# DIRECT ELECTROSYNTHESIS OF HALO AND MIXED-HALO COMPLEXES OF PALLADIUM(II AND IV) BY THE DISSOLUTION OF A SACRIFICIAL PALLADIUM ANODE IN AQUEOUS MEDIUM

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Abstract—A rapid single-step method for the electrosynthesis of chloro and bromo complexes of palladium(II and IV), viz.  $M_2[PdX_4]$  and  $M_2[PdX_6]$ , by the dissolution of a palladium anode in chloride or bromide containing media is described. Electrolysis of dilute HX solution in the presence of pyridine, 2,2'-bipyridyl or 1,10-phenanthroline gives rise to non-electrolytes, e.g. *trans*-[PdX<sub>2</sub>(py)<sub>2</sub>], [PdX<sub>2</sub>(bipy)] and [PdX<sub>2</sub>(phen)]. Anodic oxidation of palladium in HX medium in the presence of acetonitrile and benzonitrile also gives the non-electrolytes *trans*-[PdX<sub>2</sub>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>] and *trans*-[PdX<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>], respectively.

Electrochemical synthesis in which a sacrificial metal anode is dissolved in an electrolyte containing the appropriate ligand has become an established method for the preparation of widely different kinds of complexes in a single step.<sup>1,2</sup> In recent publications<sup>3-5</sup> we have demonstrated that fluoro complexes of transition metals can be conveniently prepared by the dissolution of metal anodes in aqueous HF medium. Oldham and Tuck<sup>6</sup> have reported the preparation of  $(Ph_3PH)_2[CoCl_4]$  using a cobalt anode in acetonitrile containing HCl. The electrosynthesis of H<sub>2</sub>[PtCl<sub>6</sub>] and H[AuCl<sub>4</sub>] has also been reported.<sup>7</sup> The present communication describes the electrosynthesis of palladium(II) and (IV) chloro and bromo complexes, as well as mixedligand haloamine complexes of palladium(II) in a single step using palladium as the anode in aqueous HCl or HBr medium. An interesting case in which a ligand is produced in situ by the cathodic reduction has been utilized for the synthesis of some non-electrolytic complexes of the type  $[PdX_2L_2]$ , where L is a primary amine.

### **EXPERIMENTAL**

Palladium foil (99.95% pure) was supplied by Arora Matthey Limited, India. The electrolytic cell was a tall-form beaker  $(100 \text{ cm}^3)$  fitted with a rubber stopper through which two holes were made. Palladium foil  $(2.5 \times 1.2 \times 0.25 \text{ cm})$  connected to a platinum wire formed the anode and was inserted through one hole. Platinum foil (about  $1 \times 1 \times 0.15$ cm) connected to a platinum wire served as the cathode and was introduced through the second hole. A dc power supply was the source of power.

Palladium, chloride and bromide were analysed by standard gravimetric methods. Nitrogen was determined by micro Dumas' method. IR and electronic spectra and X-ray powder diffraction patterns were recorded by the instruments as reported in our previous communication.<sup>3</sup>

#### Preparation of the compounds

 $M_2[PdCl_6]$  and  $LH_2[PdCl_6]$ , where M = Cs,  $NH_4$ and  $(CH_3)_4N$ ; L = 2,2'-bipyridyl and 1,10-phenanthroline. In the first method HCl (6 M, 10 cm<sup>3</sup>) was taken in a beaker and CsCl,  $(CH_3)_4NCl$ , 2,2'bipyridyl or 1,10-phenanthroline hydrate (0.5 g) was dissolved in it. For the preparation of the ammonium salt  $NH_4Cl$  solution (6 M, 10 cm<sup>3</sup>) alone constituted the electrolyte. The application of a voltage (2–4 V) gave a current of 50 mA. Gradually, the bright red complexes started settling.

