Synthesis of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2Br_2]$ (X = F, Cl), New and More Versatile Precursors of Pentahalophenyl Derivatives of Palladium(II)

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Abstract

The title compounds (**1**, X = F; **2**, X = Cl) were obtained in quantitative yield by refluxing together $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_4]$ and $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_4]$. Treatment of **1** or **2** with $AgClO_4$ (Pd:Ag = 1:1) gave solutions which behaved as containing '$Pd(C_6X_5)Br$'. **1**, **2** and the '$Pd(C_6X_5)Br$' solutions were checked as precursors of mono-pentahalophenyl derivatives, yielding a variety of complexes $[Pd(C_6X_5)Br(L\text{-}L)]$ (L-L = bipy, tmen, dpe, COD), $[Pd(C_6X_5)BrL_2]$ (L = *p*-TolNH$_2$, py, PPh_3, $AsPh_3$, $SbPh_3$), $[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2L_2]$ (X = F, L = $AsPh_3$; X = Cl, L = $SbPh_3$) and $(NBu_4)[Pd(C_6X_5)Br_2L]$ (X = F, L = py, $AsPh_3$, $SbPh_3$; X = Cl, L = *p*-TolNH$_2$, py, PPh_3, $AsPh_3$, $SbPh_3$). The solutions of '$Pd(C_6X_5)Br$' proved to be the best general precursors of complexes $[Pd(C_6X_5)BrL_2]$ although complexes with $OPPh_3$ could not be obtained.

Introduction

The chemistry of organopalladium and platinum compounds with pentahalophenyl ligands has been reviewed very recently [1, 2]. Over a period of twenty years a variety of complexes containing one, two, three or four C_6X_5 groups attached to the metal centre have been synthesized. Some of the complexes prepared are of particular interest for they can be used as fairly general precursors of a given type of complexes. Thus, the complexes *trans*-$[Pd(C_6X_5)_2(tht)_2]$ (X = F [3], Cl [2, 4]; tht = tetrahydrothiophen) are good synthons of the moiety '*trans*-$Pd(C_6X_5)_2$' since the labile tht ligand can be displaced easily. The anionic complexes $(NBu_4)_2[Pd(\mu\text{-}Y)_2(C_6X_5)_4]$ (X = F, Cl; Y = Cl, Br) [2, 3, 5] are even more general precursors of complexes containing the moiety '*cis*-$Pd(C_6X_5)_2$', either by direct bridge splitting and Y displacement or, better, by removing the Y ligands with $AgClO_4$ in a poorly coordinating solvent; in this way, complexes such as *cis*-$[Pd(C_6X_5)_2(THF)_2]$ [6], *cis*-$[Pd(C_6X_5)_2(CO)_2]$ [6] or *cis*-$[Pd(C_6F_5)_2(dpa)_2]$ [7] (dpa = diphenylacetylene), which could not have been obtained by displacing a tht ligand, can be made easily.

The most general precursors hitherto available for the preparation of complexes containing the moieties '$PdClC_6X_5$' (usually *trans* unless a chelating ligand is used) or 'PdC_6X_5' were the dinuclear complexes $[Pd_2(\mu\text{-}Cl)_2(C_6X_5)_2(tht)_2]$ which are prepared in two-step processes with good combined yields (56% for X = F; 40% for X = Cl) [8] and $[Pd(C_6F_5)Br]_n$ produced by the metal atom technique [9] in very modest yield (10.5%). In this paper we describe the easy synthesis of the new complexes $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2Br_2]$ which are also prepared in two step processes in even better combined yields (81% for X = F; 54% for X = Cl) than the above-mentioned tht complexes and, in addition, are more versatile precursors. We also describe their use as precursors of mono-perhaloaryl complexes.

