqslant 0$, $-22 \leqslant l \leqslant 22$
Standard reflections	$2\bar{3}\bar{1}$, 300, $0\bar{2}0$ and 006

TABLE II. Atomic Positional (×10^4) and Thermal (×10^4) Parameters^a

Atom	x	y	z	U_{eq} (A^2)
Pd	−5464(2)	18348(1)	1555(1)	310.9(5)
Cl	−2701(8)	12574(5)	−9687(4)	548(2)
P1	−5729(6)	24792(5)	12357(4)	310(2)
P2	−24328(7)	11206(5)	−102(4)	374(2)
F1	3259(2)	3135(2)	1831(1)	842(8)
F2	3606(2)	2448(2)	894(1)	839(7)
F3	2368(2)	1854(1)	1516(1)	797(7)
F4	1069(2)	4428(2)	41(1)	766(6)
F5	2868(2)	3865(2)	50(1)	766(6)
F6	2521(2)	4606(1)	979(1)	824(7)
O	1087(2)	2560(2)	208(1)	504(6)
C1	596(3)	3396(2)	1245(2)	386(7)
C2	1564(3)	3122(2)	779(2)	390(7)
C3	2715(3)	2649(2)	1255(2)	517(9)
C4	2019(3)	4006(2)	462(2)	522(9)
C5	−2546(3)	67(2)	−539(2)	600(10)
C21	−34(3)	1778(2)	2029(2)	364(7)
C22	175(3)	850(2)	1945(2)	466(8)
C23	665(4)	319(2)	2540(2)	595(10)
C24	940(4)	711(2)	3227(2)	646(10)
C25	729(3)	1621(2)	3323(2)	552(9)
C26	260(3)	2164(2)	2726(2)	451(8)
C31	−1958(2)	3104(2)	1367(2)	356(7)
C32	−2469(3)	3065(2)	1993(2)	484(8)
C33	−3522(3)	3569(3)	2045(2)	638(10)
C34	−4087(3)	4110(3)	1475(2)	678(10)
C35	−3608(3)	4157(2)	848(2)	618(10)
C36	−2543(3)	3659(2)	792(2)	456(8)
C41	−3626(3)	1876(2)	−525(2)	480(8)
C42	−4892(3)	1746(3)	−559(2)	719(11)
C43	−5778(4)	2343(3)	−946(3)	937(13)
C44	−5386(4)	3054(3)	−1319(3)	925(13)
C45	−4142(5)	3198(3)	−1303(3)	912(13)
C46	−3253(4)	2607(3)	−910(2)	632(10)
C51	−3007(3)	770(2)	796(2)	418(8)
C52	−3819(3)	1296(2)	1111(2)	545(9)
C53	−4207(4)	989(3)	1742(2)	728(11)
C54	−3778(4)	188(3)	2063(2)	785(13)
C55	−2943(4)	−333(3)	1758(2)	785(13)
C56	−2557(3)	−53(3)	1128(2)	612(10)

^{a}Positional parameters ×10^5 for Pd, Cl and P atoms. The isotropic equivalent thermal parameter is defined as: $(1/6pi^2)$-$[aB_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

methods. With all non-hydrogen atoms included, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ where the weight w is given by $4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure amplitudes, refinement converged at agreement factors $R_1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o| = 0.037$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.056$. Scattering factors for neutral, non-hydrogen atoms and real dispersion corrections were taken from ref. 5b. All 25 hydrogen atoms were located in a difference Fourier synthesis as the 25 highest peaks, ranging from 0.66(9) to 0.28(9) e Å^{-3}, and included in idealized positions (C–H 0.90 and 0.95 Å for sp^2 and sp^3 hybridization, respectively, thermal parameters 110% of those of the attached atoms). Scattering factors were taken from Stewart *et al.* [9]. With anisotropic thermal parameters for all non-hydrogen atoms, refinement converged at agreement factors $R_1 = 0.025$ and $R_2 = 0.035$ (p = 0.05, 361 variables and 3977 unique data with $F_o > 3\sigma(F_o)$). The largest shift in the final cycle was 0.02σ, and the error on an observation of unit weight 1.01 e. The highest peak in a final difference Fourier synthesis was 0.23(5) e Å^{-3} at (0.305, 0.645, 0.533) and had no chemical significance. An analysis of R_2 in terms of F_o, λ^{-1} sin θ and various combinations of indices showed no unusual trends, and indicated a satisfactory weighting scheme and no sign of secondary extinction. Positional and U(equiv) thermal parameters are given in Table II (see also 'Supplementary Material').

