Co-ordination Chemistry of Higher Oxidation States. Part 4.[1] Palladium(IV) Complexes of Nitrogen, Phosphorus, and Arsenic Donor Ligands. Crystal and Molecular Structures of $[Pd(bipy)Cl_4]$ and $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$ †

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Octahedral palladium(IV) complexes $[Pd(L\text{–}L)Cl_4]$ [L–L = $Me_2NCH_2CH_2NMe_2$, 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), $Ph_2PCH_2CH_2PPh_2$, $Me_2PCH_2CH_2PMe_2$, $Ph_2AsCH_2CH_2AsPh_2$, $o\text{-}C_6H_4(AsMe_2)_2$, and $Me_2As(CH_2)_3AsMe_2$] have been prepared by chlorine oxidation of $[Pd(L\text{–}L)Cl_2]$. The corresponding $[Pd(L\text{–}L)Br_4]$ [L–L = $Me_2PCH_2CH_2PMe_2$, $o\text{-}C_6H_4(AsMe_2)_2$, and $Me_2As(CH_2)_3AsMe_2$] have been obtained, but the $[Pd(L\text{–}L)Br_2]$ (L–L = N-donors above, $Ph_2PCH_2CH_2PPh_2$ and $Ph_2AsCH_2CH_2AsPh_2$) were not oxidised by bromine. The complexes $[Pd(L\text{–}L)X_4]$ (X = Cl or Br) reductively eliminate X_2 on gentle heating. Chlorine oxidation of $Pd(L\text{–}L)_2Cl_2$ gave $Pd(L\text{–}L)_2Cl_4$ for L–L = $Me_2PCH_2CH_2PMe_2$ and $o\text{-}C_6H_4(PMe_2)_2$, but gave $[Pd(L\text{–}L)Cl_4]$ for L–L = $Ph_2PCH_2CH_2PPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, and $o\text{-}C_6H_4(AsMe_2)_2$. The complexes *trans*-$[Pd(L\text{–}L)_2X_2][ClO_4]_2$ [X = Cl or Br; L–L = $Me_2PCH_2CH_2PMe_2$, $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, or $o\text{-}C_6H_4(PMe_2)(AsMe_2)$] were obtained by HNO_3–HX oxidation of $Pd(L\text{–}L)_2X_2$ followed by addition of $HClO_4$. Infrared, electronic, and ^1H n.m.r. spectra are reported for the complexes. Attempts to prepare Pd^{IV} complexes with multidentate phosphines and arsines are described.
The structures of the title compounds have been established by single-crystal *X*-ray studies. The complex $[Pd(bipy)Cl_4]$ is monoclinic, space group *Pn*, $a = 12.241(5)$, $b = 6.720(2)$, $c = 8.120(9)$ Å, $\beta = 104.37(5)°$, and $Z = 2$. 1 383 Observed reflections $[\sigma(F) \leqslant 2F]$ refined *R* to 0.023. The crystal contains discrete octahedral molecules [Pd–Cl 2.289(1)—2.310(1), Pd–N 2.037(4), 2.044(4) Å]. The complex $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$ is triclinic, space group $P\bar{1}$, $a = 7.903(3)$, $b = 10.670(3)$, $c = 10.141(2)$ Å, $\alpha = 110.50(2)$, $\beta = 91.75(3)$, $\gamma = 107.31(3)°$, and $Z = 1$. 1 680 Observed reflections $[\sigma(F) \leqslant 3F]$ refined *R* to 0.039. The crystal contains *trans* octahedral cations [Pd–Cl 2.302(2), Pd–As 2.452(1), 2.455(1)] and perchlorate ions [Cl–O 1.42(1) Å].

Palladium(IV) is a comparatively rare oxidation state best established in PdF_4, PdO_2, and in complexes with anionic ligands, for example in $[PdX_6]^{2-}$ (X = F, Cl, or Br), $[Pd(S_2CNR_2)_3]^+$ and $[Pd(S_2CNR_2)_2X_2]$ ($S_2CNR_2^-$ = dithiocarbamate).[2] Complexes with neutral ligands are less stable and few have been thoroughly characterised. Substituted halogeno-anions $[PdLX_5]^-$ (L = PPr^n_3, $AsEt_3$, SMe_2, $SeMe_2$, NMe_3, or C_5H_5N; X = Cl or Br) have recently been prepared[1] by halogen oxidation of the corresponding $[PdLX_3]^-$, but neutral analogues $[PdL_2X_4]$ can generally only be isolated when L = amine.

Complexes with several bidentate ligands have been described including those of propylenediamine,[3] 2,2′-bipyridyl (bipy),[4] 1,10-phenanthroline (phen),[5] and $o\text{-}C_6H_4(PMe_2)_2$,[6] but only the complexes $[Pd(L\text{–}L)_2X_2][ClO_4]_2$ [L–L = $o\text{-}C_6H_4(AsMe_2)_2$ [7] or $H_2NCH_2CH_2NH_2$; [8,9] X = Cl or Br] have been studied in any detail. The single reported complex of a polydentate ligand is $[Pd\{As(C_6H_4AsPh_2\text{-}o)_3\}Cl_2]Cl_2$.[10] We have shown [11] that Pd^{II}-dithioether complexes cannot be oxidised to Pd^{IV} by a range of oxidants. Here we describe systematic attempts to prepare Pd^{IV} complexes of bi- and poly-dentate ligands, their spectroscopic characterisation, and single-crystal *X*-ray studies of examples of the two main structural types. An account of the Pt^{IV} analogues has been published.[12] There is also growing evidence [13,14] that organopalladium(IV) intermediates are involved in the coupling of alkyl halides mediated by complexes such as $[Pd(Ph_2PCH_2CH_2PPh_2)Me_2]$ or $[Pd(PPh_2Me)_2Me_2]$.

Results

$[Pd(L\text{–}L)X_4]$ (L–L = *Bidentate Ligand*, X = Cl *or* Br).—Treatment of finely powdered $[Pd(L\text{–}L)Cl_2]$ suspended in dry carbon tetrachloride with a small excess of chlorine produced orange-red $[Pd(L\text{–}L)Cl_4]$ complexes (Table 1). Similar treatment of the distibine compounds $[Pd(L'\text{–}L')Cl_2]$ [L′–L′ = $o\text{-}C_6H_4(SbPh_2)_2$ or $Me_2SbCH_2CH_2CH_2SbMe_2$] resulted in chlorination of the stibines to the antimony(V) dichlorides, identified by their characteristic i.r. and ^1H n.m.r. spectra.[15] Nitrosyl chloride (which oxidises some Ni^{II} complexes to Ni^{III}, where chlorine causes decomposition) [16] was also investigated as an oxidant, but produced similar results to Cl_2 with all the palladium(II) complexes examined. Bromine oxidation of $[Pd(L\text{–}L)Br_2]$ [L–L = $Me_2PCH_2CH_2PMe_2$, $o\text{-}C_6H_4(AsMe_2)_2$, or $Me_2AsCH_2CH_2CH_2AsMe_2$] produced red-brown $[Pd(L\text{–}L)Br_4]$, but when L–L = $Me_2NCH_2CH_2NMe_2$, bipy, phen, $Ph_2PCH_2CH_2PPh_2$, or *cis*-$Ph_2PCH{=}CHPPh_2$, no oxidation occurred, the unchanged palladium(II) complexes being recovered even after overnight treatment with a large excess of bromine. Nitrosyl bromide and nitric acid also failed to bring about oxidation of the latter series of complexes.

The palladium(IV) complexes of N-donor ligands are stable in sealed tubes, but those of phosphorus and arsenic donor ligands decompose slowly at room temperature, although they can be stored for several months at −20 °C without significant deterioration. On moderate heating the $[Pd(L\text{–}L)X_4]$ complexes decompose, the weight losses (Experimental section)

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† (2,2′-Bipyridyl)tetrachloropalladium(IV) and *trans*-dichlorobis[*o*-phenylenebis(dimethylarsine)]palladium(IV) diperchlorate.