Experimental

Carbon, H and N analyses were carried out on a Perkin-Elmer 240 microanalyser. Conductivities were measured with a Crisson 522 conductimeter. IR spectra were recorded (in the range 4000–200 cm^{-1}) on a Perkin-Elmer 599 spectrometer, and ^1H NMR spectra on a Varian XL-200 instrument (200 MHz for ^1H). Literature methods were used to prepare the compounds $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_4]$ [2, 3, 5], $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_4]$ [10] and $[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2(tht)_2]$ [8].

The syntheses of the complexes are described below. When several syntheses differed only in the starting material or the ligand used only one complex is described as type procedure.

Synthesis of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2Br_2]$

$(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ (1)

To a solution of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_4]$ (2.5 g, 1.64 mmol) in acetone (40 cm^3) was added

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$(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_4]$ (1.93 g, 1.64 mmol). The mixture was refluxed for 10 h, and then evaporated to dryness. Addition of ^iPrOH (15 cm^3) to the resulting oil and stirring gave an orange product **1** which was filtered and air dried. 99% yield. (Λ_M = 212 ohm^{-1} cm^2 mol^{-1} in *ca.* 5×10^{-4} M solution in acetone.)

$(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6Cl_5)_2Br_2]$ **(2)** was prepared similarly. (Λ_M = 189 ohm^{-1} cm^2 mol^{-1} in *ca.* 5×10^{-4} M solution in acetone.)

Synthesis of [Pd(C$_6$X$_5$)Br(L-L)]

(a) From (NBu$_4$)$_2$[Pd$_2$(μ-Br)$_2$(C$_6$X$_5$)$_2$Br$_2$]: [Pd(C$_6$F$_5$)Br(bipy)] (3)

To a solution of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ (0.127 g, 0.09 mmol) in acetone (10 cm^3) was added bipy (0.029 g, 0.18 mmol). The mixture was stirred for 1 h. Evaporation of the solvent and addition of EtOH (10 cm^3) afforded a yellow product **3** which was filtered and air-dried.

$[Pd(C_6Cl_5)Br(bipy)]$ **(4)**, $[Pd(C_6F_5)Br(tmen)]$ **(5)**, $[Pd(C_6Cl_5)Br(tmen)]$ **(6)**, $[Pd(C_6F_5)Br(dpe)]$ **(7)** and $[Pd(C_6Cl_5)Br(dpe)]$ **(8)** were prepared similarly.

(b) From 'Pd(C$_6$X$_5$)Br' solutions: [Pd(C$_6$F$_5$)-Br(COD)] (9)

To a solution of $AgClO_4$ (0.074 g, 0.36 mmol) in freshly distilled tetrahydrofuran (20 cm^3) was added $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ (0.243 g, 0.18 mmol). After 30 min stirring the precipitate (AgBr) was filtered off; 1,5-cyclooctadiene (44.3 l, 0.36 mmol) was added to the solution. After stirring for 10 min the solution was evaporated to dryness, the residue was extracted with 100 cm^3 of Et_2O and the insoluble $(NBu_4)ClO_4$ was removed. Evaporation of this Et_2O clear solution and addition of n-hexane (5 cm^3) afforded a yellow product **9** which was filtered off and air-dried.

$[Pd(C_6Cl_5)Br(COD)]$ **(10)** was prepared similarly, but the complex was separated from $(NBu_4)ClO_4$ by washing the residue with acetone, where the $(NBu_4)ClO_4$ is very soluble and **10** is only sparingly soluble.

(c) From [Pd$_2$(μ-Br)$_2$(C$_6$X$_5$)$_2$(tht)$_2$]: [Pd(C$_6$F$_5$)-Br(COD)] (9)

To a suspension of $[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(tht)_2]$ (0.46 g, 0.52 mmol) in CH_2Cl_2 (5 cm^3) was added COD (0.4 ml, 3.24 mmol). Instantaneously the suspension changed into a clear mixture which was stirred for 2 min; n-hexane (15 cm^3) was added affording a yellow product **9** which was filtered and air-dried (yield 46%). Evaporation of the remaining solution to 5 cm^3 led to a yellow product, $[Pd(C_6F_5)Br(tht)_2]$, in 41% yield.