Structure Description

The crystals are built up from independent molecules of the title compound, with a shortest intermolecular non-bonding contact of 2.54 Å between HC34 and HC54 at (x −1, 0.5 − y, 0.5 + z). The closest Pd•••Pd approach is 5.5413(3) Å. A stereo-

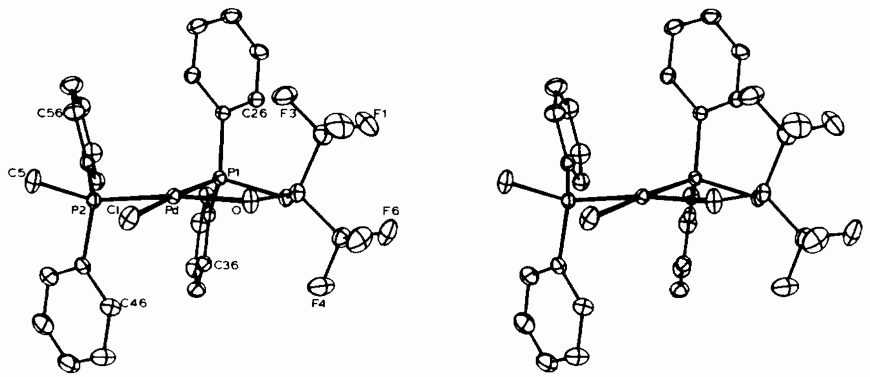

Fig. 1. Stereoscopic ORTEP view of the structure of compound 6.

TABLE III. Selected Bond Distances (Å) and Bond Angles (deg)[a]

Distances					
Pd–Cl	2.335(1)	P1–C21	1.802(3)	O–C2	1.365(3)
Pd–P1	2.231(1)	P1–C31	1.812(3)	C1–C2	1.539(4)
Pd–P2	2.259(1)	P2–C5	1.818(3)	C2–C3	1.545(4)
Pd–O	2.046(2)	P2–C41	1.823(3)	C2–C4	1.540(4)
P1–C1	1.840(3)	P2–C51	1.810(3)		
Angles					
Cl–Pd–P1	172.58(3)	C1–P1–C21	107.1(1)	Pd–O–C2	122.7(2)
Cl–Pd–P2	88.91(3)	C1–P1–C31	102.6(1)	P1–C1–C2	110.3(2)
Cl–Pd–O	88.23(6)	C21–P1–C31	108.5(1)	O–C2–C1	113.8(2)
P1–Pd–P2	98.51(3)	Pd–P2–C5	115.4(1)	O–C2–C3	108.7(2)
P1–Pd–O	84.36(6)	Pd–P2–C41	108.7(1)	O–C2–C4	107.7(2)
P2–Pd–O	173.92(6)	Pd–P2–C51	117.65(9)	C1–C2–C3	110.6(2)
Pd–P1–C1	100.7(1)	C5–P2–C41	105.0(1)	C1–C2–C4	107.6(2)
Pd–P1–C21	116.43(9)	C5–P2–C51	102.4(2)	C3–C2–C4	108.3(2)
Pd–P1–C31	119.44(9)	C41–P2–C51	106.7(1)		

[a] Numbers in parentheses in this and other Tables are estimated standard deviations in the least significant digits.

view of the molecule showing the atom numbering scheme is given in Fig. 1, and selected bond distances and angles are presented in Table III.

The coordination geometry at the palladium atom is square planar, with *cis* phosphorus atoms. Some weighted least-squares planes are given in Supplementary Table S-V; the largest deviation from planarity is that of 0.065(2) Å by the oxygen atom. The five-membered chelate ring adopts a dissymmetric envelope conformation, with the two carbon atoms displaced by 0.518(3) and 0.113(3) Å from the Pd,O,P plane. In contrast to the Ni complex of the ligand L^1 [1], the two CF_3 groups are equally disposed with respect to the chelate ring plane. Dimensions within these groups are normal, with an average C–CF_3 distance of 1.543(3) Å, and C–F distance of 1.327(3) Å, similar to those we have found in similar fluorinated alkoxides [1, 10], and the C–O distance of 1.365(3) Å is also unexceptionable for a compound of this type.

Distances from the metal atom to the two phosphine ligands are significantly different, with the Pd–P bond within the chelate ring being shorter than that to PPh_2Me. The latter value, 2.259(1) Å, agrees well with the value of 2.260(2) Å in *cis*-$PdCl_2(PPhMe_2)_2$ [11]. Our value of 2.231(1) Å for the Pd–P bond within the five-membered ring is consistent with previous values; for example, in *cis*-bis(diphenylphosphinoacetato)palladium(II) the Pd–P bonds are 2.236(2) and 2.234(2) Å [12], while in the compound $[Pd\{PPh_2CH{=}C(CF_3)O\}Cl(PPh_2OEt)]$ the Pd–P bond in the chelate ring is 2.246(2) Å [13].