Supplementary data available (No. SUP 23435, 24 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Analytical and physical data for the [Pd(L-L)X_4] complexes

	Colour	Analysis (%)[a] C	H	X	ν(Pd-X)/cm^{-1}	10^{-3} $E_{max.}$[b]/cm^{-1}	Λ_M[c]
(*a*) [Pd(L-L)Cl_4]							
L-L = $Me_2NCH_2CH_2NMe_2$[d]	Red	20.1 (19.8)	4.5 (4.4)	38.7 (38.9)	356m, 342 (sh), 336s	19.6 (vbr)	20
bipy[e]	Orange-red	29.2 (29.7)	2.0 (2.0)	34.7 (35.1)	363m (sh), 357s, 352m (sh)	32.9, 27.5, 23.1, 21.1	—
phen[f]	Dark orange	33.2 (33.6)	2.0 (1.9)	33.1 (33.1)	359br, 342m	24.9, 21.0	—
$Me_2PCH_2CH_2PMe_2$	Orange	18.2 (18.1)	4.1 (4.1)	35.6 (35.6)	345m, 328s, 320 (sh)	31.9, 27.2, 21.3	17
$Ph_2PCH_2CH_2PPh_2$	Orange-red	48.0 (48.3)	4.1 (3.7)	21.5 (21.9)	349m (sh), 341s, 330 (sh), 317w	27.3, 24.7, 20.5	—
$Me_2AsCH_2CH_2CH_2AsMe_2$	Dark orange	17.2 (16.8)	3.8 (3.6)	27.6 (28.3)	344 (sh), 327s, 318s, 300 (sh)	34.9, 28.4, 20.3	—
o-$C_6H_4(AsMe_2)_2$	Orange	22.5 (22.5)	3.0 (3.0)	21.4 (21.5)	347 (sh), 337s, 318s	34.5, 27.3, 24.5, 20.2	—
$Ph_2AsCH_2CH_2AsPh_2$	Orange	42.9 (42.5)	3.3 (3.3)	19.2 (19.3)	341 (sh), 332s, 309m	27.6, 19.8	—
(*b*) [Pd(L-L)Br_4]							
L-L = $Me_2PCH_2CH_2PMe_2$	Red-brown	12.8 (12.5)	3.0 (2.8)	56.1 (55.5)	244m, 188s, 177 (sh)	30.7, 24.7, 19.8	—
$Me_2AsCH_2CH_2CH_2AsMe_2$	Red-brown	11.9 (12.4)	2.9 (2.7)	48.0 (47.1)	248s, 196 (sh), 180s	26.6, 23.7, 19.9	—
o-$C_6H_4(AsMe_2)_2$	Dark red	16.9 (16.9)	2.2 (2.3)	44.2 (44.9)	220m (sh), 190s, 180s	21.2, 18.7	—

[a] Calculated values are given in parentheses. [b] Diffuse reflectance, diluted with $BaSO_4$, range 35 × 10^3—15 × 10^3 cm^{-1}. [c] In Ω^{-1} cm^2 mol^{-1}. CH_3CN solutions (10^{-3} mol dm^{-3}); 1 : 1 electrolytes have Λ_M = 120—160 Ω^{-1} cm^2 mol^{-1} (W. J. Geary, *Coord. Chem. Rev.*, 1971, 7, 81). [d] N = 7.9 (7.7)%. [e] N = 6.8 (6.9)%. [f] N = 6.6 (6.5)%.

Table 2. Analytical and spectroscopic data for *trans*-[Pd(L-L)$_2X_2$][ClO_4]$_2$ and Pd(L-L)$_2X_4$ (X = Cl or Br)

Complex	Colour	Analysis (%)[a] C	H	X	Λ_M[b]/ Ω^{-1} cm^2 mol^{-1}	10^{-3} $E_{max.}$[c]/ cm^{-1}	10^{-3} $E_{max.}$ (ε_{mol})/cm^{-1}[d]	^{1}H n.m.r.[e]/δ/p.p.m.
[Pd($Me_2PCH_2CH_2PMe_2$)$_2Cl_2$][ClO_4]$_2$	Orange-red	21.4 (21.3)	4.7 (4.8)	10.5 (10.5)	202	27.8, 21.8	23.2 (3 106)	1.7 (t), 6 Hz [1.75 (t), 8 Hz]
Pd($Me_2PCH_2CH_2PMe_2$)$_2Cl_4$	Orange-red	25.8 (26.3)	5.9 (5.9)	26.0 (25.9)	decomp.	33.3, 27.0 (sh), 21.7	—	1.7 (t)
[Pd($Me_2PCH_2CH_2PMe_2$)$_2Br_2$][ClO_4]$_2$	Dark red	19.2 (18.9)	4.2 (4.2)	21.1 (20.9)	211	27.3, 20.1	21.6 (1 750)	2.12 (t), 6 Hz [1.78 (t), 8 Hz]
[Pd{*o*-$C_6H_4(PMe_2)_2$}$_2Cl_2$][ClO_4]$_2$	Orange	31.0 (31.4)	4.2 (4.2)	9.2 (9.2)	180	27.2, 23.8	24.1 (4 500)	1.9 (t), 5 Hz [1.85 (t), 12 Hz]
Pd[*o*-$C_6H_4(PMe_2)_2$]$_2Cl_4$	Deep orange	37.6 (37.3)	5.0 (5.0)	21.4 (22.0)	decomp.	30.3, 24.0	—	1.9 (t)
[Pd{*o*-$C_6H_4(PMe_2)_2$}$_2Br_2$][ClO_4]$_2$	Red	27.7 (27.9)	3.8 (3.7)	18.0 (18.6)	182	26.5, 20.2	21.9 (1 520)	1.95 (t), 5 Hz [1.9 (t), 12 Hz]
[Pd{*o*-$C_6H_4(PMe_2)(AsMe_2)$}$_2Cl_2$][ClO_4]$_2$	Orange	27.5 (27.9)	3.9 (3.8)	7.5 (8.5)	199	27.7, 22.7	23.5 (2 200)	*f* [*f*, *g*]
[Pd{*o*-$C_6H_4(PMe_2)(AsMe_2)$}$_2Br_2$][ClO_4]$_2$	Red	25.6 (25.3)	3.4 (3.4)	16.4 (16.8)	189	27.0, 21.0	21.3 (2 075)	*f* [*f*, *g*]
[Pd{*o*-$C_6H_4(AsMe_2)_2$}$_2Cl_2$][ClO_4]$_2$	Orange	25.5 (25.3)	3.4 (3.4)	7.8 (7.5)	217	27.8, 23.1	22.5 (2 300)	2.15 (s) [1.9 (s)][g]
[Pd{*o*-$C_6H_4(AsMe_2)_2$}$_2Br_2$][ClO_4]$_2$	Red	23.0 (23.2)	3.2 (3.1)	15.0 (15.4)	194	26.6, 20.2	20.7 (1 400)	1.97 (s) [2.1 (s)][g]
[Pd($H_2NCH_2CH_2NH_2$)$_2Cl_2$][ClO_4]$_2$	Yellow-green				—	—	24.6 (174)[h]	
[Pd($H_2NCH_2CH_2NH_2$)$_2Br_2$]Br_2·2HBr	Orange				—	—	23.8 (810)[h]	

[a] Calculated values in parentheses. [b] Freshly prepared 10^{-3} mol dm^{-3} solution in $MeNO_2$; 2 : 1 electrolytes have Λ_M 120—200 Ω^{-1} cm^2 mol^{-1} in this solvent. [c] Diffuse reflectance, diluted with $BaSO_4$, range 30 × 10^3—15 × 10^3 cm^{-1}. [d] CH_3CN solution low-energy band only. [e] Freshly prepared solution in CD_3CN, except where stated otherwise. Data in parentheses refer to Pd^{II} analogues; coupling constants given are ^2J(PH). [f] Complex pattern due to overlap of Me_2P- and Me_2As- resonances *ca.* 1.8—2.00 p.p.m. [g] $(CD_3)_2SO$ solution. [h] Data from ref. 9, solutions in 0.1 mol dm^{-3} $HClO_4$.

monitored by t.g.a. (dynamic argon atmosphere) corresponding to those expected for reductive elimination of X_2. Examination of the residues by analysis and i.r. spectroscopy showed them to be predominantly the corresponding $[Pd(L-L)X_2]$ complexes. In the cases of complexes of the N-donor ligands,* and the alkyl-substituted diphosphines and diarsines, the reductive elimination is essentially clean, but for the phenyl-substituted diphosphine and diarsine compounds, some oxidation of the neutral ligand occurs.

The $[Pd(L-L)X_4]$ complexes are only slightly soluble in halogenocarbons and acetonitrile, and are decomposed by dimethyl sulphoxide. The complexes $[Pd(L-L)X_4]$ (L–L = diphosphine or diarsine) decompose rapidly in CH_2Cl_2 solution, to $[Pd(L-L)X_2]$, oxidised ligand, and other unidentified products. Attempts to obtain ^{1}H n.m.r. spectra by *in situ* oxidation (X_2) of $[Pd(L-L)X_2]$ failed due to rapid precipitation of $[Pd(L-L)X_4]$.