In the second method the electrolyte was HCl (6 M) alone. After electrolysis, chlorine was passed through the solution and then the complexes were

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precipitated by adding CsCl, NH<sub>4</sub>Cl, (CH<sub>3</sub>)<sub>4</sub>NCl, 2,2'-bipyridyl or 1,10-phenanthroline hydrate (0.5 g) dissolved in the minimum volume of HCl (6 M).

 $M_2[PdBr_6]$ , where M = Cs and  $(CH_3)_4N$ . These compounds were prepared by methods similar to that described above. In the first method the electrolyte was HBr (6 M, 10 cm<sup>3</sup>), containing CsBr or  $(CH_3)_4NBr$  (0.5 g). Black crystalline complexes came out during the electrolysis. In the second method the electrolyte was HBr (6 M). After electrolysis, bromine water was added followed by the addition of CsBr or  $(CH_3)_4NBr$  dissolved in HBr (6 M).

 $M_2[PdX_4]$  and  $LH_2[PdX_4]$ , where M = Rb, Cs, NH<sub>4</sub> and (CH<sub>3</sub>)<sub>4</sub>N; X = Cl and Br; L = 2,2'-bipyridyl and 1,10-phenanthroline. The electrolysis was carried out using HCl (10 cm<sup>3</sup>) or HBr (6 M, 10 cm<sup>3</sup>). After the electrolysis the brown complexes were precipitated out by adding a slight excess of the appropriate alkali metal halide, NH<sub>4</sub>Cl, (CH<sub>3</sub>)<sub>4</sub>NCl, (CH<sub>3</sub>)<sub>4</sub>NBr, 2,2'-bipyridyl or 1,10phenanthroline, dissolved in the minimum volume of HCl or HBr (6 M).

 $PdCl_2$  and  $PdBr_2$ . The electrolyte was HCl (10 cm<sup>3</sup>) or HBr (0.2 M, 10 cm<sup>3</sup>). After the electrolysis, the solutions were evaporated to a very small volume over a steam bath. The compounds came out on cooling to room temperature.

[PdX<sub>2</sub>L<sub>2</sub>], where X = Cl and Br; L = py,  $\frac{1}{2}$ bipy and  $\frac{1}{2}$ phen. The electrolysis was carried out using HCl (10 cm<sup>3</sup>) or HBr (0.2 M, 10 cm<sup>3</sup>) containing pyridine (0.15 cm<sup>3</sup>), 2,2'-bipyridyl (0.3 g) or 1,10phenanthroline hydrate (0.3 g). The compounds were obtained during the electrolysis. The complexes were also precipitated by adding the bases to the solution obtained from the electrolysis at HCl or HBr solution (0.2 M).

[PdX<sub>2</sub>L<sub>2</sub>], where X = Cl and Br;  $L = C_6H_5$ CH<sub>2</sub>NH<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>. A mixture of (a) HX (1 M, 10 cm<sup>3</sup>), ethanol (6 cm<sup>3</sup>) and benzonitrile (3 cm<sup>3</sup>) or (b) HX (0.5 M, 15 cm<sup>3</sup>) and acetonitrile (5 cm<sup>3</sup>) was electrolysed, followed by evaporation of the solution over a steam bath until the volume was reduced to *ca* 3 cm<sup>3</sup>. On cooling to room temperature brown compounds were obtained.

Details of the experimental conditions along with the yields of the complexes are given in Table 1. The data for all the hexachloro and the hexabromo complexes in the table refer to the first method. The aqueous ethanolic media used for the preparation of the benzylamine complexes necessitated the application of a higher voltage. All the complexes were separated by filtration under suction. The complexes  $[PdX_2(CH_3CH_2NH_2)_2]$ ,  $[PdX_2(C_6H_5$  $CH_2NH_2)_2]$  and those of the type  $[PdX_2L_2]$ , where  $L = py, \frac{1}{2}$  bipy and  $\frac{1}{2}$  phen, were washed with diethylether, chloroform and ethanol, respectively, while the other complexes were dried by pressing between the folds of the filter paper.

