Co-ordination Chemistry of Higher Oxidation States. Part 3.[1] Palladium(IV) Complexes with Neutral Unidentate Ligands

David J. Gulliver and William Levason *
Department of Chemistry, The University, Southampton SO9 5NH

Oxidation of $[NR_4][PdLX_3]$ with the corresponding halogen (X_2) in carbon tetrachloride gave octahedral palladium(IV) anions $[NR_4][PdLX_5]$ [L = py (pyridine), $AsEt_3$, SMe_2, or $SeMe_2$, X = Cl or Br; L = NMe_3, PPh_3S, or PPr^n_3, X = Cl; L = PEt_2Ph, X = Br]. Attempts to prepare analogues with L = $SbMe_3$, $TeMe_2$, or dmso (dimethyl sulphoxide) failed. Neutral palladium(IV) complexes *trans*-$[PdL_2X_4]$ (L = NMe_3, py, PPr^n_3, or $AsMe_2Ph$, X = Cl; L = NMe_3, X = Br) have been obtained from *trans*-$[PdL_2X_2]$ and X_2. The complexes were characterised by i.r. and electronic spectroscopy, and conductivity measurements, and their thermal decomposition examined by t.g.a.

Palladium(IV) is an unfamiliar oxidation state, most readily obtained in complexes with anionic ligands, for example $PdCl_6^{2-}$, $PdBr_6^{2-}$, $[Pd(SO_3F)_6]^{2-}$, and $[Pd(S_2CNR_2)_3]Cl$.[2] There are a number of reports of complexes with neutral bidentates, mostly amines or nitrogen heterocycles, but complexes of neutral unidentates are little known. Complexes of the latter type described in the literature are $[Pd(NH_3)_2Cl_4]$,[3-5] $[Pd(py)_2Cl_4]$ (py = pyridine),[6] $[PdL_2Cl_4]$ (L = 1-phenylethylamine),[7] and $[Pd(NH_2Me)_2Cl_4]$,[4] and even for these the published data are incomplete. There appear to be no reports of Pd^{IV} complexes with unidentate ligands containing the heavier members of Group 5B or 6B. Although no organopalladium(IV) complexes have been isolated [the pentafluorophenyl complex $Pd(PPh_3)_2Cl_2(C_6F_5)_2$ reported [8] in 1969 has been shown [9] to be a palladium(II) dimer $Pd_2(PPh_3)_2Cl_2(C_6F_5)_2$, there is growing evidence [10,11] that organopalladium(IV) intermediates are involved in the organopalladium(II) mediated coupling of alkyl halides. As part of a more general study of the chemistry of the platinum metals in the higher oxidation states, we have examined the halogen oxidation of a range of palladium(II) complexes with neutral Group 5B and 6B donor ligands.

Results

Anionic Complexes $[NR_4][PdLX_5]$ (X = Cl *or* Br, L = *unidentate ligand*, R = *alkyl*).—The treatment of finely powdered palladium(II) anions $[NR_4][PdLX_3]$ suspended in a small quantity of carbon tetrachloride with a slight excess of the appropriate halogen gave the corresponding palladium(IV) complexes $[NR_4][PdLX_5]$ (L = py, $AsEt_3$, SMe_2, or $SeMe_2$, X = Cl or Br; L = PPr^n_3, PPh_3S, or NMe_3, X = Cl; L = PEt_2Ph, X = Br), Table 1. These complexes vary in colour from orange to red-brown, and decompose slowly at room temperature, but can be stored at −20 °C for several months without decomposition. The $[NR_4][PdLX_5]$ complexes all dissolve in chlorocarbon solvents, although they are markedly less soluble than the palladium(II) anions, and the stability in solution depends greatly upon L, but seems to differ little whether X = Cl or Br. Thus the $[Pd(py)X_5]^-$ ions are stable in the presence of a little free halogen, whilst at the other extreme $[Pd(SeMe_2)X_5]^-$ decomposes immediately with the selenide being oxidised to Me_2SeX_2, identified by the characteristic [12] ^1H n.m.r. resonances at δ 3.64 (Cl) and 3.61 p.p.m. (Br). The complexes are decomposed by water or alcohols, but dissolve readily in dry nitrobenzene, in which they have conductivities consistent with 1 : 1 electrolytes (Table 1). Our attempts to halogen oxidise $[NR_4][PdLX_3]$ (L = $SbMe_3$ or $TeMe_2$) and $[NR_4][Pd(dmso)Cl_3]$ (dmso = dimethyl sulphoxide) resulted in decomposition, in the cases of the stibines and tellurides, Me_3SbX_2 and Me_2TeX_2 (identified by ^1H n.m.r. spectroscopy) were produced. Several systems including PPh_3O (X = Cl or Br), NMe_3, PPh_3S, or dmso (X = Br) could not be examined since the $[PdLX_3]^-$ starting materials could not be obtained.

