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Isolation of chloro-bridged arylpalladium complexes, $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$, in palladium catalyzed C–C cross coupling reaction of triarylbismuth with arylhalides

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The reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with triarylbismuth in dichloromethane at room temperature afforded chloro-bridged arylpalladium complexes, $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ (Ar = Ph or 4-MeC_6H_4 (tol)) in 85–90% yield as a yellow crystalline powder. These complexes were characterized by elemental analysis and NMR spectroscopy. Molecular structures of $[Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2]$ and $[Pd_2Ph_2(\mu\text{-}Cl)_2(PMePh_2)_2]$ were established by single crystal X-ray crystallography. These complexes are centrosymmetric dimers with trans configuration. The C–C coupling reaction between triarylbismuth and an arylhalide in the presence of a base is catalyzed by $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$. The reactions proceed via an arylpalladium complex formed by transmetallation reaction between $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ and Ar_3Bi. Probable reaction routes for C–C coupling have been discussed.

1. Introduction

Metal catalyzed cross coupling reaction of organic halides with organometallic reagents is one of the most important organic transformations for making C–C bonds [1] and is exploited in industry for preparing pharmaceuticals, agrochemicals and fine chemicals [2]. Palladium catalyzed cross coupling reactions are unparalleled due to their flexibility, and ease of handling and preparing palladium complexes which show tolerance to a wide range of functionalities [3]. The well known Suzuki, Negishi, Stille and Kumada C–C cross coupling reactions employ organoboron, organozinc, organotin and organomagnesium reagents, respectively [1]. These reactions require organometallic reagents in stoichiometric amounts and suffer from atom economy. In this context, triarylbismuth compounds are gaining momentum as multi-coupling organometallic compounds and can react with three equivalents of electrophilic reagents. Besides this, they are non-toxic and show high reactivity due to weak Bi–C bond energy. Barton [4], Tanaka [5], Rao [6] and others [7], has demonstrated use of organobismuth compounds in C–C coupling reactions. Both palladium(0) (e. g., $Pd(PPh_3)_4$ [5a]) and palladium(II) (e. g., $Pd(OAc)_2$ [4], $PdCl_2(PPh_3)_2$) [8]) have been used as a catalyst and have shown similar catalytic activity [9]. The formation of an organopalladium species "Ar–Pd–X" as an intermediate has been envisaged in these reactions [4,5a,10].

Coordinately unsaturated metal complexes are proposed as catalytically active species in metal catalyzed organic transformations [11], such as hydrogenation, hydroformylation, C–C coupling reactions, etc. Many palladium-catalyzed reactions are proposed to involve 14-electron, three coordinate complexes. Such complexes are generated either by oxidative addition of an arylhalide on palladium(0) species or by dissociation of a ligand moiety from a four coordinate palladium complex. In fact, Hartwig and coworker [12] have isolated and structurally characterized T-shaped three-coordinate organopalladium complexes. The ease of formation of three-coordinate palladium(II) species has been assessed by density functional theory methods [13]. These tri-coordinated palladium(II) complexes have also been used as a catalyst for polymerization of norbornenes [14] and reactions of arylhalides with organometallic species [15] and amines [16]. Recently binuclear chloro-bridged complexes, $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ have been used as a catalyst in Heck [17] and Suzuki–Miyaura [18] cross coupling reactions. In Suzuki–Miyaura cross coupling, the reaction between *p*-bromoanisole and $ArB(OH)_2$ (Ar = Ph or 4-MeC_6H_4) in the presence of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ gives 32 and 46% yields, respectively of the crossed-coupled product [18].

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With the above perspective we have examined catalytic activity of chloro-bridged binuclear palladium complexes, $Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2$ in the reactions of arylhalides with triarylbismuth. It was anticipated that a three coordinate palladium complex "$PdArCl(PR_3)$" would form as an intermediate by transmetallation reaction. Indeed we could isolate binuclear arylpalladium complexes, $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ from these reactions. Results of this work are described herein.