Displacement Reaction on [Pd(C$_6$X$_5$)Br(COD)]

To a solution of $[Pd(C_6F_5)Br(COD)]$ (0.095 g, 0.21 mmol) in CH_2Cl_2 (10 cm^3) was added $(NBu_4)Br$ (0.165 g, 0.52 mmol). The mixture changed from yellow to orange in a few minutes. After 2 h stirring, the solvent was evaporated to dryness and ^iPrOH (5 cm^3) was added. An orange compound was obtained that was identified as $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ **(1)** (0.139 g, 80% yield).

The reaction starting from $[Pd(C_6Cl_5)Br(COD)]$, which gave **2** was carried out similarly.

Synthesis of (NBu$_4$)[Pd(C$_6$X$_5$)Br$_2$L

(a) (NBu$_4$)[Pd(C$_6$Cl$_5$)Br$_2$(p-TolNH$_2$)] (11)

p-$TolNH_2$ (0.067 g, 0.67 mmol) was added to an acetone solution (15 cm^3) of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6Cl_5)_2Br_2]$ (0.17 g, 0.11 mmol). The mixture was stirred for 1 h and then evaporated to dryness. The oily residue was washed with n-hexane and stirred in this solvent overnight to give a yellow solid **(11)** which was filtered and air-dried.

(b) (NBu$_4$)[Pd(C$_6$F$_5$)Br$_2$py] (12)

To a solution of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ (0.1 g, 0.07 mmol) in acetone (10 cm^3) was added py (23.8 μl, 0.29 mmol). The mixture was stirred for 1 h and then evaporated to dryness. Addition of Et_2O (10 cm^3) led to a yellow compound **12** which was filtered and air-dried.

$(NBu_4)[Pd(C_6Cl_5)Br_2py]$ **(13)** was prepared similarly.

(c) (NBu$_4$)[Pd(C$_6$Cl$_5$)Br$_2$(PPh$_3$)] (14)

To a solution of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6Cl_5)_2Br_2]$ (0.112 g, 0.07 mmol) in acetone (10 cm^3) was added PPh_3 (0.039 g, 0.15 mmol) whereupon the orange solution changed to yellow. The mixture was stirred for 1 h, then evaporated to dryness and EtOH (10 cm^3) was added. The yellow product obtained, **14**, was filtered and air-dried.

$(NBu_4)[Pd(C_6F_5)Br_2(SbPh_3)]$ 17 and $(NBu_4)[Pd(C_6F_5)Br_2(AsPh_3)]$ **(15)** were prepared similarly. When the mother liquors of **15** were set aside $[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(AsPh_3)_2]$ **(16)** was obtained in 4% yield.

Synthesis of [Pd$_2$(μ-Br)$_2$(C$_6$Cl$_5$)$_2$(SbPh$_3$)$_2$] (19)

$SbPh_3$ (0.071 g, 0.2 mmol) was added to an acetone solution (15 cm^3) of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6Cl_5)_2Br_2]$ (0.152 g, 0.1 mmol) and the mixture was stirred for 90 min. Evaporation to *ca.* 5 cm^3 afforded a yellow product **19** which was filtered and air-dried (yield 25%). The remaining solution was evaporated to dryness and EtOH (10 cm^3) was added; a deep-yellow product was obtained and identified as a mixture of $(NBu_4)[Pd(C_6Cl_5)Br_2(SbPh_3)]$ **(18)** and **19**. This mixture was suspended

in EtOH and stirred for 15 h whereupon **18** changed to **19**. The yellow precipitate **19** was then filtered and air-dried.

Synthesis of [Pd(C_6X_5)BrL$_2$]

(A) From $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2Br_2]$

(a) cis-[Pd(C_6F_5)Br(PPh_3)$_2$] (24). To a suspension of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ (0.226 g, 0.19 mmol) in EtOH (20 cm^3) was added PPh_3 (0.205 g, 0.78 mmol). The mixture was stirred for 1 h and the resulting yellow product (**24**) was filtered and air-dried.