For a substituted octahedral $[MLX_5]^-$ ion (C_{4v}), theory [13] predicts four metal–halide stretching vibrations A_1(MX), $A_1(MX_4)$, $B_1(MX_4)$, and $E(MX_4)$, of which the B_1 is Raman active only. The deep colours and instability of the $[PdLX_5]^-$ ions prevented Raman studies, but the far-i.r. bands tentatively assigned as Pd−X vibrations are listed in Table 2. Generally three bands were observed as predicted, although in a few cases fewer bands could be distinguished presumably due to coincidence of the absorptions. In the absence of Raman data, the assignment of individual bands is uncertain, but a comparison with the far-i.r. spectra of the $[PtLX_5]^-$ ions [13] is interesting. The latter exhibit A_1(PtX) at considerably lower frequencies than the $A_1,E(PtX_4)$, but for $[PdLX_5]^-$ the three bands are closer together. The low value of the A_1(PtX) ν(Pt−X) *trans* to L is attributed to the large *trans* influence of L, and since any π component will be small for these high oxidation states, the *trans* influence must operate largely *via* anisotropic σ-bonding effects. It appears that the *trans* influence of the neutral ligand L is considerably less in $[PdLX_5]^-$ than in $[PtLX_5]^-$, consistent with Pd^{IV} being harder and less polarisable than Pt^{IV} and hence less influenced by the unequal ligand σ-bonding requirements.

The diffuse reflectance electronic spectra of the $[PdLX_5]^-$ ions contain intense overlapping bands at 18 000—30 000 cm^{-1} (Table 2). The lowest energy charge-transfer band in $PdCl_6^{2-}$, $Pd(e_g)\leftarrow Cl$, is at 29 400 cm^{-1} [14] which after correction for ligand field splitting gives an optical electronegativity for Pd^{IV} of 2.75. Combining this with $\chi_{opt.}$ for the neutral ligands [14] suggests that most of the absorptions observed are charge transfer in origin. Most of the complexes decomposed too rapidly in solution for absorption coefficients to be measured, and only for $[NBu^n_4][Pd(py)Cl_5]$ was a reproducible solution spectrum obtained.

Thermogravimetric analysis (t.g.a.) of representative $[PdLX_5]^-$ salts showed that most were decomposed on fairly gentle heating, the weight losses in the initial process corresponding to $-X_2$, *i.e.* conversion of $[PdLX_5]^-$ to $[PdLX_3]^-$ (*e.g.* L = $AsEt_3$, X = Cl or Br; L = SMe_2, X = Cl). The anions with the *N*-donors NMe_3 and py decomposed at higher temperatures, but the weight losses were very large indicating complete breakdown of the complex; in the case of the NMe_3 complex at least this is to be expected in view of the low stability of the Pd^{II} complex.[15]

Attempts were made to study the oxidation of $[NR_4][PdLCl_3]$ by cyclic voltammetry, but in acetonitrile containing 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$ as base electrolyte (sweep rates