2. Results and discussion

Halide- bridged palladium complexes, $[Pd_2Y_2(\mu\text{-}X)_2L_2]$ (X = halide, L = neutral donor ligand) are versatile synthons employed for the preparation of a myriad coordination and organometallic complexes [19]. The reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with Ar_3Bi in dichloromethane proceeds smoothly affording chloro-bridged arylpalladium complexes, $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$ (Ar = Ph or 4-MeC_6H_4 (tol)) (eq. (1)) as a pale yellow powder in 85–90% yield. Although as prepared complexes were spectroscopically pure for further reactions, they could be recrystallized from dichlormethane-hexane mixture as pale yellow crystals in 42–59% yield. It is noteworthy that the method is a convenient synthetic approach for the isolation of arylpalladium complexes, $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$. The method reported by Anderson [20] for the preparation of such complexes involved a reaction between $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ and diorganomercurials, Ar_2Hg. The products were isolated in moderate yields due to difficulties in removing RHgCl. Other synthetic methods involve (i) decomposition of a formate-bridged complex, $[Pd_2Ph_2(\mu\text{-}O_2CH)_2(PPh_3)_2]$, either in iodobenzene [21] or in the presence of iodobenzene and 9-iodo-*m*-carborane [22], and (ii) oxidative addition of arylhalides (halide = Br or I) on a two coordinate palladium(0) species, $[Pd\{P(o\text{-}tol)_3\}_2]$ [23]. Interestingly the corresponding methylpalladium complexes, $[Pd_2Me_2(\mu\text{-}Cl)_2(PR_3)_2]$ are obtained in excellent yield by transmetallation reaction of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with either $AlMe_3$ [24] or Me_4Sn [25–27]. In an alternative method for the synthesis of $[Pd_2Me_2(\mu\text{-}Cl)_2(PR_3)_2]$ complexes, [CODPdMeCl] is treated with one equivalent of tertiary phosphine in an appropriate solvent [14,28–31].

$$[Pd_2Cl_2(\mu - Cl)_2(PR_3)_2] + Ar_3Bi \rightarrow [Pd_2Ar_2(\mu - Cl)_2(PR_3)_2] + ArBiCl_2 \tag{1}$$

(where PR_3 = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3; Ar = Ph or 4-MeC_6H_4 (tol))

To assess the utility of chloro-bridged derivatives for the synthesis of other binuclear complexes, reaction of $[Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ with $Pb(EPh)_2$ were carried out and complexes of the type $[Pd_2Ph_2(\mu\text{-}EPh)_2(PMe_2Ph)_2]$ (E = S or Se) (eq. (2)) were isolated.

$$\begin{aligned}&[Pd_2Ph_2(\mu - Cl)_2(PMe_2Ph)_2]\\&\quad + Pb(EPh)_2 \rightarrow [Pd_2Ph_2(\mu - EPh)_2(PMe_2Ph)_2]\end{aligned} \tag{2}$$

The ^1H NMR spectra (Table 1) of chloro-bridged complexes exhibited expected resonances. The $^{31}P\{^1H\}$ NMR spectra displayed a single resonance indicating the presence of one isomeric form. The analogous platinum complexes, $[Pt_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$, exists in a mixture of cis and trans isomers in solution [19]. The palladium complexes are known to undergo rapid cis $\rightleftharpoons$ trans isomerization in solution [19,25], consequently resulting in the observation of a single ^{31}P NMR resonance. Unlike chloro-bridged complexes, the $^{31}P\{^1H\}$ NMR spectra of phenyl dichalcogenolato bridged

Table 1
Physical, analytical and NMR (^1H and ^{31}P) spectral data of organopalladium complexes.