Although very few alkoxides of palladium have been reported, some comparison of Pd–O bond lengths with analogous systems may be made. The perfluoropinacol derivative $[Pd\{OC(CF_3)_2C(CF_3)_2O\}(PPh_3)_2]$ is known [14]; its Pd–O bond lengths [15] of 2.043 and 2.016 Å in a five-membered chelate ring with phosphines *trans* to oxygen are close to our value of 2.046(2) Å. In the tetrachlorocatechol com-

TABLE IV. NMR Data on Complexes[a]

Complex	CH_2		CF_3		CH_3[b]		P_A[c]		P_B[c]		$^2J(P_A,P_B)$ (Hz)[e]
	δ (ppm)	$^2J(P,H)$ (Hz)	δ (ppm)	$^4J(P,F)$ (Hz)	δ (ppm)	$^2J(P,H)$ (Hz)	δ (ppm)	$\Delta\delta$[d] (ppm)	δ (ppm)	$\Delta\delta$[d] (ppm)	
2 $Pd(L^1)_2$	3.47	12.5	−76.6	3.7			40.6	74.2			
4 $[Pd(L^1)Cl]_2$	3.5	13	−76.1	4			47.3	81.0			
5 $Pd(L^1)Cl(PPh_3)$	3.25	11.8	−77.1	3.5			50.1	83.7	26.52	32.4	5.3
6 $Pd(L^1)Cl(PPh_2Me)$	3.27	12.1	−77.2	2.8	1.92	11.1[f]	49.2	82.8	12.20	40.2	6.1
7 $Pd(L^1)Cl(PPhMe_2)$	3.25	12.0	−77.3	3.5	1.59	11.4[f]	48.8	82.4	−1.13	45.9	8.5
8 $Pd(L^1)Cl(PMe_3)$	3.32	12.1	−77.2	3.6	1.33	12.1	49.3	82.9	−6.96	55.0	8.4
9 $Pd(L^1)Cl(SMe_2)$	3.21	12.4	−77.2	4.8	2.39		43.0	76.6			
10 $Pd(L^1)Cl(pyr)$	3.30	12.4	−77.0	3.6	[g]		42.5	76.1			

[a] Ambient temperature; solvent $CDCl_3$ or CD_2Cl_2. [b] CH_3–P or CH_3–S group. [c] P_A is in the L^1 ligand; P_B is in the additional PR_3 ligand. [d] The coordination shift; $\Delta\delta = \delta$(coord L^1 anion) − δ(free HL^1). [e] Absolute values. [f] $^4J(P,H) = 1.3$ Hz. [g] Pyridine ^1H signals at 8.80–8.85 ppm.

plex $[Pd(C_6Cl_4O_2)(PPh_3)_2]$, Pd–O bonds (again *trans* to phosphine) are 2.028(5) and 2.038(5) Å [16]. Shorter Pd–O bonds are found in delocalised, cyclic, acac chelate rings, of which an interesting example is the dinuclear complex $[(F_6acac)Pd(\mu\text{-}OMe)_2Pd(F_6acac)]$ [17]. The four bonds from palladium to hexafluoroacetylacetonyl oxygen average 1.993(7) Å, while the four bonds to bridging methoxide average 1.996(7) Å. In all of the above systems, the bond is shorter than the values of 2.074(5) and 2.078(5) Å found in the phosphino–acetato complex [12], consistent with the more ionic character of the Pd–O bond to be expected in the latter.

Discussion

The synthetic approach outlined above for the preparation of mixed-ligand complexes of palladium(II) was generally successful. The synthesis of chloride-bridged, dinuclear complexes by the reaction of $PdCl_2(PhCN)_2$ with other palladium(II) derivatives is an established route, typically used to prepare phosphine complexes $[(PR_3)ClPd(\mu\text{-}Cl)_2PdCl(PR_3)]$ [18]. The geometry of such complexes is invariably *trans* [19], and we therefore show the bidentate L^1 groups arranged with the phosphino functions *trans* in **4**, although its geometry has not been established. Of the many known chloro-bridged dinuclear palladium complexes containing bidentate terminal ligands, the great majority contain metal–carbon bonds, and of those that do not, none has a phosphorus atom in the chelate ring. They are generally prepared by direct reaction of the bidentate ligand with $PdCl_2$ [20], and we do not know of a precedent for the displacement of a bidentate ligand from a bis-chelate in the formation of a chloride-bridged, dinuclear, species. The considerable stability of **4** is further shown by its passage intact through the mass spectrometer.

Using neutral ligands L^2, the dinuclear complex **4** was then cleaved to give complexes $Pd(L^1)Cl(L^2)$, where $L^2 = PR_3$, SMe_2, or pyridine, and *cis* or *trans* geometry is possible in each case. Early studies [21] had suggested that bis(phosphine) complexes of Pd^{2+} were invariably *trans*, but Grim and Keiter [22] subsequently used ^{31}P NMR to show examples of *cis-trans* isomerism in complexes $PdCl_2(PPh_nR_{3-n})_2$ (R = alkyl; $n = 0$–3). Similar NMR studies on our new complexes show that all four phosphine cleavage products are *cis*, and data are given in Table IV.