### **RESULTS AND DISCUSSION**

In strong HCl or HBr medium (6 M) the palladium anode readily dissolved with the formation of  $[PdX_4]^{2-}$ , which is consistent with the relatively low standard reduction potentials of the couples  $[PdCl_4]^{2-}/Pd$  and  $[PdBr_4]^{2-}/Pd$  (0.59 and 0.49 V, respectively, in 1 M HX medium<sup>8</sup>). The electrochemical efficiency  $E_F$  (defined as the number of moles of palladium oxidized per Faraday) was slightly lower than the expected value of 0.5 mol  $F^{-1}$  (Table 1). This is attributed to the liberation of a little chlorine or bromine at the anode, which escaped.

Electrolysis of a strong solution of ammonium chloride or HCl/HBr (6 M) in the presence of heavy cations resulted in the oxidation of palladium anode to palladium(IV) with the simultaneous precipitation of M<sub>2</sub>[PdCl<sub>6</sub>], LH<sub>2</sub>[PdCl<sub>6</sub>] or M<sub>2</sub>[PdBr<sub>6</sub>]. Despite the relatively higher standard reduction potentials of the systems  $[PdCl_6]^{2-}/[PdCl_4]^{2-}$  and  $[PdBr_6]^{2-}/[PdBr_4]^{2-}$  (1.29 and 0.99 V, respectively, in 1 M HX medium<sup>9,10</sup>), oxidation to the tetravalent state is favoured due to the lower solubility of hexahalopalladate(IV) salts. The hexabromo complexes of palladium(IV) with  $bipyH_2^{2+}$ or  $phenH_2^{2+}$  as the cation could not be prepared in this way probably due to the bromination of the amines. The electrochemical efficiency under these conditions was close to the expected value of 0.25 mol  $F^{-1}$  (Table 1). The slightly lower value may be attributed to the liberation and escape of some chlorine and bromine. Salts of the hexachloropalladates(IV) could also be prepared by the oxidation of  $[PdCl_4]^{2-}$  and  $[PdBr_4]^{2-}$  (generated electrolytically in 6 M acid medium) with chlorine/bromine, followed by the addition of the respective cations. However, the salts  $LH_2[PdBr_6]$ (L = 2,2'-bipyridyl and 1,10-phenanthroline) could not be prepared by this method.

Electrolysis of a solution containing amine hydrochlorides or hydrobromides (halide concentration *ca* 0.2 M) using a palladium anode resulted in the precipitation of  $[PdX_2L_2]$  (where  $L = pyridine, \frac{1}{2}bipy$  and  $\frac{1}{2}phen$ ). The electrochemical efficiency was close to 0.5 (Table 1) and there was virtually no liberation of chlorine or bromine. Hydrogen was liberated at the cathode and a slight liberation of oxygen occurred at the anode.

Interesting reactions occurred when dilute solutions of HCl or HBr (0.25 or 0.5 M) were electrolysed in the presence of acetonitrile and benzo-