Compound	Re-crystallization solvent (% yield)	m.p (°C)	% Analysis Found (calc.)		NMR data	
			C	H	$^{31}P\{^1H\}$	^1H
$[Pd_2Ph_2(\mu\text{-}Cl)_2(PEt_3)_2]$	Dichloromethane–hexane (48)	120	43.01 (42.75)	6.08 (5.98)	27.0	1.15 (d, t, 6H, CH_3CH_2P); 1.49–1.55 (m, 4H, CH_2P); 6.95 (m, 6H, 3, 4, 5 C_6H_5Pd); 7.31–7.34 (m, 4H, 2, 6 C_6H_5Pd), 7.60 (d, 8 Hz)
$[Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2]$	Dichloromethane–hexane (52)	120	45.02 (44.49)	6.37 (6.32)	27.2	1.18–1.21 (m, 6H, CH_3CH_2P); 1.51 (q, 4H, CH_2P); 2.20 (s, 6H, $CH_3–C_6H_4Pd$); 6.81 (br, 4H, C_6H_4); 7.18 (br, 4H, C_6H_4)
$[Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$	Dichloromethane–hexane (59)	135	47.10 (47.08)	4.44 (4.51)	3.7	1.43 (d, 11 Hz, Me_2P), 6.85 (br, 6H, 3, 4, 5 C_6H_5Pd); 7.07 (br, 4H, 2, 6 C_6H_5Pd); 7.35–7.47 (m, 6H, 3, 4, 5 C_6H_5P); 7.60 (d, 4H, 2, 6 C_6H_5P)
$[Pd_2tol_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$	Dichloromethane-hexane (52)	145	48.63 (48.54)	4.94 (4.89)	3.9	1.43 (d, 11 Hz, Me_2P); 2.17 (s, 6H, $H_3C\text{-}C_6H_5Pd$); 6.71 (br, C_6H_4); 6.94 (br, C_6H_4); 7.42 (m, 6H, 3, 4, 5 C_6H_5P); 7.63 (br, 4H, 2, 6 C_6H_5P)
$[Pd_2Ph_2(\mu\text{-}Cl)_2(PMePh_2)_2]$	Dichloromethane-hexane (51)	140	53.98 (54.43)	4.34 (4.32)	16.8	1.49 (d, 10.5 Hz, CH_3P), 6.75 (m, 6H, 3, 4, 5 C_6H_5Pd); 7.07 (m, 4H, 2, 6 C_6H_5Pd); 7.33 (m, 6H, 3, 4, 5 C_6H_5P); 7.59 (m, 4H, 2, 6 C_6H_5P)
$[Pd_2tol_2(\mu\text{-}Cl)_2(PMePh_2)_2]$	Dichloromethane-hexane (55)	110	55.45 (55.44)	4.84 (4.65)	16.6	1.49 (d, 10.5 Hz, CH_3P); 2.11 (s, 6H, $H_3C\text{-}C_6H_5Pd$); 6.62 (d, C_6H_4); 6.90 (dd, C_6H_4); 7.42 (m, 6H, 3, 4, 5 C_6H_5P); 7.60 (m, 4H, 2, 6 C_6H_5P)
$[Pd_2Ph_2(\mu\text{-}Cl)_2(PPh_3)_2]$	Dichloromethane-hexane (42)	170	59.44 (59.89)	3.86 (4.19)	31.6	6.60 (br, 6H, 3,4,5 C_6H_5Pd); 6.96 (br); 7.23–7.62 (m, *Ph*)
$[Pd_2tol_2(\mu\text{-}Cl)_2(PPh_3)_2]$	Dichloromethane-hexane (45)	150	58.71 (60.62)	4.39 (4.47)	31.3	2.40 (s, 6H, $H_3C\text{-}C_6H_5Pd$); 6.60 (m, 6H, 3, 4, 5 C_6H_5Pd); 6.96 (m, 4H, 2, 6 C_6H_5Pd); 7.23–7.79 (m, *Ph*)
$[Pd_2Ph_2(\mu\text{-}SPh)_2(PMe_2Ph)_2]$	Benzene–hexane (51)	125	55.47 (55.75)	4.85 (4.91)	−2.9, −3.4	1.14 (d, 9.3 Hz, Me_2P); 1.23 (d, 9.6 Hz); 1.75 (d, 13.2 Hz); 6.66–6.95 (m); 7.42–7.76 (m)(*Ph*)
$[Pd_2Ph_2(\mu\text{-}SePh)_2(PMe_2Ph)_2]$[a]	Benzene–hexane (40)	125	50.6 (50.28)	4.51 (4.43)	−5.8, −6.5	1.16 (d, 6H, Me_2P); 6.61–7.59(m,Ph).

[a] $^{77}Se\{^1H\}$ NMR, cis isomer: 66.8 (t, $^2J(^{77}Se–^{31}P)$ = 138 Hz); −201.2 (s). trans isomer; −110.4 (d, $^2J(^{77}Se - {}^{31}P)$ = 134 Hz).

derivatives exhibited two resonances attributable to cis and trans isomers. The analogous hydroxo-bridged complex, $[Pd_2Ph_2(\mu\text{-}OH)_2(PPh_3)_2]$, has been shown to exist as a 1:4 mixture of cis and trans isomers in solution [32].