Table 1. Physical data

Complex	Colour	Analysis (%) [a] C	H	X	N	Λ_M [b]/ S cm^2 mol^{-1}
$[Pd(NMe_3)_2Cl_4]$	Orange	19.5 (19.7)	5.0 (4.95)	38.9 (38.7)	7.3 (7.65)	
$[Pd(NMe_3)_2Br_4]$	Dark red	13.4 (13.25)	3.2 (3.3)	59.1 (58.7)	5.1 (5.15)	
$[Pd(py)_2Cl_4]$	Orange	29.7 (29.6)	2.6 (2.5)	35.2 (34.9)	7.0 (6.9)	2
$[Pd(PPr^n{}_3)_2Cl_4]$	Red	37.8 (38.0)	7.0 (7.4)	24.9 (24.9)		
$[Pd(AsMe_2Ph)_2Cl_4]$	Orange	30.95 (31.4)	3.6 (3.6)			
$[NPr_4][Pd(NMe_3)Cl_5]$	Orange	34.1 (34.05)	7.3 (7.05)	33.3 (33.5)	2.5 (2.65)	30
$[NBu^n{}_4][Pd(py)Cl_5]$	Orange	42.1 (42.7)	6.9 (6.8)	29.0 (29.3)	4.7 (4.6)	22
$[NBu^n{}_4][Pd(py)Br_5]$	Brown	31.0 (30.5)	5.1 (5.0)	48.7 (48.3)	3.6 (3.4)	27
$[NEt_4][Pd(PPr^n{}_3)Cl_5]$	Orange-red	35.8 (35.6)	7.0 (7.2)	31.3 (30.9)	2.6 (2.45)	29
$[NMe_4][Pd(PEt_2Ph)Br_5]$	Dark brown	22.9 (22.6)	3.8 (3.7)	52.9 (53.5)	1.6 (1.9)	30
$[NEt_4][Pd(AsEt_3)Cl_5]$	Orange	28.9 (29.2)	6.1 (6.1)	30.2 (30.8)	2.3 (2.4)	21
$[NMe_4][Pd(AsEt_3)Br_5]$	Dark brown	16.8 (16.2)	3.8 (3.7)	54.3 (53.8)	1.7 (1.9)	29
$[NEt_4][Pd(SMe_2)Cl_5]$	Orange	24.8 (25.2)	5.7 (5.5)	37.3 (37.25)	3.0 (2.95)	28
$[NMe_4][Pd(SMe_2)Br_5]$	Red-brown	11.4 (11.2)	2.6 (2.8)	62.0 (62.2)	2.1 (2.2)	30
$[NBu^n{}_4][Pd(PPh_3S)Cl_5]$	Fawn	49.7 (49.8)	6.1 (6.3)	21.1 (21.6)	1.5 (1.7)	23
$[NBu^n{}_4][Pd(SeMe_2)Cl_5]$	Fawn	34.2 (34.05)	6.5 (6.7)	27.4 (27.9)	2.2 (2.2)	29
$[NBu^n{}_4][Pd(SeMe_2)Br_5]$	Red-brown	26.0 (26.35)	4.9 (4.9)	47.2 (46.6)	1.6 (1.65)	31.5

[a] Calculated values in parentheses. [b] In 10^{-3} mol dm^{-3} nitrobenzene; 1 : 1 electrolytes have Λ_M 20—30 S cm^2 mol^{-1} in this solvent (W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81).

Table 2. Spectroscopic data

Complex	I.r. [a]/cm^{-1}	$10^{-3}E_{max.}$ [b]/cm^{-1}
$[Pd(NMe_3)_2Cl_4]$	338s (br)	35.5, 28.0, 20.7
$[Pd(NMe_3)_2Br_4]$	225s	28.0 (sh), 25.5, 22.4 (sh), 18.6
$[Pd(py)_2Cl_4]$	353	33.0 (br), 27.0 (sh), 22.6 (br)
$[Pd(PPr^n{}_3)_2Cl_4]$	335 (br)	35.0, 28.7, 22.6, 20.0
$[Pd(AsMe_2Ph)_2Cl_4]$	336 (br)	35.5, 28.8 (sh), 22.5 (sh), 20.4
$[NPr^n{}_4][Pd(NMe_3)Cl_5]$	340 (sh), 335s, 320 (sh)	35.0, 26.8, 22.7 20.5
$[NBu^n{}_4][Pd(py)Cl_5]$	350s, 325 (sh), 308w (sh)	27.2, 23.1, 20.5 [c]
$[NBu^n{}_4][Pd(py)Br_5]$	274 (sh), 256s	36.0 (br), 29.0 (br), 22.9, 18.7
$[NEt_4][Pd(PPr^n{}_3)Cl_5]$	338s, 315 (sh)	35.0, 27.0, 24.0, 19.8
$[NMe_4][Pd(PEt_2Ph)Br_5]$	245vs	25.0 (br), 18.7
$[NEt_4][Pd(AsEt_3)Cl_5]$	342 (sh), 338s, 317 (sh)	34.8, 26.8, 25.0, 20.0
$[NMe_4][Pd(AsEt_3)Br_5]$	251vs, 236 (sh), 204m	29.0, 21.0, 16.8 (sh)
$[NEt_4][Pd(SMe_2)Cl_5]$	344 (sh), 338s, 315w (sh)	34.5, 26.7, 23.3, 20.3
$[NMe_4][Pd(SMe_2)Br_5]$	262 (sh), 248s, 243s (br)	35.5, 26.3, 23.1, 19.3
$[NBu^n{}_4][Pd(PPh_3S)Cl_5]$ [d]	346 (sh), 335s, 318m	27.6, 21.5
$[NBu^n{}_4][Pd(SeMe_2)Cl_5]$	347s, 334s, 305w	35.0 (br), 28.0, 21.8 (sh), 19.8
$[NBu^n{}_4][Pd(SeMe_2)Br_5]$	257, 238 (sh)	28.5, 22.6, 18.5