(b) trans-[Pd(C_6F_5)Br(PPh_3)$_2$] (25). PPh_3 (0.13 g, 0.49 mmol) was added to an acetone solution (15 cm^3) of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ (0.168 g, 0.12 mmol), and the mixture was stirred for 1 h. The solution was evaporated to dryness and EtOH (15 cm^3) was added; this led to a pale-yellow solid **25**, which was filtered and air-dried.

cis-$[Pd(C_6Cl_5)Br(PPh_3)_2]$ (**26**), $[Pd(C_6F_5)Br(AsPh_3)_2]$ (**27**), $[Pd(C_6Cl_5)Br(AsPh_3)_2]$ (**28**), $[Pd(C_6F_5)Br(SbPh_3)_2]$ (**29**) and $[Pd(C_6Cl_5)Br(SbPh_3)_2]$ (**30**) were prepared similarly.

(B) From 'Pd(C_6X_5)Br' solutions: [Pd(C_6F_5)Br(p-TolNH$_2$)$_2$] (20)

To a solution of $AgClO_4$ (0.025 g, 0.12 mmol) in freshly distilled tetrahydrofuran (20 cm^3) was added $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ (0.083 g, 0.06 mmol) and the mixture was stirred for 30 min. The solution was evaporated to dryness, the residue was extracted in dry Et_2O (70 cm^3) and the insolubles AgBr and $(NBu_4)ClO_4$ were filtered off. *p*-TolNH_2 (0.026 g, 0.24 mmol) was added to the filtered solution and the mixture was stirred for 30 min. Then the solvent was evaporated and n-hexane (5 cm^3) was added to obtain a yellow product **20** which was filtered and air-dried.

$[Pd(C_6Cl_5)Br(p\text{-}TolNH_2)_2]$ (**21**), $[Pd(C_6F_5)Brpy_2]$ (**22**) and $[Pd(C_6Cl_5)Brpy_2]$ (**23**) were prepared similarly.

^1H NMR data

20: 2.23(s, 3H, Me); 4.75(br.s, 2H, NH_2); 6.77-($2H_A$ aromatic); 6.94($2H_B$ aromatic) J_{AB} = 8.11 Hz.

21: 2.21(s, 3H, Me); 4.73(br.s, 2H, NH_2); 6.70-($2H_A$ aromatic); 6.89($2H_B$ aromatic) J_{AB} = 8.05 Hz.

22: 7.31(dt, $H^3 + H^5$); 7.73(t, H^4); 8.79(d, $H^2 + H^6$); $^3J_{2-3}$ = 6.0 Hz; $^3J_{3-4}$ = 7.7 Hz.

23: 7.31(dt, $H^3 + H^5$); 7.73(t, H^4); 8.92(d, $H^2 + H^6$); $^3J_{2-3}$ = 5.07 Hz; $^3J_{3-4}$ = 7.66 Hz.

Results and Discussion

Synthesis of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2Br_2]$ and 'Pd(C_6X_5)Br'

The complexes $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2Br_2]$ (**1**), (**2**) are easily obtained in virtually quantitative yields by refluxing together stoichiometric amounts of $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_4]$ [2, 3, 5] and $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2Br_4]$ [10] in acetone, whereupon a transarylation occurs. The compounds behave as 2:1 electrolytes in acetone solution and the observation of only one X-sensitive absorption of mainly ν(M–C) character [3, 5] (C_{2h}, B_u) is consistent with a *trans* arrangement of the two C_6X_5 groups in the dimeric anion. Table 1 collects some relevant data of these and the rest of the complexes dealt with in this paper.