Molecular structures of $[Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2]$ and $[Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ were established unequivocally by single crystal X-ray diffraction analyses. ORTEP drawings with crystallographic numbering scheme are shown in Figs. 1 and 2, and the selected interatomic parameters are given in Table 2. The complexes are centrosymmetric sym trans dimers with the inversion center in the planar Pd_2Cl_2 rhombus. The coordination environment around each distorted square planar palladium atom is defined by two cis-bridging chloride ligands, phosphorus atom of tertiary phosphine and the C_σ carbon atom of the aryl group. The Pd–Cl distances (~2.41 and ~2.45 Å) differ significantly. The Pd–Cl bond trans to the aryl group is longer than the one trans to the phosphine ligand, and is consistent with the aryl group exerting greater trans influence than the phosphine ligand. These distances are in accord with the binuclear organopalladium complexes [19,26,31]. The Pd–C distances (2.00 Å) are significantly shorter than the binuclear chloro-bridged methylpalladium complexes, $[Pd_2Me_2(\mu\text{-}Cl)_2(L)_2]$ (L = PR_3, $AsPr^i_3$) (2.029–2.100 Å) [14,26,29–31] but are comparable to halo-bridged complexes, $[Pd_2Ph_2(\mu\text{-}I)_2(PPh_3)_2]$ (Pd-C = 1.993(1)Å) [22] and $[Pd_2(C_6H_4Bu^n\text{-}p)_2(\mu\text{-}Br)_2(P\text{-}o\text{-}tol_3)_2]$ (Pd-C = 2.02(1)Å) [23]. The Cl–Pd–Cl angles are within the range (~85°) reported for chloro-bridged binuclear palladium complexes [22,25,28,32].

$$Ar_3Bi + 3Ar'X \xrightarrow[\text{Dioxane, }100^\circ C]{[Pd_2Cl_2(\mu-Cl)_2(PR_3)_2]/\text{Base}} 3-n\,Ar-Ar' + n\,Ar-Ar \tag{3}$$

2.1. C–C coupling reactions

The C–C cross coupling reactions (eq. (3)) between triarylbismuth and a variety of arylhalides in the presence of base and a chloro-bridged palladium complex $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (R = Et or Ph) as a catalyst in refluxing dioxane gave cross-coupled biaryls in addition to homo-coupled products (Table 3). The relative ratio of cross-coupled product and homo-coupled product in each reaction was evaluated by ^1H NMR integration. The cross-coupled and homo-coupled products in the reactions of Ph_3Bi with iodobenzene (entry no. 1) and tol_3Bi with p-tolylhalides (entry nos. 15–17) could not be ascertained as in these reactions only one product is expected (Ph–Ph in the former and tol–tol in the latter).

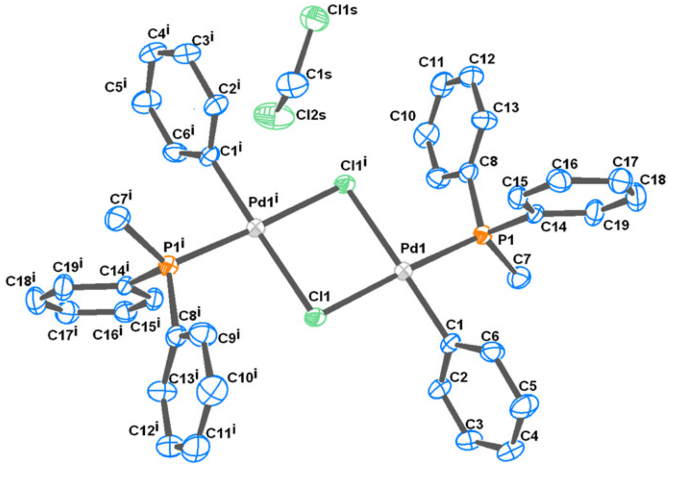


Fig. 1. Molecular structure of $[Pd_2Ph_2(\mu\text{-}Cl)_2(PMePh_2)]$ (ORTEP diagram with 50% probability).