The far-i.r. spectra of the $[Pd(L-L)Cl_4]$ complexes (Table 1) exhibit three or four overlapping bands assigned as ν(Pd–Cl), consistent with the expected *cis* pseudo-octahedral structures (theory predicts four i.r.-active Pd–Cl stretches, $2A_1 + B_1 + B_2$). This structure has been confirmed for $[Pd(bipy)Cl_4]$ by an *X*-ray study (see below), and from the similarity of the i.r. spectra, clearly pertains for all the $[Pd(L-L)X_4]$ complexes. Comparison of the i.r. spectra of these complexes with those of the $[Pt(L-L)X_4]$ analogues [12] is interesting. For the Pt^{IV} complexes the vibrations of the axial halides ($A_1 + B_2$) occur at higher frequencies than those of the in-plane PtX_2 unit, whilst for the Pd^{IV} complexes, the vibrations span a much smaller frequency range. We [1] noted a similar difference in the spectra of $[PtLX_5]^-$ and $[PdLX_5]^-$ ions, and ascribe it to the reduced *trans*-influence of the neutral ligand L–L on the much harder Pd^{IV} ion.

The electronic spectra of these complexes are mainly composed of broad intense charge-transfer bands, although the rather weaker absorptions (*ca.* $\leqslant 20\,000$ cm^{-1}) may be essentially *d–d* in character.

$[Pd(L-L)_2Cl_2]^{2+}$ (L–L = *Bidentate Ligand*, X = Cl *or* Br).—Chlorine oxidation of $Pd(L-L)_2Cl_2$ [L–L = $Ph_2PCH_2CH_2PPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, or o-$C_6H_4(AsMe_2)_2$] in CCl_4 suspension produced $[Pd(L-L)Cl_4]$ and oxidised ligand. Only for complexes of $Me_2PCH_2CH_2PMe_2$ and o-$C_6H_4(PMe_2)_2$ was it possible to produce $Pd(L-L)_2Cl_4$. Similar displacement of one bidentate ligand occurs on chlorination of platinum(II) $Pt(L-L)_2Cl_2$ complexes of aryl diarsines, but $Pt(L-L)_2Cl_4$ were isolated [12] with $Ph_2PCH_2CH_2PPh_2$, o-$C_6H_4(AsMe_2)_2$, and $Me_2PCH_2CH_2PMe_2$. A more successful approach [6,7] to $[Pd(L-L)_2X_2]^{2+}$ ions was oxidation of $Pd(L-L)_2X_2$ with a mixture of concentrated nitric acid–concentrated HX (X = Cl or Br) at 0 °C and after addition of excess 70% perchloric acid (**CAUTION**: potential explosion hazard), $[Pd(L-L)_2X_2][ClO_4]_2$ [L–L = o-$C_6H_4(AsMe_2)_2$, o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(PMe_2)(AsMe_2)$, and $Me_2PCH_2CH_2PMe_2$] (Table 2) were isolated. Curiously, $[Pd(Ph_2PCH_2CH_2PPh_2)_2]Y_2$ (Y = ClO_4 or Cl) were not oxidised by this acid mixture. Bis(ligand)-palladium(II) complexes cannot be prepared in the presence of halide ions for $Me_2NCH_2CH_2NMe_2$, bipy, or phen,[18] but Mason's data [9] on $[Pd(H_2NCH_2CH_2NH_2)_2X_2]^{2+}$ have been included in Table 2 for comparison.

The $[Pd(L-L)_2X_2][ClO_4]_2$ complexes decompose slowly in the solid state, and more rapidly in solution, with the diphosphine chloro-complexes the most stable, and $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Br_2][ClO_4]_2$ the least. In freshly prepared 10^{-3} mol dm^{-3} nitromethane solution the diperchlorate complexes are 1 : 2 electrolytes, but the $Pd(L-L)_2Cl_4$ complexes decompose rapidly in solution and do not give reproducible conductivities [*cf.* $Pt(L-L)_2Cl_4$].[12] The cation in $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$ was shown to have a *trans* geometry by an *X*-ray study (see below), and similar structures are assigned to all the complexes based upon the ^{1}H n.m.r. spectra (Table 2). The diarsine complexes exhibit single As–Me resonances, and the diphosphines broader ' triplet ' P–Me resonances consistent with local D_{4h} symmetry for the cations. The far-i.r. spectra of the complexes show a number of medium intensity absorptions attributable to the neutral ligands, but the expected $B_{1u}(PdX_2)$ vibrations have not been identified. The i.r. spectra of the corresponding pairs $[Pd(diphosphine)_2Cl_2][ClO_4]_2$ and $Pd(diphosphine)_2Cl_4$ are identical (except for the ClO_4^- ion absorptions), confirming the latter should be formulated *trans*-$[Pd(diphosphine)_2Cl_2]Cl_2$.

The electronic spectra of the $[Pd(L-L)_2X_2]^{2+}$ cations are similar in the solid state and in CH_3CN solution (Table 2) consisting of one clearly defined absorption in the range (25—20) × 10^3 cm^{-1}, and more intense broad bands at $>26 \times 10^3$ cm^{-1}. The latter are clearly charge-transfer bands, but the lower energy band is tentatively assigned as the first spin-allowed *d–d* band $^1A_1 \longrightarrow {}^1E$ of the d^6 cations. On this basis the complexes exhibit the spectrochemical trends Cl > Br, and $H_2NCH_2CH_2NH_2 > o\text{-}C_6H_4(PMe_2)_2 > Me_2PCH_2CH_2PMe_2 > o\text{-}C_6H_4(AsMe_2)_2$. The high position of ethylenediamine is not unexpected for a hard metal ion and has been observed previously, *e.g.* with Cr^{III},[6,19] whereas in lower oxidation states and with softer metals the P and As donors exert a stronger ligand field, probably due to the greater relative importance of the π-acceptor component in their bonding. The absorption coefficients are very high for *d–d* bands, and this can be associated with ' intensity borrowing '[20] from the nearby Laporte allowed bands.

Complexes of Multidentate Ligands.—Oxidation of the palladium(II) chloro-complexes of $PhP(CH_2CH_2PPh_2)_2$, $P(CH_2CH_2PPh_2)_3$, $MeAs(CH_2CH_2CH_2AsMe_2)_2$, and $As(CH_2CH_2CH_2AsMe_2)_3$, with either chlorine or concentrated HNO_3–$HClO_4$, under a variety of conditions, produced materials of variable composition, all of which showed evidence in the i.r. spectra for oxidation of the neutral ligand. This is in contrast with the corresponding platinum complexes,[12] where *mer*-$[Pt(tridentate)Cl_3]^+$ and $[Pt(tetradentate)Cl_2]^{2+}$ have been isolated. In the case of $[Pd\{PhP(CH_2CH_2PPh_2)_2\}Cl]Cl$, chlorine oxidation in CCl_4 suspension produced an orange solid of composition $Pd[PhP(CH_2CH_2PPh_2)_2]Cl_4$, which showed only a weak peak at 1 177 cm^{-1} due to a small amount of phosphine oxide,[21] and subsequent displacement of the ligand (Experimental section) confirmed it was unchanged triphosphine with only a small amount of phosphine oxide. We conclude on the basis of its properties and these measurements that the substance is predominantly $[Pd\{PhP(CH_2CH_2PPh_2)_2\}Cl_3]Cl$. The failure to isolate complexes with the other multidentate ligands studied is probably due to the preference of the palladium(IV) to bind four chloride ligands, rather than more than two neutral donors, and the oxidising conditions ensure conversion of any unco-ordinated phosphorus or arsenic group to the corresponding oxide or chloride.

Structural Data.—The title compounds are the first palladium(IV) complexes containing neutral ligands to be structurally characterised. Crystals of other palladium(IV) complexes, namely $[Pd(Ph_2PCH_2CH_2PPh_2)Cl_4]$, $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}Cl_4]$, $[Pd(Me_2PCH_2CH_2PMe_2)_2Br_2][ClO_4]_2$, and $[Pd\{o\text{-}C_6H_4(AsMe_2)(PMe_2)\}_2Br_2][ClO_4]_2$ were successfully grown, but these deteriorated during preliminary data

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* The thermal decomposition of $[Pd(bipy)Cl_4]$ to $[Pd(bipy)Cl_2]$ has been reported previously, see ref. 17.