Treatment of **1** or **2** with the stoichiometric amount of $AgClO_4$ in a variety of solvents allows the selective removal of one bromide per palladium (eqn. (1)). Filtration of the insoluble AgBr affords solutions which behave as containing 'Pd(C_6X_5)Br', although probably either the solvent or the perchlorate groups are coordinated to the palladium to complete a square-planar coordination. If the presence of $(NBu_4)ClO_4$ is inconvenient, it can be removed by evaporating to dryness and extracting the 'Pd(C_6X_5)Br' in diethyl ether (probably as the complex with two Et_2O ligands) where the $(NBu_4)ClO_4$ is only sparingly soluble, following the same strategy used for the species 'Pd$(C_6X_5)_2$' [6]; this is hardly achieved for X = Cl due to its lower solubility in diethyl ether. On the other hand, the increased unstability of 'Pd(C_6X_5)Br' compared to 'Pd$(C_6X_5)_2$' makes the isolation of the diethyl ether complexes as solids inadvisable.

$$\mathbf{1}\ (\text{or } \mathbf{2}) + 2AgClO_4 \longrightarrow 2\text{'Pd}(C_6X_5)\text{Br'} + 2AgBr + 2(NBu_4)ClO_4 \quad (1)$$

Both types of complexes, $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2Br_2]$ and 'Pd(C_6X_5)Br' in solution have been tested as potential general precursors of monopentahalophenyl complexes and the results are discussed below.

Reactions with Chelating Ligands

When good coordinating chelating ligands are used (2,2′-bipyridine, bipy; *N,N,N′,N′*-tetramethylethylenediamine, tmen; 1,2-bis(diphenylphosphino)ethane, dppe), the result is always the monomeric complex [Pd(C_6X_5)Br(L-L)] both starting from the anionic complexes or from 'Pd(C_6X_5)Br' and regardless of the L-L:Pd ratio used. Thus, if a ratio L-L:Pd = 1:2 is used on the anionic dimers half of the starting material is recovered unchanged and the ligand does not coordinate as exo-bidentate (eqn. (2)). Moreover, the Br^- ligands in solution do not

TABLE 1. Analytical Results, Yields and Relevant IR Data (cm^{-1}) for the Complexes[a]