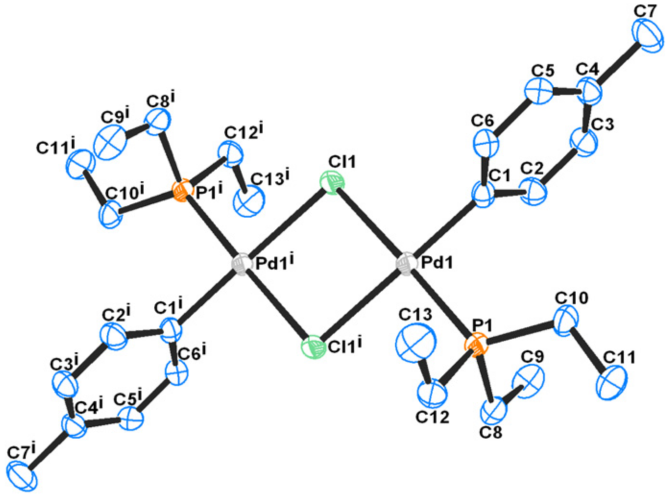


Fig. 2. Molecular structure of $[Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)]$ (ORTEP diagram with 50% probability).

As is evident from Table 3, cross coupling reaction with aryliodides, as expected, is better than the corresponding arylbromides. The arylbromides containing electron releasing groups (e.g. Me) gave better yields than those containing electron withdrawing groups in para position (e.g. OMe) (entries 2 and 8). An increase in yield of biaryls was observed with tetrabutylammonium hydroxide as a base in comparison with K_2CO_3 (entries, 5, 6; 10, 11 and 12, 14). However, in some cases a reverse trend was noticed (entries 3, 4). The PPh_3 complex, $[Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2]$ (entries 6, 16) showed better catalytic activity than the one containing more basic phosphine, $[Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (entries 4, 15).

The C–C cross coupling reactions are often accompanied with a homo-coupled product. Considering the formation of both homo- and cross-coupled products, one can conceive a number of

Table 2
Selected bond lengths (Å) and angles (°) for $[Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2]$ and $[Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$.

	$[Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2]$	$[Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$
Pd1–Cl1	2.4102(16)	2.402(2)
Pd1–Cl1^i	2.4573(18)	2.459(2)
Pd1–P1	2.2187(16)	2.216(2)
Pd1–C1	2.002(6)	2.004(8)
Pd1…Pd1^i	3.538	3.564
Cl1–Pd1–Cl1^i	86.74(6)	85.70(8)
Cl1–Pd1–C1	92.33(17)	92.4(2)
Cl1–Pd1–P1	178.13(5)	177.17(9)
Cl1^i–Pd1–C1	178.97(5)	177.0(2)
Cl1^i–Pd1–P1	91.59(6)	96.76(8)
C1–Pd1–P1	89.34(17)	85.2(2)
Pd1–Cl1–Pd1^i	93.26(6)	94.30(8)

Table 3

Cross coupling reaction of triarylbismuth with arylhalide.