	<b>T</b> '	Metal			r		
	vonage	Current	Time	dissolved	Y lei		
Compound	(V)	(A)	(min)	(g)	g	~~~ 	(mol F ')
$(NH_4)_2[PdCl_6]$	3	0.05	120	0.082	0.24	92	0.21
Cs <sub>2</sub> [PdCl <sub>6</sub> ]	4	0.05	60	0.049	0.24	87	0.23
$[(CH_3)_4N]_2[PdCl_6]$	3	0.05	120	0.072	0.26	81	0.18
(bipyH <sub>2</sub> )[PdCl <sub>6</sub> ]	3	0.05	120	0.078	0.30	86	0.20
(phenH <sub>2</sub> )[PdCl <sub>6</sub> ]	3	0.05	120	0.072	0.30	91	0.18
$Cs_2[PdBr_6]$	3	0.05	60	0.039	0.29	93	0.20
$[(CH_3)_4N]_2[PdBr_6]$	3	0.05	60	0.041	0.25	87	0.21
$(NH_4)_2[PdCl_4]$	3	0.10	45	0.140	0.20	56	0.47
Cs <sub>2</sub> [PdCl <sub>4</sub> ]	3	0.05	120	0.167	0.56	71	0.42
$[(CH_3)_4N]_2[PdCl_4]$	3	0.10	60	0.185	0.60	87	0.46
(bipyH <sub>2</sub> )[PdCl <sub>4</sub> ]	2	0.10	60	0.165	0.46	74	0.42
(phenH <sub>2</sub> )[PdCl <sub>4</sub> ]	2	0.10	60	0.175	0.57	76	0.44
Rb <sub>2</sub> [PdBr <sub>4</sub> ]	3	0.10	60	0.180	0.72	72	0.45
$[(CH_{3})_{4}N]_{2}[PdBr_{4}]$	3	0.10	60	0.180	0.59	61	0.45
bipyH <sub>2</sub> [PdBr <sub>4</sub> ]	3	0.10	60	0.175	0.60	63	0.44
phenH <sub>2</sub> [PdBr₄]	3	0.10	60	0.170	0.62	65	0.43
PdCl <sub>2</sub>	2	0.10	60	0.185	0.23	76	0.47
PdBr <sub>2</sub>	3	0.10	60	0.185	0.32	69	0.46
$[PdCl_2(py)_2]$	3	0.05	120	0.190	0.40	63	0.48
[PdCl <sub>2</sub> (bipy)]	3	0.10	60	0.190	0.41	70	0.48
[PdCl <sub>2</sub> (phen)]	3	0.10	60	0.180	0.45	74	0.45
$[PdBr_2(py)_2]$	3	0.05	120	0.171	0.44	61	0.43
[PdBr <sub>2</sub> (bipy)]	2	0.05	120	0.167	0.43	68	0.42
[PdBr <sub>2</sub> (phen)]	2	0.05	120	0.163	0.45	68	0.41
$[PdCl_2(CH_3CH_2NH_2)_2]$	3	0.10	90	0.202	0.12	24	0.33
$[PdCl_2(C_6H_5CH_2NH_2)_2]$	25	0.10	60	0.116	0.10	23	0.29
$[PdBr_2(CH_3CH_2NH_2)_2]$	5	0.10	90	0.208	0.14	20	0.35
$[PdBr_2(C_6H_5CH_2NH_2)_2]$	25	0.10	90	0.180	0.20	25	0.31

Table 1. Experimental conditions for the electrochemical synthesis of compounds

nitrile. The palladium anode was oxidized to palladium(II) and simultaneously the nitriles suffered reduction to the corresponding primary amines (L). The products,  $[PdX_2L_2]$ , crystallized out on evaporation. The electrochemical efficiency with respect to oxidized palladium was much lower (about 0.3 mol F<sup>-1</sup>) than the theoretical value, which may be due to other reactions occurring at the anode. The yields of the complexes based on the amount of palladium oxidized were low (about 25%), since theoretically only 0.5 mol of the amines would be formed per mol of Pd<sup>2+</sup>.

At the anode,  $Pd \longrightarrow Pd^{2+} + 2e$ 

At the cathode,  $RCN + 4H^+ + 4e \longrightarrow$ 

 $RCH_2NH_2$ 

All the complexes gave satisfactory elemental analyses (Table 2). The molecular conductances of dimethylformamide solutions  $(1.0 \times 10^{-3} \text{ M})$  of the

complexes [PdX<sub>2</sub>L<sub>2</sub>], where L = py, CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>2</sub>,  $\frac{1}{2}$ bipy and  $\frac{1}{2}$ phen at 25°C, were very low (1 to 5  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>). The X-ray powder diffraction data of the few complexes which are available in the powder diffraction file agree with our experimental values (Table 2).