Complex	Analysis[b]			Yield (%)	IR		Reference
	C	H	N		C_6X_5 [c]	L	
trans-$(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2Br_2]$ (1)	38.8 (39.0)	5.1 (5.4)	2.3 (2.1)	99	795		
trans-$(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6Cl_5)_2Br_2]$ (2)	35.0 (34.9)	4.7 (4.8)	2.1 (1.8)	99	625		
$[Pd(C_6F_5)Br(bipy)]$ (3)				99			9, 11
$[Pd(C_6Cl_5)Br(bipy)]$ (4)	32.6 (32.5)	1.3 (1.4)	4.6 (4.7)	95	628	1595, 1560	
$[Pd(C_6F_5)Br(tmen)]$ (5)				70			11
$[Pd(C_6Cl_5)Br(tmen)]$ (6)	25.9 (26.1)	3.1 (2.9)	5.2 (5.1)	70	620	810, 770	
$[Pd(C_6F_5)Br(dpe)]$ (7)				90			11
$[Pd(C_6Cl_5)Br(dpe)]$ (8)	45.7 (46.1)	2.8 (2.9)		85	610	570, 490 475	
$[Pd(C_6F_5)Br(COD)]$ (9)				80			9
$[Pd(C_6Cl_5)Br(COD)]$ (10)	31.0 (30.9)	2.2 (2.2)		77	620	1570 773, 750	
$(NBu_4)[Pd(C_6Cl_5)Br_2(p\text{-}TolNH_2)]$ (11)	39.9 (40.3)	5.1 (5.2)	3.0 (3.2)	70	625	3360–3310 1510	
$(NBu_4)[Pd(C_6F_5)Br_2py]$ (12)	42.7 (42.9)	5.2 (5.5)	3.6 (3.7)	80	790	1600, 760	
$(NBu_4)[Pd(C_6Cl_5)Br_2py]$ (13)	38.5 (38.7)	4.7 (4.9)	3.7 (3.3)	75	625	1600, 760	
$(NBu_4)[Pd(C_6Cl_5)Br_2(PPh_3)]$ (14)	46.7 (47.0)	5.0 (5.0)	1.4 (1.4)	70	615	520, 505 495	
$(NBu_4)[Pd(C_6F_5)Br_2(AsPh_3)]$ (15)	48.7 (48.9)	5.1 (5.2)	1.6 (1.4)	70	790	480, 470 350–320	
$[Pd_2(\mu\text{-}Br)_2(C_6F_5)_2(AsPh_3)_2]$ (16)				4			8, 12
$(NBu_4)[Pd(C_6F_5)Br_2(SbPh_3)]$ (17)	46.4 (46.7)	5.0 (5.0)	1.4 (1.4)	68	790	450, 460	
$(NBu_4)[Pd(C_6Cl_5)Br_2(SbPh_3)]$ (18)				mixture	625	450, 460	
$[Pd_2(\mu\text{-}Br)_2(C_6Cl_5)_2(SbPh_3)_2]$ (19)				80			8
trans-$[Pd(C_6F_5)Br(p\text{-}TolNH_2)_2]$ (20)	42.3 (42.3)	3.3 (3.2)	4.9 (4.9)	60	790	3640–3550 1510, 1490	
trans-$[Pd(C_6Cl_5)Br(p\text{-}TolNH_2)_2]$ (21)	37.1 (36.9)	2.9 (2.8)	4.2 (4.3)	40	620	3660–3550 1580, 1510	
trans-$[Pd(C_6F_5)Brpy_2]$ (22)				60			8, 9
trans-$[Pd(C_6Cl_5)Brpy_2]$ (23)	32.5 (32.3)	1.7 (1.7)	4.7 (4.7)	40	620	1600 770, 755	
cis-$[Pd(C_6F_5)Br(PPh_3)_2]$ (24)	57.7 (57.5)	3.5 (3.4)		85	790	535, 525 510, 500	3
trans-$[Pd(C_6F_5)Br(PPh_3)_2]$ (25)				85			13
cis-$[Pd(C_6Cl_5)Br(PPh_3)_2]$ (26)	52.4 (52.5)	3.4 (3.1)		70	620	532, 520 508, 488	
$[Pd(C_6F_5)Br(AsPh_3)_2]$ (27)				90			9, 12
$[Pd(C_6Cl_5)Br(AsPh_3)_2]$ (28)	48.1 (48.1)	3.1 (2.9)		80	625	690, 480 470, 330	
$[Pd(C_6F_5)Br(SbPh_3)_2]$ (29)	47.4 (47.6)	2.7 (2.8)		80	786	690, 450	
$[Pd(C_6Cl_5)Br(SbPh_3)_2]$ (30)	44.0 (44.2)	2.5 (2.6)		80	620	690, 450	

[a]For complexes described in the literature by other methods, only our yield and the reference of the earlier synthesis are given. [b]Calculated values in parentheses. [c]Other absorptions: C_6F_5 = 1500, 1050, 950; C_6Cl_5 = 1330–1310.

lead to the formation of $(NBu_4)_2[Pd(C_6X_5)Br_3]$; even in the presence of an excess of $(NBu_4)Br$ it is the dinuclear species which is formed upon crystallization.

$$\mathbf{1}\text{ (or }\mathbf{2}) + \text{L-L} \longrightarrow [Pd(C_6X_5)Br(\text{L-L})] + 2(NBu_4)Br + \tfrac{1}{2}\mathbf{1}\text{ (or }\mathbf{2}) \quad (2)$$