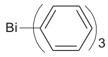
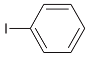
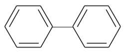
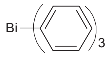
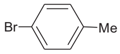
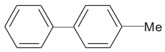
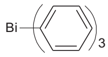
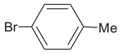
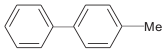
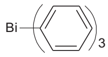
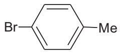
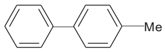
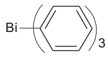
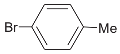
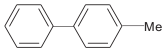
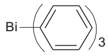
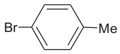
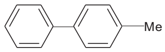
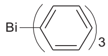
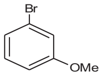
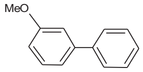
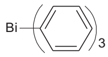
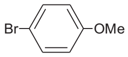
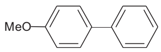
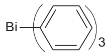
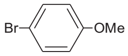
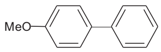
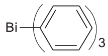
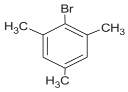
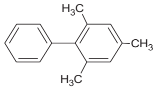
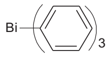
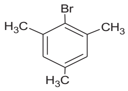
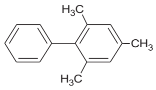
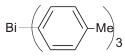
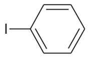
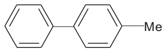
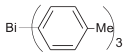
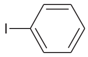
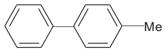
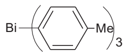
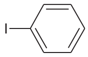
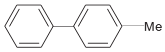
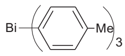
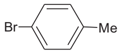
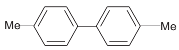
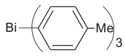
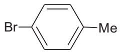
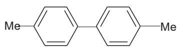
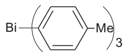
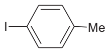
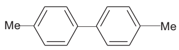
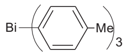
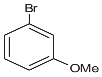
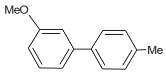
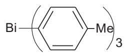
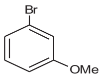
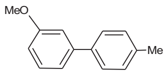
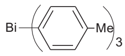
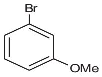
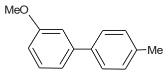
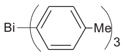
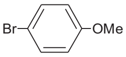
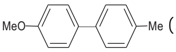
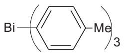
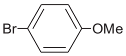
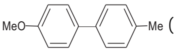
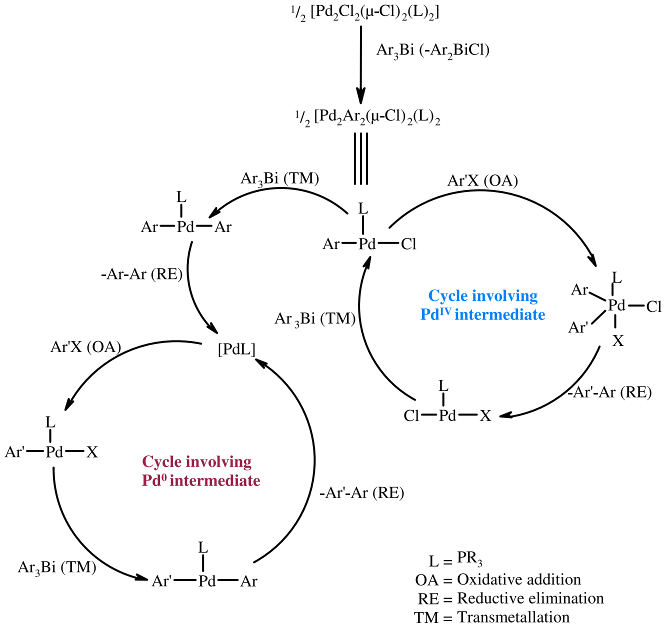
Entry No.	Reactant		Catalyst	Base	Reaction time	% yield[a]	Product(% of cross-coupled product)
	Ar_3Bi	ArBr					
1			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	Bu_4NOH	4 h	98	 (98)
2			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	K_2CO_3	4 h	34	 (93)
3			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	K_2CO_3	5h	75	 (85)
4			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	Bu_4NOH	6 h	35	 (66)
5			$Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2$	K_2CO_3	10 h	51	 (97)
6			$Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2$	Bu_4NOH	6 h	58	 (79)
7			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	K_2CO_3	4 h	71	 (96)
8			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	K_2CO_3	4 h	18	 (96)
9			$Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2$	K_2CO_3	4 h	50	 (98)
10			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	K_2CO_3	4 h	78	 (95)
11			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	Bu_4NOH	4 h	90	 (97)
12			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	K_2CO_3	4 h	66	 (30)
13			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	Bu_4NOH	3 h	84	 (58)
14			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	Bu_4NOH	4 h	90	 (73)
15			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	Bu_4NOH	3 h	46	 (100)
16			$Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2$	Bu_4NOH	2 h	65	 (100)
17			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	Bu_4NOH	3 h	72	 (100)
18			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	K_2CO_3	4 h	16	 (5)
19			$Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2$	K_2CO_3	6 h	45	 (51)
20			$Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2$	K_2CO_3	9 h	72	 (18)

Table 3 (*continued*)

Entry No.	Reactant		Catalyst	Base	Reaction time	% yield[a]	Product(% of cross-coupled product)
	Ar_3Bi	ArBr					
21			$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$	K_2CO_3	4 h	44	 (5)
22			$Pd_2Cl_2(\mu\text{-}Cl)_2(PPh_3)_2$	K_2CO_3	4 h	75	 (45)

[a] Corresponds to cross-coupled and homo-coupled product.