It is well-established that, in bis(phosphine) complexes of palladium(II), phosphorus–phosphorus coupling in *trans* geometry is much greater than in *cis*; for example, the values of $^2J(P,P')$ in *cis*- and *trans*-$PdCl_2(PMe_3)_2$ are −8.0 and +610 Hz respectively [23]. The small values of $|^2J|$ found in **5**–**8** therefore indicate *cis* geometry in each case, but the more surprising observation is that the *trans* isomer is never observed. In contrast, in solution studies of *cis*–*trans* isomerism in $PdCl_2(PR_3)_2$ by Grim and Keiter [22] and by Redfield and Nelson [24], no instance was found of a complex that was exclusively *cis*. We have previously shown [1] that the bis-complexes $Pd(L^1)_2$ and $Pt(L^1)_2$ are *cis* in solution, while $Ni(L^1)_2$ is *trans* in the solid crystal, but a solvent-dependent, *cis*–*trans* mixture in solution, and this difference we ascribed to the greater importance of the antisymbiotic effect [27] in complexes of the softer metal ions. In complexes **5**–**8**, it appears that this effect is stabilising the complexes in a configuration with the two soft phosphine donors mutually *cis*. While steric effects normally disfavor this geometry, because of repulsion between bulky phosphines, this is markedly reduced in the present series because of the small bite angle of the chelated ligand L^1. The P(1)–Pd–O angle in **6** is only 84.36(6)°, which relieves the steric interaction between the phosphines as the P(1)–Pd–P(2) angle increases to 98.51(3)°.

In complexes **5–8**, the coordination shift, $\Delta\delta$, of the monodentate phosphine $PPh_{3-n}Me_n$ increases steadily as n increases, and there is a parallel, but smaller, increase in $^2J(P_A, P_B)$. This accords with the usual trend that $\Delta\delta$ increases with increasing σ-donor power in the phosphine ligand. A parallel effect is reported for complexes *cis*-$PdCl_2(PPh_{3-n}Me_n)$, where $\Delta\delta$ is 47.2 [22], 53.3 [22] and 60.1 [26] ppm for $n = 0$, 1, and 2 respectively. The new complexes also show the linear correlation between $\Delta\delta$ and the chemical shift of the free phosphine which has been noted previously [27].

In each case where similar complexes *cis*-$PdCl_2(PR_3)_2$ and *cis*-$Pd(L^1)Cl(PR_3)$ can be compared for the same phosphine, the value of $\Delta\delta$ is 5–7 ppm less in the latter. This is consistent with our previous observation that the *trans*-influence of fluorinated alkoxide is greater than that of chloride [2]. The same trend is seen in the coordination shift of P_A, the phosphine in ligand L^1, which is 74.2 ppm in *cis*-$Pd(L^1)_2$ (alkoxide *trans*), 81.0 ppm in **4** (bridging Cl^- *trans*) and 82–84 ppm in **5–8** (Cl^- *trans*).

It is more difficult to assign geometry to the complexes $Pd(L^1)Cl(SMe_2)$ (**9**) and $Pd(L^1)Cl(pyr)$ (**10**), because of the absence of $^3J(P_A,P_B)$. However, they have values of $\Delta\delta$ of 76.6 and 76.1 ppm for the coordinated ligand phosphine, significantly lower than in **5–8**, and strongly suggesting that chloride has been replaced by a ligand of stronger *trans* influence in the site *trans* to phosphine. Since the *trans* influence of thioether and pyridine is known to be greater than that of Cl^- (but less than that of PR_3) [28], this is consistent with a geometry for **9** and **10** in which L^2 is *trans* to ligand phosphine and Cl^- is *cis*. The difference between these two complexes and **5–8** is due to the greater importance of the antisymbiotic effect in the latter; when this is reduced, steric effects predominate. Similarly, the complexes $PdCl_2(PR_3)(L)$, where L is a nitrogen donor, are exclusively *trans* [29].

Conclusions

This work has demonstrated a versatile new approach to the synthesis of mixed-ligand complexes of palladium containing one bidentate ligand in conjunction with chloride and a unidentate ligand. Steric effects in systems of this type are reduced by the small bite angle dictated by a five-membered ring, and antisymbiotic influences then predominate in determining geometry. The palladium–oxygen bond length in alkoxides increases steadily with the ionic character of the bond.

Supplementary Material

Tables of analytical data, hydrogen atom parameters, anisotropic thermal parameters, root-mean-square amplitudes of vibration, supplementary dimensions, weighted least-squares planes and torsion angles have been deposited with the Editor-in-Chief.

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