Although the anionic dimers are, thus, the most convenient precursors to $[Pd(C_6X_5)Br(L\text{-}L)]$ complexes with strong ligands, the advantages of the '$Pd(C_6X_5)Br$' solutions become apparent when poorer ligands such as diolefins are used. Thus, 1,5-cyclooctadiene (COD) does not react with the anionic dimers; on the contrary the reverse reaction occurs and $(NBu_4)Br$ displaces COD in $[Pd(C_6X_5)Br(COD)]$ (eqn. (3)). The tht dimers only give a 50% of conversion while the rest of the dimer acts as acceptor of the displaced tht (eqn. (4)). However the '$Pd(C_6X_5)Br$' solutions provide a high yield route to these COD complexes (eqn. (5)), only one of which (X = F) had been described before [9] in a very modest (7%) yield.

$$2[Pd(C_6X_5)Br(COD)] + 2(NBu_4)Br \longrightarrow \mathbf{1}\text{ (or }\mathbf{2}) + 2COD \quad (3)$$

$$[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2(tht)_2] + COD(\text{excess}) \longrightarrow [Pd(C_6X_5)Br(COD)] + [Pd(C_6X_5)Br(tht)_2] \quad (4)$$

$$\text{'}Pd(C_6X_5)Br\text{'} + COD \longrightarrow [Pd(C_6X_5)Br(COD)] \quad (5)$$

Reactions of the Anionic Dimers with Monodentate Ligands

When the anionic dimers $(NBu_4)_2[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2Br_2]$ are reacted with monodentate neutral ligands L in an L:Pd = 1:1 ratio three possible behaviours are to be expected: (i) simple bridge splitting (eqn. (6) in Table 2); (ii) bridge splitting and Br displacement; this reaction needs a L:Pd ratio of 2:1 and hence half of the starting material cannot react (eqn. (7) in Table 2); and (iii) Br displacement with no bridge splitting (eqn. (8) in Table 2). All three behaviours are observed depending on the ligand and the results are summarized in Table 2.

When the L:Pd ratio used is 2:1 it is obvious that, if the second molecule of ligand coordinates to the palladium, the only possible product is $[Pd(C_6X_5)BrL_2]$ (eqn. (9) in Table 2). Not every ligand is able to drive the reaction this way as can be seen in Table 2.

An examination of the results summarized in Table 2 shows that the behaviour exhibited by the ligands roughly follows their nucleophilicities as measured by n_{Pt} [14] p-$TolNH_2 < py < Br^- < SbPh_3 < AsPh_3 < PPh_3$. The ligand $OPPh_3$ has not been assigned n_{Pt}, but it is likely the worst nucleophile and in fact it does not react with **1** or **2**, no matter the excess of ligand used.

The ligands p-$TolNH_2$ and py are unable to take the reaction beyond the initial bridge splitting (eqn. (6)) and the former reveals some differences in reactivity towards **1** and **2** since it only splits the bridges of **2**.

TABLE 2. Summary of Reactions with Monodentate Ligands

$$\mathbf{1}\text{ (or }\mathbf{2}) + 2L \longrightarrow \begin{cases} 2(NBu_4)[Pd(C_6X_5)Br_2L] & (6) \\ [Pd(C_6X_5)BrL_2] + (NBu_4)Br + \tfrac{1}{2}\mathbf{1}\text{ (or }\mathbf{2}) & (7) \\ [Pd_2(\mu\text{-}Br)_2(C_6X_5)_2L_2] + 2(NBu_4)Br & (8) \end{cases}$$

$$[Pd(C_6X_5)BrL_2] + (NBu_4)Br + \tfrac{1}{2}\mathbf{1}\text{ (or }\mathbf{2}) + 2L \longrightarrow 2[Pd(C_6X_5)BrL_2] + 2(NBu_4)Br \quad (9)$$

Complex	L	L:Pd = 1:1[a]	L:Pd = 2:1[a]
1	$OPPh_3$	no	no
2	$OPPh_3$	no	no
1	p-$TolNH_2$	no	no
2	p-$TolNH_2$	no	6
1	py	6	6
2	py	6	6
1	PPh_3	7, *cis*	9, *cis* or *trans*[b]
2	PPh_3	6	6 + 9[c]
1	$AsPh_3$	6 + 8[d]	9
2	$AsPh_3$	7	9
1	$SbPh_3$	6	6 + 9[d]
2	$SbPh_3$	6 + 8[b]	9

[a]The numbers under this heading refer to the equations above. [b]Depending on the conditions used (see 'Experimental'). [c]Excess of L led to eqn. (9). [d]Depending on the solvent used for precipitating the compound (see text).