[a] Far-i.r. spectra 400—170 cm^{-1} (Nujol mull). Bands believed to be due to ν(Pd–X). [b] Electronic spectra of solids diluted with $BaSO_4$. [c] CH_2Cl_2 solution 28 100 (ε = 2 094), 24 200 (1 080), 20 800 (sh) (441 dm^3 mol^{-1} cm^{-1}). [d] ν(P=S) = 535, ν(P=S) free ligand = 638 cm^{-1}.

0.01—1 V s^{-1}) only several irreversible oxidation processes were observed, consistent with breakdown of the complexes. This is not surprising in that the products of the oxidation, $[PdLX_3]$ or more likely $[PdLX_3]^+$, will be extremely unstable. Addition of $[NR_4]Cl$ did not alter the irreversibility suggesting that co-ordination of chloride to the oxidised palladium ion is too slow to effect stabilisation.

Neutral Complexes $[PdL_2X_4]$.—Treatment of a suspension of *trans*-$[PdL_2Cl_2]$ (L = NMe_3 or py) with a small excess of chlorine in CCl_4 produced orange $[PdL_2Cl_4]$ (Table 1), and the dark red $[Pd(NMe_3)_2Br_4]$ was obtained similarly from $[Pd(NMe_3)_2Br_2]$ and bromine. However, $[Pd(py)_2Br_2]$ did not oxidise, being recovered unchanged on treatment with bromine. These *N*-donor complexes are reasonably stable solids which can be stored at 0 °C for some months without decomposition. Thermogravimetric analysis confirms [16] that $[Pd(py)_2Cl_4]$ reductively eliminates chlorine to form $[Pd(py)_2Cl_2]$, but the trimethylamine complexes again decompose completely on heating. These complexes are shown to be the *trans*-$[PdL_2X_4]$ isomer by the presence of a single strong band in the far-i.r. spectra (Table 2) assignable as $E_u(PdX_4)$.

The attempted oxidation of $[PdL_2Cl_2]$ (L = PMe_2Ph, PPh_3, $AsEt_3$, $AsPh_3$, or $SbMe_3$) with the stoicheiometric amount of chlorine in CCl_4 produced intractable red oils, but by careful control of the conditions $[Pd(PPr^n{}_3)_2Cl_4]$ and $[Pd(AsMe_2Ph)_2Cl_4]$ were isolated. Both are of borderline stability, very difficult to produce in a state of reasonable purity, and decompose in a few days at room temperature. They were assigned *trans* structures on the basis of their far-i.r. spectra (Table 2). Chlorine oxidation of *trans*-$[Pd(SR_2)_2Cl_2]$ (R = Me or Ph) produced deep orange solids which decompose during drying and could not be characterised. From the properties of the crude materials they are probably the Pd^{IV} complexes, which is interesting since *cis*-$[PdLCl_2]$ (L = dithioether) do not oxidise,[17] being recovered unchanged after treatment with Cl_2–CCl_4. Treatment of $[PdL_2Br_2]$ (L = PR_3, AsR_3, or SMe_2) with bromine gave only red oils.

Use of excess chlorine in the oxidation of Pd^{II} complexes of phosphine, arsine, or thioether ligands results in the formation of $PdCl_6{}^{2-}$ (*cf.* ref. 4) and oxidised ligand, *e.g.* Ph_3PO from $[Pd(PPh_3)_2Cl_2]$, a mixture of Ph_3AsO and Ph_3AsCl_2 from $[Pd(AsPh_3)_2Cl_2]$, and Me_2SCl_2 from $[Pd(SMe_2)_2Cl_2]$ identified by a combination of i.r., ^1H n.m.r., and mass spectra.