Table 3. Selected bond lengths (Å) and angles (°) for [Pd(bipy)Cl$_4$] with estimated standard deviations in parentheses

(*a*) Distances

Pd-Cl(1)	2.290(1)	Pd-Cl(4)	2.310(1)
Pd-Cl(2)	2.289(1)	Pd-N(1)	2.037(4)
Pd-Cl(3)	2.302(1)	Pd-N(2)	2.044(4)
N(1)-C(1)	1.338(6)	N(2)-C(6)	1.349(7)
C(1)-C(2)	1.403(8)	C(6)-C(7)	1.392(7)
C(2)-C(3)	1.360(13)	C(7)-C(8)	1.372(8)
C(3)-C(4)	1.398(10)	C(8)-C(9)	1.370(9)
C(4)-C(5)	1.359(7)	C(9)-C(10)	1.376(8)
C(5)-N(1)	1.356(6)	C(10)-N(2)	1.330(6)
C(5)-C(6)	1.477(7)	N(1) ··· N(2)	2.64

(*b*) Angles

Cl(1)-Pd-Cl(2)	89.1(1)	N(1)-Pd-Cl(2)	95.4(1)
Cl(1)-Pd-Cl(3)	89.9(1)	N(1)-Pd-Cl(3)	89.0(1)
Cl(1)-Pd-Cl(4)	91.9(1)	N(1)-Pd-Cl(4)	89.1(1)
Cl(2)-Pd-Cl(3)	91.3(1)	N(2)-Pd-Cl(1)	94.9(1)
Cl(2)-Pd-Cl(4)	90.4(1)	N(2)-Pd-Cl(3)	89.3(1)
Cl(3)-Pd-Cl(4)	177.6(1)	N(2)-Pd-Cl(4)	88.9(1)
		N(1)-Pd-N(2)	80.5(2)
Pd-N(1)-C(1)	124.6(4)	Pd-N(2)-C(6)	114.1(3)
Pd-N(1)-C(5)	114.6(3)	Pd-N(2)-C(10)	124.9(4)

All internal ring angles are in the range 119.3(5)—121.0(5)

N(1)-C(5)-C(6)	114.9(4)	N(2)-C(6)-C(5)	115.9(4)
C(4)-C(5)-C(6)	123.7(5)	C(7)-C(6)-C(5)	124.3(5)

(*c*) Planes (referred to fractional crystal co-ordinates)

Plane 1. N(1), C(1)—C(5)

$$8.2939X - 3.5358Y + 2.6775Z = -0.6831$$

Plane 2. N(2), C(6)—C(10)

$$8.4970X - 3.3905Y + 2.6404Z = -0.6376$$

Dihedral angle between plane 1 and plane 2 is 1.56°.

collection (at room temperature), and in the absence of low temperature facilities their study was abandoned.

The structure of [Pd(bipy)Cl$_4$] consists of discrete octahedral molecules. Selected bond lengths and angles are given in Table 3; Figures 1 and 2 show the discrete molecule and the molecular packing arrangement respectively. The molecule has no crystallographic symmetry, but inspection of Table 3 shows approximate C_{2v} symmetry is present. The only Pd$^{\mathrm{IV}}$ compound with which comparison can be made is [NH$_4$]$_2$[PdCl$_6$],[21] for which Pd-Cl is reported as 2.300(7) Å, against values in the range 2.290—2.310 Å in [Pd(bipy)Cl$_4$]. It is notable that in the latter the mutually *trans* chlorines have significantly longer (10 σ) bonds to Pd, than the chlorine atoms *trans* to nitrogen. A similar difference between Pt-I bonds *trans* to iodine (2.67 Å) and *trans* to nitrogen (2.61 Å) has been found in [Pt(phen)I$_6$] [which contains Pt(phen)I$_4$ octahedra with I$_2$ molecules linking the octahedra].[22] The neutral Pt$^{\mathrm{IV}}$ complex *trans*-[Pt(PEt$_3$)$_2$Cl$_4$] has Pt-Cl = 2.332(5) Å.[23] The dimensions and geometry of the Pd-bipy unit do not show any significant deviations from those found in related structures, and in particular may be compared with [Pt(bipy)Cl$_2$][24] [Pt-N 2.001(6), Pt-Cl 2.306 Å, N-Pt-N 80(1)°], [Pd(bipy)$_2$][NO$_3$]$_2$·H$_2$O[25] [Pd-N 2.034 Å (average), N-Pd-N 80.0(2)°], and [Sn(bipy)Et$_2$Cl$_2$].[26] The two rings in bipy have a dihedral angle of 1.56°, and as noted previously[24-26] the angles N(1)C(5)C(6) [114.9(4)°] and N(2)C(6)C(5) [115.9(4)°] are less than the expected 120°, corresponding to an N(1)-N(2) separation (the chelate ' bite ') of 2.64 Å.

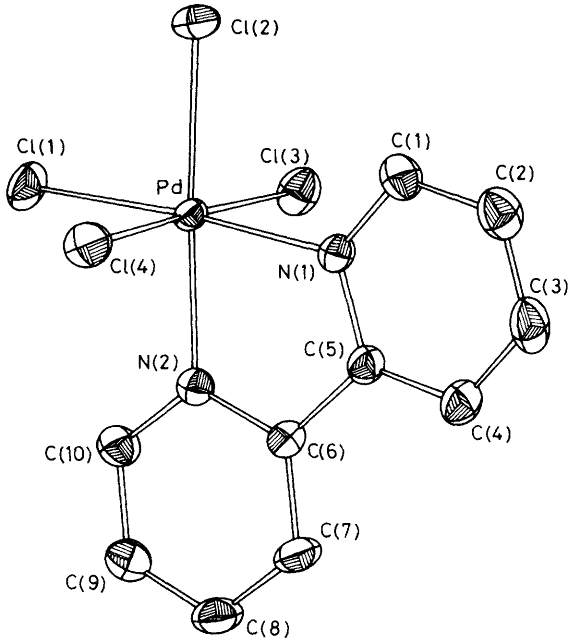

Figure 1. Discrete molecule of [Pd(bipy)Cl$_4$] excluding H atoms and with 40% probability thermal ellipsoids

Table 4. Selected bond lengths (Å) and angles (°) for [Pd{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}$_2$Cl$_2$][ClO$_4$]$_2$ with estimated standard deviations in parentheses

(*a*) Cation

Pd-Cl(1)	2.302(2)	As(1) ··· As(2)	3.355(2)
Pd-As(1)	2.452(1)	As(1) ··· As(2′)	3.580(2)
Pd-As(2)	2.455(1)		
As-C max.	1.935(8)	C-C max.	1.40(1)
min.	1.910(8)	min.	1.36(1)
Cl(1)-Pd-As(1)	88.3(1)	Cl(1′)-Pd-As(1)	91.7(1)
Cl(1)-Pd-As(2)	89.5(1)	Cl(1′)-Pd-As(2)	90.5(1)
As(1)-Pd-As(2)	86.3(1)	As(1)-Pd-As(2′)	93.7(1)
Pd-As(1)-C(5)	106.6(2)	Pd-As(2)-C(10)	106.1(2)
C-C-C max.	121.2(9)	As-C-C max.	121.3(6)
min.	118.4(7)	min.	119.6(5)

Equation of plane passing through C(5)—C(10) is $-5.3631X + 9.5327Y - 3.6990Z = 0.0626$.

Dihedral angle between the planes passing through PdAs(1)As(2) and C(5)—C(10) is 3.49°.

(*b*) Anion

Cl(2)-O(1)	1.430(7)	Cl(2)-O(3)	1.424(7)
Cl(2)-O(2)	1.421(7)	Cl(2)-O(4)	1.423(7)
O-Cl(2)-O max.		110.7(4)	
min.		107.6(5)	

Primed atoms are related to unprimed atoms by the centre of symmetry at 0,0,0.