pathways for the reaction between triarylbismuth with arylhalides catalyzed by $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (Scheme 1). Initially transmetallation reaction between $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ and Ar_3Bi yields a three-coordinate arylpalladium complex "PdClArL" (L = PR_3) which undergoes second transmetallation, when excess of Ar_3Bi is present, to give "Ar_2PdL". In the absence of excess of triarylbismuth, as during the synthesis of $[Pd_2Ar_2(\mu\text{-}Cl)_2(PR_3)_2]$, dimerization of "PdClArL" [13] takes place to afford isolable chloro-bridged arylpalldium complexes. The diarylpalladium species "Ar_2PdL" undergoes reductive elimination of biaryl (a homo-coupled product) with concomitant formation of a palladium(0) (PdL) species. In a control experiment a reaction between tol_3Bi and $[Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ in the presence of Bu_4NOH in refluxing dioxane gave a cross-coupled product (Ph-tol) suggesting the formation of "PhtolPd" species which reductively eliminates the biaryl. Alper et.al, has shown the formation of '[PdL]' as a catalytically active species involved in palladium catalyzed carbonylation reactions [21,33]. The stability of this species is dependent on the nature of the L [33]. The '[PdL]' undergoes oxidative addition reactions with various substrates (Ar'X, Ar_3Bi, Ar_2BiX, etc.) to generate palladium(II) derivatives which on transmetallation followed by reductive elimination of biaryls regenerates "PdL" (Scheme 1). An alternative pathway can also be considered. This route may involve oxidative addition of an arylhalide on a three-coordinate palladium(II) species, [PdClArL], to give a five coordinate palladium(IV) intermediate, '[PdArAr'ClXL]' which on reductive elimination of a cross-coupled product (Ar–Ar') generates 'PdClXL'. In a control experiment, reactions between *p*-tolylbromide and isolated $[Pd_2Ph_2(\mu\text{-}Cl)_2(PR_3)_2]$ (PR_3 = PEt_3 and PMe_2Ph) in 2: 1 stoichiometry in refluxing dioxane in the presence of Bu_4NOH, though sluggish, gave a crossed-coupled product (tol–Ph) indicating the formation of a '[PdArAr'ClXL]' species. The latter after transmetallation by arylbismuth compounds (it may be noted that the transmetallation of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ by Ph_2BiCl affording $[Pd_2Ph_2(\mu\text{-}Cl)_2(PEt_3)_2]$ was equally facile) yield the parent three-coordinate palladium complex, '[PdClArL]'. The oxidative addition of an organic halide on palladium(II) to give organopalladium(IV) complexes and reductive elimination of a C–C coupled product from the latter is well documented in literature [34,35].



Scheme 1. Proposed catalytic cycle.

3. Experimental

3.1. Material and methods

The compounds $[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ (PR_3 = PEt_3, PMe_2Ph, $PMePh_2$, PPh_3) [36] and Ar_3Bi (Ar = Ph, 4-MeC_6H_4 (tol)) [37] were prepared according to literature methods. All reactions were carried out under an argon atmosphere in dry and distilled solvents. Microanalyses were carried out on a Thermo Fischer EA 1110–CHNS instrument. IR spectra were recorded as Nujol mulls between CsI plates on a Bomem MB-102 FT IR spectrometer. The ^1H, $^{31}P\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a Bruker Avance-II 300 MHz NMR spectrometer operating at 300.13, 121.49 and 57.24 MHz, respectively. Chemical shifts are relative to internal $CHCl_3$ for ^1H and external 85% H_3PO_4 for ^{31}P and Me_2Se for ^{77}Se NMR (secondary reference Ph_2Se_2, δ 463 ppm)

3.2. Syntheses

3.2.1. Synthesis of $[Pd_2Ph_2(\mu\text{-}Cl)_2(PEt_3)_2]$

To a dichloromethane (20 ml) solution of $[Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (163 mg, 0.275 mmol), a benzene solution of Ph_3Bi (122 mg, 0.277 mmol) was added with stirring under a nitrogen atmosphere. The reactants were stirred for 3 h and then filtered through a G-3 filtering unit. The filtrate was evaporated under vacuum to give a pale yellow solid (164 mg, 88%) which was recrystallized from dichloromethane–hexane mixture in 48% yield. Pertinent data are given in Table 3. Similarly, other chloro-bridged complexes have been isolated.

3.2.2. Synthesis of $[Pd_2Ph_2(\mu\text{-}SPh)_2(PMe_2Ph)_2]$

To a dichloromethane (20 ml) solution of $[Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2]$ (58 mg, 0.081 mmol) solid $Pb(SPh)_2$ (39 mg, 0.091 mmol) was added with stirring which continued for 3 h. The solution was filtered through a celite column and the filterate was

Table 4
Crystallographic and structural refinement data for [$Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2$] and [$Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2$].