Discussion

The results described above show that palladium(IV) complexes with unidentate ligands can be isolated, but are much less stable than the platinum(IV) analogues.[13] As expected for a high oxidation state the anionic $[PdLX_5]^-$ are more stable than the neutral $[PdL_2X_4]$. The stability of the Pd^{IV} complexes is very dependent upon L, but for the anions at least, the differences between chloride and bromide are small.

On thermodynamic grounds the decreased stability of Pd^{IV} relative to Pt^{IV} is expected in view of the greater ionisation potential $[Pd_{(g)} \rightarrow Pd^{4+}{}_{(g)} = 10\,652$ kJ mol^{-1}, $Pt_{(g)} \rightarrow Pt^{4+}{}_{(g)} = 9\,364$ kJ mol^{-1} [18]], which is only slightly offset by the lower enthalpy of atomisation of palladium [381 (Pd), 546 (Pt) kJ mol^{-1} [19]]. The $t_{2g}{}^6e_g{}^0$ configuration of the M^{IV} complexes results in maximum ligand field stabilisation energy for the octahedral complexes, and here too the larger Δ values for 5*d* elements (approximately 30% greater) contribute to greater stability for the Pt^{IV} complexes.[20]

The influence of the neutral donor L upon the relative stability of the $[PdLX_5]^-$ ions, $NR_3 \gg PR_3 \sim AsR_3 \sim SR_2 > SeR_2$ ($\gg SbR_3$, TeR_2), is evidence that Pd^{IV} is considerably harder than Pt^{IV}, which in contrast forms its most stable complexes with phosphines and arsines, and bonds tertiary amines much less strongly.[13,17]

Experimental

Physical measurements were made as described previously.[17] The i.r. spectra were obtained using NaCl plates (4 000—600 cm^{-1}) and Polythene plates (400—180 cm^{-1}) since CsI plates were rapidly attacked by the Pd^{IV} complexes. Most of the Pd^{II} starting materials were obtained by literature routes or minor modifications thereof: *viz.* NMe_3,[15] PR_3,[21,22] $AsEt_3$,[21], SMe_2,[23] py.[6]

Although $PdBr_2$ was reported [15] not to react with NMe_3, we found that freshly prepared $PdBr_2$, obtained by repeatedly evaporating $PdCl_2$ with concentrated HBr, readily gave $[Pd(NMe_3)_2Br_2]$ on reaction in acetone (Found: C, 13.4; H, 3.2; N, 5.1. $C_6H_{18}Br_2N_2Pd$ requires C, 13.2; H, 3.3; N, 5.2%); ν(Pd–Br) 215 cm^{-1}; $E_{max.}$ 31 300, 26 700, 23 000 diffuse reflectance (d.r.).

$[NBu_4][PdLCl_3]$ (L = $SeMe_2$, $TeMe_2$, dmso, PPh_3S, or py).—$[NBu_4]_2[Pd_2Cl_6]$. To $Na_2[PdCl_4]$ (1.47 g, 5 mmol) in methanol (30 cm^3) was added $[NBu^n{}_4]Cl$ (1.39 g, 5 mmol in methanol (30 cm^3). After 1 h the solution was rotary evaporated to ~5 cm^3 and the product precipitated with water (100 cm^3), collected, and dried *in vacuo* (2.14 g, 94%).

To $[NBu_4]_2[Pd_2Cl_6]$ (0.23 g, 0.25 mmol) dissolved in acetone (50 cm^3) was added the calculated amount of L (0.5 mmol) and the mixture stirred for 4 h. The solution was then reduced to a small volume ~5 cm^3 and the crude product precipitated with diethyl ether. The oil which is invariably obtained initially crystallises on stirring with diethyl ether over a period of ~2 h. The solid obtained was recrystallised from dichloromethane–diethyl ether. Yields 70—90%.

L = $SeMe_2$. Found: C, 38.4; H, 7.4; N, 2.5. $C_{18}H_{42}Cl_3NPdSe$ requires C, 38.3; H, 7.5; N, 2.5%; ν(Pd–Cl) at 338, 314, 295 (sh) cm^{-1}; $E_{max.}$ 32 000, 22 500 (d.r.).