The second compound, *trans*-[Pd{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}$_2$Cl$_2$][ClO$_4$]$_2$, is as the formula implies composed of centrosymmetric cations and perchlorate anions. The very similar unit-

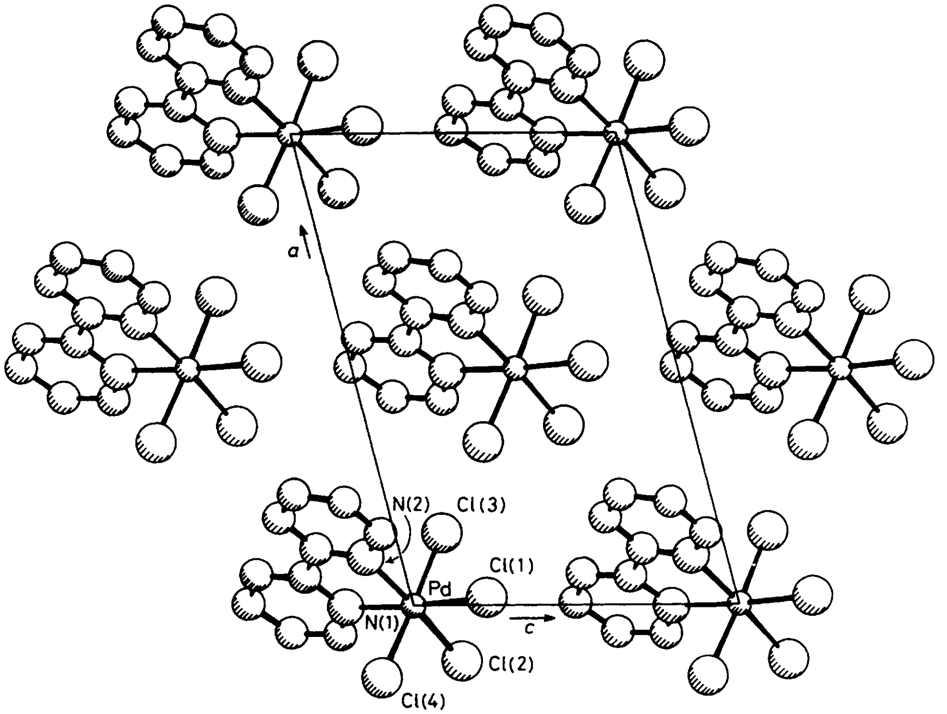

Figure 2. Unit-cell packing arrangement for $[Pd(bipy)Cl_4]$ viewed down the *b* axis

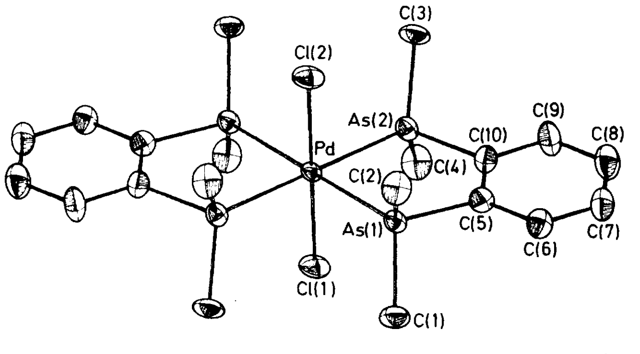

Figure 3. Cation in $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$ excluding H atoms and with 40% probability thermal ellipsoids

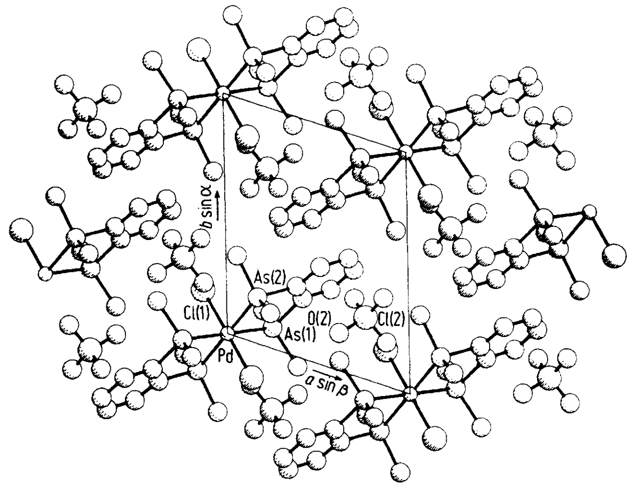

Figure 4. Unit-cell packing arrangement for $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$ viewed down the *c* axis

cell dimensions of the Pt^{IV} analogue (Experimental section) confirm that the compounds are isostructural. Selected bond lengths and angles are in Table 4, and Figures 3 and 4 show the isolated cation and the packing arrangement respectively. The Pd–Cl distance in the cation [2.302(2) Å] is not significantly different from that in the $[PdCl_6]^{2-}$ anion [2.300(7) Å][21] despite the differences in the charges on the ions. It is interesting that a similar comparison of Pt^{IV}–Cl distances in *trans*-$[Pt(en)_2Cl_2]^{2+}$ (en = $H_2NCH_2CH_2NH_2$) [2.313(4) Å][27] and $[PtCl_6]^{2-}$ [2.323(1) Å][28] reveals slight differences in the expected direction, *i.e.* shorter Pt–Cl bonds in the cation. The cation geometry is similar to that found in *trans*-$[Pt(en)_2Cl_2]^{2+}$.[27] The structural data on metal complexes of *o*-phenylenebis(dimethylarsine) have been summarised.[29] The dimensions of the diarsine ligand in $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^{2+}$ are unexceptional. The *o*-phenylene ring is planar with the two arsenic atoms displaced from the ring by 0.06 and 0.14 Å, the dihedral angle between the PdAs(1)As(2) plane and the aromatic ring being 3.49°. The Pd–As distance in the Pd^{IV} complex [2.454(2) Å] and the AsPdAs angle [86.3(1)°] can be compared with the data reported for the essentially planar bivalent metal complexes $M\{o\text{-}C_6H_4(AsMe_2)_2\}_2X_2$ (MX_2 = PdI_2,[30] PtI_2,[31] or $PtCl_2$[32]), which have M–As in the range 2.38—2.40 Å and As–M–As = 84—86°. Although the data on the bivalent metal complexes are not of high precision, the M–As distances are in good agreement with those reported[29] recently in $Pd\{o\text{-}C_6H_4(AsPhMe)_2\}_2X_2$. Hence it appears that the Pd–As distance in the octahedral complex is *ca.* 0.05—0.07 Å longer than that in the four-co-ordinate M^{II} complexes. This is similar to the differences observed[23,33] in the M–P bond lengths between $[Pt(PR_3)_2Cl_4]$ (R = alkyl) and $[Pt(PR_3)_2Cl_2]$ (*ca.* 0.08 Å). Whilst part of the increase in length found in the M^{IV} complexes may be due to the change in co-ordination number, it may also reflect some π-component in the M^{II}–P-(As) bonds, which is less important (possibly negligible) in the higher oxidation state complexes. The intramolecular As $\cdots$ As separation in $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^{2+}$ is also longer [3.355(2) Å] than in the M^{II} analogues (3.19—3.24 Å), but the intermolecular As $\cdots$ As distance 3.580(2) Å is in the range observed previously.[29] No evidence was found for disorder of the perchlorate ions.

Discussion

The palladium(IV) complexes prepared in this study and elsewhere [1] can be usefully compared with each other, and with the analogous platinum(IV) compounds.[12] Taking the Pd^{IV}–Pt^{IV} comparison first, the most obvious difference is that whilst for Pt^{IV} the stabilising effects of chloride and bromide ligands were not noticeably different, for Pd^{IV} the chloro-complexes $[Pd(L\text{–}L)Cl_4]$ are more stable and can be obtained with a wider range of neutral ligands, whilst $[Pd(L\text{–}L)Br_4]$ were isolated only with alkyl-substituted diphosphines and diarsines. For the cations $[Pd(L\text{–}L)_2X_2]^{2+}$ those with X = Br are much more easily reduced than when X = Cl. Platinum(IV) formed very stable complexes with bidentate P- or As-donors, and rather less stable complexes with tertiary-N- and S-donor ligands,[12] but for Pd^{IV} the stability as a function of donor atom appears to be $N > P \geqslant As$ ($\gg S$), at least for the $[Pd(L\text{–}L)Cl_4]$ type, although our failure to obtain $[Pd(\text{diamine})Br_4]$ was unexpected. Both M^{IV} centres have a clearly exhibited preference to bind four halide ions, but this tendency is particularly marked for Pd^{IV}, as evidenced by the smaller range of $[M(L\text{–}L)_2X_2]^{2+}$ ions obtainable, especially in the presence of halide counter anions, and this is further illustrated by our failure to prepare Pd^{IV} complexes with tri- and tetradentates. Platinum(IV) complexes with P_3X_3 and P_4X_2 (or As_3X_3 and As_4X_2) donor sets were readily synthesised.[12]

The chemistry of the Pd^{IV} compounds studied suggests that $[Pd(L\text{–}L)_2X_2]^{2+}$ are more 'stable' than $[Pd(L\text{–}L)X_4]$ species for constant L–L and X, which is unexpected for a high oxidation state. It is probable however that the 'stability' here is kinetic in origin, the $[Pd(L\text{–}L)X_4]$ type having *cis* halides and hence able to reductively eliminate X_2 easily (as shown by their thermal decomposition) whilst the *trans* cations do not have this decomposition route available. Since $[Pd(L\text{–}L)_2X_2]^{2+}$ ions have only been prepared with very strong σ-donor alkyldiphosphines and -diarsines, the contribution of the crystal field stabilization energy to the thermodynamic stability may also be important for these d^6 ions ($t_{2g}{}^6e_g{}^0$). The greater stability of Pd^{IV} in a complex anion $[PdLX_5]^-$ (L = unidentate) is not unexpected, and it is notable that complexes with L = SMe_2 and $SeMe_2$ have been obtained.[1]

More detailed comparisons are not possible in the absence of thermodynamic data, and whilst kinetic studies of Pd^{IV} complexes are few,[34] the latter do indicate that although as expected (d^6) Pd^{IV} complexes are inert, the rates of reaction are *ca.* 10^3—10^4 times greater [9] than in the Pt^{IV} analogues, a significant contribution to the reactivity of Pd^{IV} complexes.