Complex	[$Pd_2tol_2(\mu\text{-}Cl)_2$ ($PEt_3)_2$]	[$Pd_2Ph_2(\mu\text{-}Cl)_2$ ($PMePh_2)_2$]0.2(CH_2Cl_2)
Chemical formula	$C_{26}H_{44}Cl_2P_2Pd_2$	$C_{38}H_{36}Cl_2P_2Pd_2$ 2(CH_2Cl_2)
Formula weight	702.25	1008.16
Crystal size (mm^3)	0.15 × 0.15 × 0.30	0.1 × 0.1 × 0.2
Crystal system	monoclinic	Triclinic
Space group	$P2_{1/n}$	P-1
Unit cell dimensions		
a(Å)	6.893(3)	6.860(4)
b(Å)	17.315(4)	13.000(5)
c(Å)	12.744(6)	13.469(4)
α(°)	–	68.30(2)
β(°)	94.46(4)	77.74(4)
γ(°)	–	76.59(4)
Volume ($Å^3$)	1516.5(11)	1074.9(8)
ρ calcd. ($g\ cm^{-3}$)	1.538	1.557
Z	2	1
μ (mm^{-1})/F(000)	1.480/712	1.311/504
Limiting indices	$-8 \le h \le 8$	$-8 \le h \le 4$
	$-22 \le k \le 0$	$-16 \le h \le 16$
	$-9 \le l \le 16$	$-17 \le h \le 17$
θ range of data collection (°)	2.85 to 27.48	2.74 to 27.51
Reflections collected/unique	3467/2227	4909/2470
Data/restraints/parameters	3467/0/149	4909/0/227
Final R_1, ωR_2 indices	0.0482/0.1146	0.0622/0.1441
R_1, ωR_2 (all data)	0.0987/0.1351	0.1684/0.1830
Goodness of fit on F^2	1.021	0.985

dried *in vacuo* to give an orange solid (62 mg, 90%). Similarly [$Pd_2Ph_2(\mu\text{-}SePh)_2(PMe_2Ph)_2$] was prepared employing [Pb(SePh)$_2$].

3.3. C–C cross coupling reaction between an arylhalide and organobismuth compound

To a dioxane (3 ml) solution of 2-bromomesitylene (110 mg, 0.55 mmol) and Ph_3Bi (72.9 mg, 0.17 mmol) was added powdered K_2CO_3 (92.4 mg, 0.67 mmol) and [$Pd_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2$] (10 mg, 0.017 mmol). (A lower concentration of the catalyst ArX:Pd (35:1) also gave similar results). The whole was heated at 100 °C in an oil bath with stirring for 4 h. The contents were cooled to room temperature and acidified with dilute HCl (10 ml) and extracted with ethylacetate (15 ml × 3). The combined extracts were washed with water (2 × 15 ml) and brine (15 ml) and dried over anhydrous Na_2SO_4. This was filtered and dried under vacuum to give colorless oil (75 mg, 78% yield) and was characterized as Mes-Phenyl by ^1H NMR spectroscopy. Similarly, other C–C coupling reactions were carried out and yields were calculated based on aryl groups of Ar_3Bi consumed in the reactions.

3.4. Crystallography

Intensity data for [$Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2$] and [$Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2$] were collected at room temperature (298 ± 2 K) on a Rigaku AFC 7S diffractometer fitted with Mo-Kα (λ-0.71069 Å) radiation so that $\theta_{max} = 27.5°$. The intensity data were corrected for Lorenz, polarization and absorption effects with an empirical procedure [38,39]. The structures were solved by direct methods [40] and refinement was on F^2 [41]. The non-hydrogen atoms were modeled with anisotropic displacement parameters while the hydrogen atoms were fixed in their calculated positions. Molecular structures were drawn using ORTEP [42]. Crystal data and refinement details are given in Table 4.

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Appendix A. Supplementary material

CCDC 823413 and 823414 contain the supplementary crystallographic data for [$Pd_2Ph_2(\mu\text{-}Cl)_2(PMe_2Ph)_2$] and [$Pd_2tol_2(\mu\text{-}Cl)_2(PEt_3)_2$], respectively for this paper. These data can be obtained free of charge atwww.ccdc.cam.ac.uk/conts/retrieving.htmlor from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; E-mail : deposit@ccdc.cam.ac.uk).

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