L = $TeMe_2$. Found: C, 35.0; H, 6.5; N, 2.4. $C_{18}H_{42}Cl_3NPdTe$ requires C, 35.3; H, 6.9; N, 2.3%; ν(Pd–Cl) at 338, 298 cm^{-1}; $E_{max.}$ 28 800, 23 000 (d.r.).

L = dmso. Found: C, 40.1; H, 7.5; N, 5.2. $C_{18}H_{42}Cl_3NOPdS$ requires C, 40.5; H, 7.9; N, 5.3%; ν(Pd–Cl) at 347, 319, 298 (sh) cm^{-1}; $E_{max.}$ 32 800, 27 700, 23 200 (d.r.); ν(S=O) = 1 125 cm^{-1}.

L = PPh_3S. Found: C, 54.2; H, 6.9; N, 1.8. $C_{34}H_{51}Cl_3NPPdS$ requires C, 54.5; H, 6.9; N, 1.9%; ν(Pd–Cl) at 358, 317 cm^{-1}; $E_{max.}$ 27 900, 22 100 (d.r.); ν(P=S) = 585 cm^{-1}.

L = py. Found: C, 47.1; H, 7.5; N, 5.3. $C_{21}H_{41}Cl_3N_2Pd$ requires C, 47.2; H, 7.7; N, 5.2%; ν(Pd–Cl) at 326 (vbr) cm^{-1}; $E_{max.}$ 31 000 (br), 22 900 (d.r.).

No reaction occurred between PPh_3O and $[NBu^n{}_4]_2[Pd_2Cl_6]$ in cold or refluxing acetone solutions.

$[NBu_4][PdLBr_3]$ (L = SMe_2, $TeMe_2$, *or* py).—These were prepared from $[NBu^n{}_4]_2[Pd_2Br_6]$ and L in acetone as described above for the chlorides. No reaction occurred between L = dmso, PPh_3S, and PPh_3O in cold or refluxing acetone solutions. The compound $[NBu^n{}_4]_2[Pd_2Br_6]$ was prepared analogously to the chloride using $Na_2[PdCl_4]$ (1.47 g, 5 mmol) exchanged by stirring overnight in MeOH (100 cm^3) with NaBr (2.06 g, 20 mmol).

L = $SeMe_2$. Found: C, 30.8; H, 6.1; N, 2.1. $C_{18}H_{42}Br_3NPdSe$ requires C, 31.0; H, 6.1; N, 2.0%; ν(Pd–Br) at 265, 249 cm^{-1}; $E_{max.}$ 27 700, 23 800, 20 500 (sh) (d.r.).

L = $TeMe_2$. Found: C, 29.2; H, 5.3; N, 1.9. $C_{18}H_{42}Br_3NPdTe$ requires C, 29.0; H, 5.7; N, 1.9%; ν(Pd–Br) at 257, 233 cm^{-1}; $E_{max.}$ 26 700, 22 200 (d.r.).

L = py. Found: C, 37.8; H, 6.2; N, 4.1. $C_{21}H_{41}Br_3N_2Pd$ requires C, 37.8; H, 6.2; N, 4.2%; ν(Pd–Br) at 267, 244 cm^{-1}; $E_{max.}$ 30 600, 24 800, 21 200 (sh) (d.r.).

$[NR_4][PdLCl_5]$ (L = py, NMe_3, $PPr^n{}_3$, $AsEt_3$, SMe_2, PPh_3S, *or* $SeMe_2$).—The finely ground Pd^{II} complex was suspended in a small volume of dry carbon tetrachloride and rapidly stirred whilst a small excess of chlorine was slowly bubbled in. The mixture was stirred for 30 min when the product was filtered off, but not pumped dry (care should be taken not to pump damp air through the products), and then dried *in vacuo*. Yields were generally >90%.

$[NR_4][PdLBr_5]$ (L = py, PEt_2Ph, $AsEt_3$, SMe_2, *or* $SeMe_2$).—These were prepared analogously to the chlorides by the addition of a small excess of bromine.

$[PdL_2X_4]$ (L = NMe_3, X = Cl *or* Br; L = py, $PPr^n{}_3$, *or* $AsMe_2Ph$, X = Cl).—These were prepared by the methods described above for $[NR_4][PdLX_5]$.

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