Experimental

Electronic spectra were recorded on a Perkin-Elmer 554 spectrometer; other physical measurements were made as described previously.[11] The following palladium(II) complexes were made by literature routes or minor modifications thereof: $[Pd(L\text{–}L)Cl_2]$ for L–L = $Me_2NCH_2CH_2NMe_2$,[35] bipy,[4] phen,[5] $Ph_2PCH_2CH_2PPh_2$,[36] $Ph_2AsCH_2CH_2AsPh_2$,[36] $Me_2SbCH_2CH_2CH_2SbMe_2$,[37] and $o\text{-}C_6H_4(SbPh_2)_2$.[38] The corresponding bromides were prepared similarly using $Na_2[PdCl_4]$ exchanged with NaBr in ethanol. The complexes $Pd(L\text{–}L)_2Cl_2$ where L–L = $Ph_2PCH_2CH_2PPh_2$ [36] or $o\text{-}C_6H_4(AsMe_2)_2$,[7] were made as described.

[1,2-Bis(dimethylphosphino)ethane]dichloropalladium(II), $[Pd(Me_2PCH_2CH_2PMe_2)Cl_2]$.—The complex $[Pd(Me_2NCH_2CH_2NMe_2)Cl_2]$ (0.294 g, 1 mmol) in acetone (50 cm^3) was stirred with $Me_2PCH_2CH_2PMe_2$ (0.15 g, 1 mmol) for 2 d under nitrogen. The crude product was filtered off, rinsed with diethyl ether, and recrystallised from CH_2Cl_2–Et_2O (0.23 g, 71%) [Found: C, 22.3; H, 5.0. $C_6H_{16}Cl_2P_2Pd$ requires C, 22.0; H, 4.9%. ν(Pd–Cl) at 322s, br cm^{-1}. $E_{max.}$ 26 000, 20 400 (sh) cm^{-1}, diffuse reflectance (d.r.)]. The complex $[Pd(Me_2PCH_2CH_2PMe_2)Br_2]$ was prepared analogously from $[Pd(Me_2NCH_2CH_2NMe_2)Br_2]$ [Found: C, 17.6; H, 3.4. $C_6H_{16}Br_2P_2Pd$ requires C, 17.3; H, 3.9%. ν(Pd–Br) at 229, 220 (sh) cm^{-1}. $E_{max.}$ 28 000, 24 600, 21 200 (sh) cm^{-1} (d.r.).]

[1,3-Bis(dimethylarsino)propane]dichloropalladium(II), $[Pd(Me_2AsCH_2CH_2CH_2AsMe_2)Cl_2]$.—The compound $Me_2AsCH_2CH_2CH_2AsMe_2$ (0.35 g, 1.4 mmol) was added under nitrogen to a solution of $Na_2[PdCl_4]$ (0.41 g, 1.4 mmol) in ethanol (100 cm^3) and the mixture refluxed for 2 h. The resulting solution was evaporated to dryness, extracted with CH_2Cl_2, and filtered. The filtrate was reduced to a small volume and the product crystallised out upon dropwise addition of EtOH–Et_2O mixture (1 : 1 v/v) (0.52 g, 86%) [Found: C, 19.4; H, 4.2. $C_7H_{18}As_2Cl_2Pd$ requires C, 19.6; H, 4.2%. ν(Pd–Cl) at 302, 266 cm^{-1}. $E_{max.}$ 28 000, 25 200 (sh) cm^{-1} (d.r.)].

$[Pd(Me_2AsCH_2CH_2CH_2AsMe_2)Br_2]$. [Found: C, 16.5; H, 3.3. $C_7H_{18}As_2Br_2Pd$ requires C, 16.2; H, 3.5%. ν(Pd–Br) at 196m, br cm^{-1}. $E_{max.}$ 26 800, 22 600 cm^{-1} (d.r.)].

*Dichloro[*o*-phenylenebis(dimethylarsine)]palladium*(II), $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}Cl_2]$.—A solution of $Na_2[PdCl_4]$ (0.71 g, 2.4 mmol) in methanol (50 cm^3) was treated with $o\text{-}C_6H_4(AsMe_2)_2$ (0.69 g, 2.4 mmol) in methanol (50 cm^3) under nitrogen. The mixture was stirred for 2 h and the solid collected and dried *in vacuo*. The solid dissolved slowly in hot *NN*-dimethylformamide (50 cm^3) and the resultant solution was reduced to *ca.* 5 cm^3 by rotary evaporation. Addition of diethyl ether precipitated the crude product which was further recrystallised from CH_2Cl_2–Et_2O to give a yellow solid (0.58 g, 52%) [Found: C, 25.9; H, 3.5. $C_{10}H_{16}As_2Cl_2Pd$ requires C, 25.9; H, 3.5%. ν(Pd–Cl) at 314, 298 cm^{-1}. $E_{max.}$ 27 600, 22 000 cm^{-1} (d.r.)].

$[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}Br_2]$. [Found: C, 21.9; H, 2.9. $C_{10}H_{16}As_2Br_2Pd$ requires C, 21.8; H, 2.9%. ν(Pd–Br) at 212, 193 cm^{-1}. $E_{max.}$ 25 000, 21 700 cm^{-1} (d.r.)].

Bis[1,2-bis(dimethylphosphino)ethane]palladium(II) *Dichloride*, $[Pd(Me_2PCH_2CH_2PMe_2)_2]Cl_2$.—A solution of $Na_2[PdCl_4]$ (0.25 g, 0.85 mmol) in methanol (100 cm^3) was treated with $Me_2PCH_2CH_2PMe_2$ (0.255 g, 1.7 mmol) under nitrogen and the mixture stirred for 2 h to give a clear solution. This was rotary evaporated to dryness, extracted with CH_2Cl_2, and filtered, and the filtrate concentrated to small volume. The solid was precipitated by slow addition of diethyl ether (0.325 g, 80%) [Found: C, 30.0; H, 6.5. $C_{12}H_{32}Cl_2P_4Pd$ requires C, 30.2; H, 6.8%. $E_{max.}$ 29 400 (sh) cm^{-1} (d.r.)].

$[Pd(Me_2PCH_2CH_2PMe_2)_2]Br_2$. [Found: C, 25.9; H, 6.0. $C_{12}H_{32}Br_2P_4Pd$ requires C, 25.4; H, 5.7%. $E_{max.}$ 29 100 (sh) cm^{-1} (d.r.)].

*Bis[*o*-phenylenebis(dimethylphosphine)]palladium*(II) *Dichloride*, $[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2]Cl_2$.—The ligand (0.24 g, 2.38 mmol) was added under nitrogen to $Na_2[PdCl_4]$ (0.35 g, 1.19 mmol) in methanol (50 cm^3) and the mixture stirred overnight. The solution was rotary evaporated to dryness, and the solid recrystallised from CH_2Cl_2–Et_2O (0.48 g, 71%) [Found: C, 41.6; H, 5.3%. $C_{20}H_{32}Cl_2P_2Pd$ requires C, 41.9; H, 5.6%. $E_{max.}$ 26 800 cm^{-1} (d.r.)].

The following complexes were prepared in a similar manner: $[Pd\{o\text{-}C_6H_4(PMe_2)_2\}_2]Br_2$ [Found: C, 36.4; H, 4.7. $C_{20}H_{32}Br_2P_4Pd$ requires C, 36.3; H, 4.9%. $E_{max.}$ 26 000 cm^{-1} (d.r.)]; $[Pd\{o\text{-}C_6H_4(PMe_2)(AsMe_2)\}_2]Cl_2$ [Found: C, 36.2; H, 4.5. $C_{20}H_{32}As_2Cl_2P_2Pd$ requires C, 36.3; H, 4.9%. $E_{max.}$ 26 800, 23 200 cm^{-1} (d.r.)]; and $[Pd\{o\text{-}C_6H_4(PMe_2)(AsMe_2)\}_2]Br_2$ [Found: C, 32.0; H, 4.6. $C_{20}H_{32}As_2Br_2P_2Pd$ requires C, 32.0; H, 4.3%. $E_{max.}$ 25 800 cm^{-1} (d.r.)].