The Pd-Cl and Pd-Br stretching frequencies in the IR spectra of  $PdCl_2$  and salts of  $[PdCl_6]^{2-}$ ,  $[PdCl_4]^{2-}$ ,  $[PdBr_6]^{2-}$  and  $[PdBr_4]^{2-}$  agree with the literature values.<sup>11-15</sup> The Pd-X stretching frequencies in the IR spectra of *trans*-[PdCl<sub>2</sub>(py)<sub>2</sub>], trans-[PdBr<sub>2</sub>(py)<sub>2</sub>], [PdCl<sub>2</sub>(bipy)] and [PdCl<sub>2</sub>(phen)] are also consistent (Table 2) with the literature values.<sup>16,17</sup> The IR spectra of [PdCl<sub>2</sub>(py)<sub>2</sub>],  $[PdBr_2(py)_2],$  $[PdCl_2(CH_3CH_2NH_2)_2]$ and  $[PdCl_2(C_6H_5CH_2NH_2)_2]$ exhibit only one v(Pd-X), which suggests that the *trans* forms exist.<sup>16</sup> Despite considerable difficulty in the assignment of v(Pd-N) in the pyridine compounds containing chloride and bromide, this band has been

Compound	% Pd	% Cl	% N	v(Pd—X) (cm <sup>-1</sup> )	X-ray powder diffraction data, d(Å)
(NH₄) <sub>2</sub> [PdCl <sub>6</sub> ]	29.8(30.0)	59.0(59.8)	8.2(7.8)	355	5.65(100), 4.88(75), 2.39(54), 2.92(40), 2.17(30), 2.83(25), 1.71(25), 3.45(20), 1.85(20), 1.62(16)
Ca <sub>2</sub> [PdCl <sub>6</sub> ]	18.8(18.2)	37.1(36.5)		342	
$(Me_4N)_2[PdCl_6]$	23.3(22.8)	45.9(45.5)	6.4(6.1)	346	
(bipyH <sub>2</sub> )[PdCl <sub>6</sub> ]	21.7(22.3)	43.9(44.6)	6.4(5.8)	356	
$(PhenH_2)[PdCl_6]$	21.7(21.2)	42.1(42.4)	5.5(5.5)	342	
Cs <sub>2</sub> [PdBr <sub>6</sub> ]	12.8(12.9)	56.9(56.4)		260	
$(Me_4N)_2[PdBr_6]$	14.8(14.5)	65.4(65.3)	4.1(3.8)		
Cs <sub>2</sub> [PdCl <sub>4</sub> ]	21.6(20.8)	27.1(27.7)		331, 317	3.45(100), 7.41(90), 2.89(40), 3.61(30), 2.55(25), 3.90(20), 2.04(18), 2.60(16), 5.12(14)
$(NH_4)_2[PdCl_4]$	38.4(38.6)	51.8(51.3)	9.8(10.1)	329	7.2(100), 3.65(50), 4.22(45), 3.23(40), 2.52(30), 2.58(20), 2.2(20), 5.16(18), 3.21(16), 2.0(16)
$(Me_4N)_2[PdCl_4]$	26.4(26.9)	36.1(35.8)	7.1(7.0)	320	
$(bipyH_2)[PdCl_4]$	26.4(26.2)	34.6(34.9)	6.6(6.9)	339	
$(PhenH_2)[PdCl_4]$	24.4(24.8)	33.4(32.9)	6.8(6.5)	334	
Rb <sub>2</sub> [PdBr <sub>4</sub> ]	18.0(17.8)	52.9(53.5)		250	
(bipyH <sub>2</sub> )[PdBr <sub>4</sub> ]	18.7(18.3)	54.2(54.6)	4.2(4.7)		
$(PhenH_2)[PdBr_4]$	17.8(17.5)	52.0(52.5)	4.7(4.6)		
PdCl <sub>2</sub>	61.0(60.0)	40.8(39.9)		330, 292	5.32(100), 2.63(80), 1.63(40), 3.09(28), 3.25(24), 1.76(24), 1.60(20), 1.83(13), 1.60(13), 1.83(10)
PdBr <sub>2</sub>	40.6(40.0)	60.9(60.0)			``´
$[PdCl_2(py)_2]$	30.4(29.7)	19.3(19.8)	7.6(7.8)	354	
[PdCl <sub>2</sub> (bipy)]	31.6(32.0)	21.3(21.2)	8.4(8.3)	347	
[PdCl <sub>2</sub> (phen)]	29.4(29.8)	20.1(19.8)	7.9(7.8)	341	
$[PdBr_2(py)_2]$	24.1(23.8)	35.4(35.6)	6.3(6.2)	270	
[PdBr <sub>2</sub> (bipy)]	25.5(25.2)	37.4(37.8)	6.5(6.6)	270	
[PdBr <sub>2</sub> (phen)]	23.3(23.9)	35.8(35.6)	6.1(6.3)		
$[PdCl_2(CH_3CH_2NH_2)_2]$	39.9(39.8)	26.4(26.5)	9.9(10.4)	315	
$[PdCl_2(C_6H_5CH_2NH_2)_2]$	27.4(27.2)	18.4(18.1)	7.2(7.1)	334	
$[PdBr_2(CH_3CH_2NH_2)_2]$	30.0(29.9)	44.3(44.8)	7.9(7.8)		
$[PdBr_2(C_6H_5CH_2NH_2)_2]$	22.3(22.2)	32.8(33.2)	6.1(5.8)		