The stronger nucleophiles PPh_3, $AsPh_3$ and $SbPh_3$, when added in ratio L:Pd 2:1, are able to displace Br^- to give $[Pd(C_6X_5)BrL_2]$ (eqn. (9)) although, in the case of **1**/$SbPh_3$, with some difficulty; in this case the influence of the solvent used for crystallization is determinant, ethanol favouring the displacement of Br^- (eqn. (10)).

$$[Pd(C_6X_5)Br_2(SbPh_3)]^- + SbPh_3 \underset{\text{acetone}}{\overset{\text{EtOH}}{\rightleftharpoons}} [Pd(C_6X_5)Br(SbPh_3)_2] + Br^- \quad (10)$$

Finally when these same ligands (PPh_3, $AsPh_3$, $SbPh_3$) are added in a L:Pd = 1:1 ratio the behaviour is most variable. For the couples **1**/PPh_3 and **2**/$AsPh_3$ only 50% of the starting material reacts to give $[Pd(C_6X_5)BrL_2]$ (eqn. (7)); thus the displacement of Br^- from $[Pd(C_6X_5)Br_2L]^-$ initially formed seems to be preferred to the bridge splitting of the remaining starting **1** or **2** in these cases.

For the rest of the couples, the product of the reaction is $[Pd(C_6X_5)Br_2L]^-$ (eqn. (6)); the picture, however, is complicated in the couples **1**/$AsPh_3$ and **2**/$SbPh_3$ by the fact that the solvent used for crystallization can induce elimination of Br^- from $[Pd(C_6X_5)Br_2L]^-$ to give $[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2L_2]$ (eqn. (11)) thus leading to the behaviour represented in eqn. (8).

$$2[Pd(C_6X_5)Br_2L]^- \xrightarrow{\text{EtOH}} [Pd_2(\mu\text{-}Br)_2(C_6X_5)_2L_2] + 2Br^- \quad (11)$$

For the complexes $(NBu_4)[Pd(C_6X_5)Br_2L]$ two ν(Pd–Br) absorptions are expected whatever the geometry and consequently their geometry cannot be ascertained. The dinuclear complexes $[Pd_2(\mu\text{-}Br)_2(C_6X_5)_2L_2]$ are assigned a *trans* geometry from the observation of only one C_6X_5 X-sensitive absorption [3, 5]. For the $[Pd(C_6X_5)BrL_2]$ complexes the geometry can be assigned from the IR data only for L = PPh_3 [15] in this case the *cis* isomer is initially formed and can be easily isolated if the reaction is carried out in such a way that the complex precipitates, but it isomerizes in solution to the more stable *trans* isomer in the presence of excess of PPh_3.

Reactions of 'Pd(C_6X_5)Br' with Monodentate Ligands

The reactions of solutions containing 'Pd(C_6X_5)Br' with monodentate ligands in the ratio L:Pd = 2:1 are straightforward. Only $OPPh_3$ fails to react and the rest of the ligands give the corresponding $[Pd(C_6X_5)BrL_2]$ complexes. Thus, this route allows us to obtain these complexes for L = py, *p*-TolNH_2 (which could not be obtained from **1** or **2**) and is a cleaner way to $[Pd(C_6X_5)Br(SbPh_3)_2]$. In short, it is the most general route to complexes of this stoichiometry. The ^1H NMR spectra (at 200 MHz) demonstrate that in the complexes $[Pd(C_6X_5)BrL_2]$ (L = *p*-TolNH_2, py; complexes **20**–**23**) both L are equivalent as expected for the *trans* isomer; these data are given in 'Experimental'.

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