[Bis(2-diphenylphosphinoethyl)phenylphosphine]chloropalladium(II) *Chloride*, $[Pd\{PPh(CH_2CH_2PPh_2)_2\}Cl]Cl$.—Addition of a dichloromethane (30 cm^3) solution of $PPh(CH_2CH_2PPh_2)_2$ (0.55 g, 1.0 mmol) to $Na_2[PdCl_4]$ (0.30 g, 1.0 mmol) in ethanol (70 cm^3) quickly gave a yellow solution. The mixture was stirred for 2 h and rotary evaporated to dryness. The residue was extracted with dichloromethane (200 cm^3), filtered, and the solution reduced to a small volume and treated with diethyl ether to give a pale yellow solid (0.62 g, 85%) [Found: C, 57.5; H, 4.9. $C_{34}H_{33}Cl_2P_3Pd$ requires C, 57.4; H, 4.7%. ν(Pd–Cl) at 309s. $E_{max.}$ 28 300 cm^{-1} (d.r.)].

[Bis(3-dimethylarsinopropyl)methylarsine]chloropalladium(II) *Chloride*, $[Pd\{AsMe(CH_2CH_2CH_2AsMe_2)_2\}Cl]Cl$.—A solution of $MeAs(CH_2CH_2CH_2AsMe_2)_2$ (0.57 g, 1.5 mmol) in dichloromethane (30 cm^3) was added to a solution of $Na_2[PdCl_4]$ (0.44 g, 1.5 mmol) in ethanol (70 cm^3) under nitrogen and the mixture stirred for 2 h. This was rotary evaporated to dryness and the residue extracted with dichloromethane and filtered. The solution was reduced to a small volume and the product crystallised out with ethanol and diethyl ether (0.53 g, 63%) [Found: C, 23.5; H, 4.8. $C_{11}H_{27}As_3Cl_2Pd$ requires C, 23.5; H, 4.9%. ν(Pd–Cl) at 302m. $E_{max.}$ 27 800, 25 000 (sh) cm^{-1} (d.r.)].

Chloro[tris(2-diphenylphosphinoethyl)phosphine]palladium(II) *Chloride*, $[Pd\{P(CH_2CH_2PPh_2)_3\}Cl]Cl$.—A solution of $Na_2[PdCl_4]$ (0.30 g, 1.0 mmol) in ethanol (60 cm^3) was mixed with a solution of $P(CH_2CH_2PPh_2)_3$ (0.70 g, 1.0 mmol) in dichloromethane (30 cm^3). A bright red solution is rapidly formed. After stirring overnight the solvent was removed by rotary evaporation and the residue extracted with dichloromethane. Reduction to *ca.* 1 cm^3 and addition of a small volume of EtOH–Et_2O precipitates the highly soluble product (0.57 g, 65%) [Found: C, 59.5; H, 5.0. $C_{48}H_{54}Cl_2P_4Pd$ requires C, 59.5; H, 5.0%. $E_{max.}$ 20 600 cm^{-1} (d.r.)].

Chloro[tris(3-dimethylarsinopropyl)arsine]palladium(II) *Chloride*, $[Pd\{As(CH_2CH_2CH_2AsMe_2)_3\}Cl]Cl$.—A solution of $Na_2[PdCl_4]$ (0.294 g, 1 mmol) in ethanol (70 cm^3) was mixed with a solution of $As(CH_2CH_2CH_2AsMe_2)_3$ (0.52 g, 1 mmol) in CH_2Cl_2 (30 cm^3) under nitrogen, and stirred overnight. The product was rotary evaporated to dryness, extracted with CH_2Cl_2, filtered, and the filtrate evaporated to small volume. The product was precipitated by addition of EtOH–Et_2O mixture (0.395 g, 57%) [Found: C, 25.4; H, 5.0. $C_{15}H_{36}As_3Cl_2Pd$ requires C, 26.0; H, 5.2%. $E_{max.}$ 27 800, 23 700 cm^{-1} (d.r.)].

All Pd^{IV} complexes were stored in sealed containers at −20 °C to minimise decomposition. All measurements were made on freshly prepared materials (wherever possible within 24 h of preparation).

$[Pd(L–L)Cl_4]$ *Complexes, General Method.*—A suspension of the finely powdered Pd^{II} complex (*ca.* 1 mmol) was suspended in dry carbon tetrachloride (5 cm^3) and rapidly stirred whilst a small excess of chlorine was slowly bubbled in. The mixture was stirred for 30 min, the product filtered off, and dried *in vacuo*. Yields are generally >80%. The complexes $[Pd(L–L)Br_4]$ were prepared similarly using a small excess of bromine.

Thermogravimetric results for $[Pd(L–L)Cl_4]$. The required value refers to loss of Cl_2 and the temperature (°C) is that at which reductive elimination is complete. $[Pd(Me_2PCH_2CH_2PMe_2)Cl_4]$ [Found: 18.2, requires 17.8%, at 150 (±5)], $[Pd(Ph_2PCH_2CH_2PPh_2)Cl_4]$ [Found: 12.0, requires 11.0%, at 115 (±5)], $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}Cl_4]$ [Found: 12.0, requires 13.3%, at 145 (±5)], and $[Pd(Ph_2AsCH_2CH_2AsPh_2)Cl_4]$ [Found: 10.5, requires 9.7%, at 110 (±5)].

Complexes $Pd(L–L)_2Cl_4$ [L–L = $Me_2PCH_2CH_2PMe_2$ *or* $o\text{-}C_6H_4(PMe_2)_2$] *and* $Pd(L–L–L)Cl_4$ [L–L–L = $PPh(CH_2CH_2PPh_2)_2$].—These complexes were prepared analogously to $[Pd(L–L)Cl_4]$.

Recovery of the ligand from $[Pd\{PPh(CH_2CH_2PPh_2)_2\}Cl_3]Cl$. The complex $[Pd\{PPh(CH_2CH_2PPh_2)_2\}Cl_3]Cl$ was suspended in distilled water and SO_2 passed through for 10 min and the mixture stirred for 2 h. A ten-fold molar excess of NaCN was added and the mixture stirred for 4 h. Dichloromethane was added and the organic layer separated and dried over Na_2SO_4. Filtration and rotary evaporation to dryness gave a cream solid. The i.r. showed a weak ν(P=O) band at 1 177 cm^{-1} and the mass spectrum was generally consistent with $PPh(CH_2CH_2PPh_2)_2$ [$PPh(CH_2CH_2PPh_2)_2^+$ (58), $Ph_2PCH_2CH_2PPhCH_2CH_2^+$ (100), $Ph_2PCH_2CH_2PPh^+$ (50), Ph_3P^+ (57), PPh_2^+ (65), and $C_{12}H_8P^+$ (81)] but also showed a small amount of phosphine oxide [$PPh(CH_2CH_2PPh_2)_2O^+$ (1)].[39]

$[Pd(L–L)_2Cl_2][ClO_4]_2$ [L–L = $Me_2PCH_2CH_2PMe_2$, $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, *or* $o\text{-}C_6H_4(PMe_2)(AsMe_2)$].—The palladium(II) complex $Pd(L–L)_2Cl_2$ (0.5 mmol) was stirred with a mixture of concentrated nitric acid and concentrated hydrochloric acid (5 cm^3, 10 : 1 v/v) at 0 °C for 10 min. The contents were then treated with concentrated (70%) perchloric acid (40 cm^3) at 0 °C (**CAUTION**: explosion hazard). The palladium(IV) complex precipitated, was filtered off, rinsed with dilute perchloric acid (*ca.* 5%), and dried *in vacuo*. Yield *ca.* 60%.

(**CAUTION**: No explosions were experienced in this work, but perchlorate complexes of high oxidation state metals are often explosive, and due care should be taken.)

The complexes $[Pd(L–L)_2Br_2][ClO_4]_2$ were prepared similarly using $Pd(L–L)_2Br_2$, concentrated HNO_3, and a trace of concentrated HBr.

X-Ray Crystal Structure Analysis.—Both crystals studied were examined photographically, using Weissenberg and precession methods, before being transferred to a Nonius CAD-4 diffractometer. Accurate cell dimensions were obtained from 25 accurately centred reflections and data were collected with graphite monochromated Mo-K_α radiation (λ = 0.7107 Å). Air-stable crystals of $[Pd(bipy)Cl_4]$ were obtained by slow diffusion of Cl_2 gas into a solution of $[Pd(bipy)Cl_2]$ in dichloromethane over a period of *ca.* one week. Air-stable crystals of $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$ were prepared by treating $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]$ with concentrated HNO_3–HCl (4 : 1 v/v) followed by addition of a small volume of concentrated (60%) $HClO_4$ and cooling in a refrigerator. Needle crystals formed readily which were cleaved to a suitable length for *X*-ray work.