Table 2. Elemental analyses," IR spectral bands and X-ray powder diffraction data of the complexes

<sup>a</sup> The values in parentheses are calculated.

reported<sup>16</sup> to occur at 278 and 306 cm<sup>-1</sup>, respectively, in the spectra of *trans*-[PdCl<sub>2</sub>(py)<sub>2</sub>] and *trans*-[PdBr<sub>2</sub>(py)<sub>2</sub>], which could be reproduced by us.

The band positions in the electronic spectra of the complexes  $[PdCl_6]^{2-}$ ,  $[PdCl_4]^{2-}$ ,  $[PdBr_4]^{2-}$  and  $[PdCl_2(bipy)]$  agree with the values reported earlier.<sup>18-23</sup> We have checked that the spectral features of the solutions left after the electrolysis of HCl (6 M and 0.2 M) using a palladium anode were identical, displaying absorption maxima at 21,200, 30,000, 35,700 and 45,400 cm<sup>-1</sup>, which show that

the same species, viz.  $[PdCl_4]^{2-}$ , is formed under both the conditions.<sup>24</sup>

The existing methods<sup>25</sup> for the preparation of the salts of  $[PdX_4]^{2-}$  use the precursors  $PdCl_2$  and  $PdBr_2$ , which are prepared by the high-temperature chlorination or bromination of palladium. Another procedure uses  $[PdX_6]^{2-}$  as the starting material. A common method for the preparation of  $[PdCl_6]^{2-}$ is the dissolution of palladium in the foul smelling and obnoxious aqua regia, or in a mixture of HCl and chlorine.<sup>25</sup> Our method is neat, rapid and single step and uses palladium directly with aqueous HCl or HBr at room temperature. The yield is also high. Compounds of the type  $[PdX_2L_2]$  are prepared mainly using  $[PdX_4]^{2-}$  as the starting material. The present work demonstrates that these can also be synthesized electrochemically in a single step. With two typical compounds, e.g. (NH<sub>4</sub>)<sub>2</sub>[PdCl<sub>6</sub>] and  $PdCl_2$ , we have checked that the syntheses can be scaled up by applying a higher current and allowing more time for electrolysis. Our method for the synthesis of non-electrolytic complexes where L is a primary amine is rather novel, since it involves simultaneous anodic oxidation of the metal and cathodic reduction of the nitrile generating the ligand in situ. Although the yield in this case is low, this method is promising for those ligands which can be electrolytically generated with a one- or twoelectron change of the reagent.

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