Crystal data. (*i*) $[Pd(bipy)Cl_4]$. $C_{10}H_8Cl_4N_2Pd$, M = 404.4, Monoclinic, a = 12.241(5), b = 6.720(2), c = 8.120(9) Å, β = 104.37(5)°, U = 647.0 $Å^3$, D_c = 2.075, Z = 2, D_m (flotation) = 2.03(2) g cm^{-3}, $F(000)$ = 392, μ(Mo-K_α) =

Table 5. Fractional atomic co-ordinates (× 10^4) for [Pd(bipy)Cl_4] excluding hydrogen atoms

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	0	1 962(1)	0
Cl(1)	165(1)	3 997(2)	2 311(2)
Cl(2)	−1 182(1)	−47(2)	1 042(2)
Cl(3)	1 550(1)	185(2)	1 448(2)
Cl(4)	−1 526(1)	3 740(2)	−1 552(2)
N(1)	−38(4)	271(6)	−2 096(5)
N(2)	1 028(4)	3 636(6)	−1 086(6)
C(1)	−622(5)	−1 420(8)	−2 479(7)
C(2)	−588(5)	−2 450(9)	−3 969(8)
C(3)	44(10)	−1 742(7)	−5 001(13)
C(4)	659(6)	14(9)	−4 559(7)
C(5)	600(4)	980(7)	−3 113(6)
C(6)	1 191(4)	2 868(7)	−2 542(7)
C(7)	1 863(5)	3 877(8)	−3 422(7)
C(8)	2 357(5)	5 641(8)	−2 785(8)
C(9)	2 193(5)	6 360(8)	−1 285(8)
C(10)	1 520(4)	5 330(7)	−452(7)

21.29 cm^{-1}. Systematic absences (*hkl*, none; *h*0*l*, $h + l = 2n + 1$; 0*k*0, none) indicate space group *Pn* (no. 7) or *P*2/*n* (no. 15). The non-centrosymmetric space group *Pn* was indicated by the distribution of conventional normalised structure factors (*E*) and confirmed by the subsequent refinement.

(*ii*) [Pd{*o*-$C_6H_4(AsMe_2)_2$}$_2$$Cl_2$][$ClO_4$]$_2$. $C_{20}H_{32}As_4Cl_4O_8Pd$, $M = 948.4$, Triclinic, $a = 7.903(3)$, $b = 10.670(3)$, $c = 10.141(2)$ Å, $\alpha = 110.50(2)$, $\beta = 91.75(3)$, $\gamma = 107.31(3)°$, $U = 755.9$ Å^3, $D_c = 2.083$, $Z = 1$, D_m (flotation) = 2.05(3) g cm^{-3}, $F(000) = 462$, μ(Mo-K_α) = 52.9 cm^{-1}. Space group *P*1 or *P*$\bar{1}$ and the latter centrosymmetric space group confirmed by the subsequent analysis.

Yellow crystals of [Pt{*o*-$C_6H_4(AsMe_2)_2$}$_2$$Cl_2$][$ClO_4$]$_2$ were prepared by an identical method to [Pd{*o*-$C_6H_4(AsMe_2)_2$}$_2$$Cl_2$][$ClO_4$]$_2$. Cell parameters $a = 7.971(15)$, $b = 10.136(3)$, $c = 10.673(4)$ Å, $\alpha = 110.41(3)$, $\beta = 107.65(11)$, $\gamma = 91.73(9)°$.

Data collection and structure determination. (*i*) [Pd(bipy)Cl_4]. The data were recorded on a room temperature crystal (0.20 × 0.20 × *ca.* 0.2 mm) using three check reflections which showed no deterioration during the experiment. After suitable averaging 1 417 reflections were obtained ($\theta_{min.} = 3°$, $\theta_{max.} = 27°$) and an empirical ψ scan absorption correction was applied to the data. Treating those reflections where $\sigma(F) > 2F$ as ' less-thans ' (34) gave 1 383 reflections that were used in the subsequent structure determination and refinement. Examination of the distribution of *E*'s suggested a non-centrosymmetric space group and the analysis was carried out in the space group *Pn* (equivalent positions x, y, z; $x + \frac{1}{2}, -y, z + \frac{1}{2}$). The Patterson map readily located the palladium atom and a sequence of structure factor and electron-density syntheses located all the non-hydrogen atoms. Least-squares refinement (isotropic atoms) reduced *R* to 0.06 and introducing an empirical weighting scheme, $w = 1/[\sigma^2(F) + 0.0004 F_o^2]$, and anisotropic atoms for Pd and Cl reduced *R* to 0.0294. A difference electron-density map revealed the majority of the hydrogen atoms and these were introduced into the model in geometrically calculated positions [d(C–H) = 1.08 Å] and with a common isotropic thermal parameter. Final least-squares refinement (anisotropic atoms) gave $R = 0.0234$, $R' = 0.0233$, and a difference electron-density map gave all features in the range −0.98 to +0.87 e Å^{-3}. The number of parameters was 153 and the ratio reflections/parameters = 9.04. The final refinement was repeated for the other absolute configuration and gave $R = 0.0246$, $R' = 0.0247$. The Hamilton *R* factor ratio test indicates that the absolute configuration of the crystal used is as reported.

Table 6. Fractional atomic co-ordinates (× 10^4) for [Pd{*o*-$C_6H_4(AsMe_2)_2$}$_2$$Cl_2$][$ClO_4$]$_2$ excluding hydrogen atoms

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	0	0	0
As(1)	2 505(1)	869(1)	−1 171(1)
As(2)	1 707(1)	1 942(1)	2 207(1)
Cl(1)	−1 295(3)	1 501(2)	−461(2)
Cl(2)	7 631(3)	2 571(2)	6 134(2)
O(1)	7 013(10)	3 205(7)	5 272(7)
O(2)	6 152(10)	1 576(8)	6 378(9)
O(3)	8 739(11)	1 818(10)	5 379(8)
O(4)	8 621(10)	3 624(7)	7 453(7)
C(1)	2 027(12)	1 472(10)	−2 681(9)
C(2)	3 852(11)	−390(9)	−1 937(9)
C(3)	2 405(12)	1 451(10)	3 729(9)
C(4)	620(12)	3 374(9)	3 053(10)
C(5)	4 204(10)	2 527(8)	281(8)
C(6)	5 745(10)	3 273(9)	−72(9)
C(7)	7 007(11)	4 396(9)	980(10)
C(8)	6 744(12)	4 780(10)	2 391(11)
C(9)	5 204(11)	4 052(9)	2 736(10)
C(10)	3 890(10)	2 925(8)	1 695(8)

(*ii*) [Pd{*o*-$C_6H_4(AsMe_2)_2$}$_2$$Cl_2$][$ClO_4$]$_2$. A room temperature crystal (0.35 × 0.07 × 0.07 mm) was used to record the data. No deterioration was observed in the two check reflections but the peaks were rather broad with rather weak intensities due to the small crystal size. After suitable averaging, 2 106 reflections were obtained ($\theta_{min.} = 1.5°$, $\theta_{max.} = 23°$) and omitting reflections where $F < 3\sigma(F)$ left 1 680 reflections which were used in the structure determination and refinement. An empirical ψ scan absorption correction was applied to the data. The distribution of *E*'s favoured the centrosymmetric space group and the structure was solved in *P*$\bar{1}$ by conventional heavy-atom methods. Introducing anisotropic Pd, As, and Cl atoms and isotropic C and O reduced *R* to 0.0535 at which stage a difference electron-density synthesis showed all the hydrogen atoms in the range 0.78—0.43 e Å^{-3}. Hydrogen atoms were introduced into the model in calculated positions [d(C–H) = 1.08 Å] with the methyl hydrogen atoms having a common thermal parameter and the aromatic protons treated similarly. Full-matrix least-squares refinement {183 parameters, anisotropic non-hydrogen atoms, empirical weights $w = 1/[\sigma^2(F) + AF_o^2]$, $A = 0.0001$} reduced *R* to a final value of 0.0395 ($R' = 0.0331$). A final difference electron-density synthesis showed all features in the range −0.88 to +0.80 e Å^{-3}.

Scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX[40] (Cl, O, N, C, H) and ref. 41 (Pd, As). All calculations were performed on an ICL 2970 computer using the programs SHELX,[40] XANADU,[42] ORTEP,[43] and PLUTO[44] and various local programs. The final atomic positional co-ordinates for [Pd(bipy)Cl_4] are in Table 5 and the corresponding details for [Pd{*o*-$C_6H_4(AsMe_2)_2$}$_2$$Cl_2$][$ClO_4$]$_2$ are in Table 6.

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