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Selectivity in reductive elimination and organohalide transfer from methyl(aryl)benzylpalladium(IV) complexes of bidentate nitrogen donor ligands, $PdBrMe(Ar)(CH_2Ph)(L_2)$

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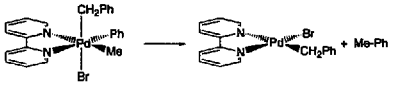
Abstract

Oxidative addition of iodoarenes to bis(dibenzylideneacetone)palladium(0) in the presence of *N,N,N',N'*-tetramethylethylenediamine (tmeda) affords $PdI(Ar)(tmeda)$ ($Ar = 4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $4\text{-}Me(O)CC_6H_4$, $4\text{-}O_2NC_6H_4$, $3\text{-}MeOC_6H_4$) in high yield. Some of these complexes ($Ar = 4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $3\text{-}MeOC_6H_4$) react with LiMe to form $PdMeAr(tmeda)$, and the methyl(aryl)palladium(II) complexes react with 2,2'-bipyridyl (bpy) or 1,10-phenanthroline (phen) to afford $PdMeAr(L_2)$; $PdMePh(phen)$ may be obtained similarly. All of the diorganopalladium(II) complexes of bpy and phen react with benzyl bromide to form $PdBrMeAr(CH_2Ph)(L_2)$ but a complex could not be isolated for $Ar = 3\text{-}MeOC_6H_4$, L_2 = bpy. The isolated palladium(IV) complexes react with $PdMe_2(bpy)$ at $-20\,^{\circ}C$ in $(CD_3)_2CO$ to selectively transfer benzyl bromide to give $PdMeAr(L_2)$ and $PdBrMe_2(CH_2Ph)(bpy)$ respectively. The complexes $PdBrMeAr(CH_2Ph)(bpy)$ (Ar = Ph, $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$) undergo selective reductive elimination of Ar–Me in $CDCl_3$ to form $PdBr(CH_2Ph)(L_2)$, but $PdBrMeAr(CH_2Ph)(phen)$ (Ar = Ph, $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $3\text{-}MeOC_6H_4$) give mixtures of $PdBr(CH_2Ph)(phen)$ and Me–Ar together with lesser amounts of $PdBrMe(phen)$ and $Ar\text{–}CH_2Ph$ (ca. 10–20%).

Keywords: Palladium; Oxidative addition; Reductive elimination; Redox reactions; Alkyl transfer

1. Introduction

Reductive elimination from triorganopalladium(IV) complexes is providing interesting examples of selectivity in C–C bond formation at a transition metal centre [1–8], as illustrated by Eq. (1) for the decomposition of $PdBrMePh(CH_2Ph)(bpy)$ (bpy = 2,2'-bipyridine) in acetone to give toluene as the only coupling product [7]. Selectivity in coupling of organic groups at palladium(IV) centres has been proposed as a step in several organic synthesis procedures [5,9–15], and in most of these syntheses an aryl group is part of the coordination sphere of palladium [9,11,13–15]. Selectivity also occurs in alkyl halide transfer reactions between palladium(IV) reagents containing three different organo groups and dimethylpalladium(II) reagents, for which transfer of benzyl bromide is exclusively favoured over methyl and phenyl bromide transfer, as illustrated in Eq. (2) [7].



(1)

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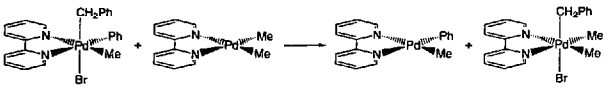

(2)

Transfer reactions similar to that in Eq. (2) could possibly occur during organic syntheses involving palladium(II) and palladium(IV) intermediates, and thus both the selectivities in coupling of different organic groups at the palladium(IV) centre and in transfer reactions may play a crucial role in the syntheses. We report here the preparation of a range of complexes $PdBrMeAr(CH_2Ph)(L_2)$ [L_2 = bpy or phen (1,10-phenanthroline)] containing substituted Ar groups, and studies of their decomposition and alkyl halide transfer reactivity in order to determine whether the high selectivities in the reactions of Eqs. (1) and (2) represent general phenomena in palladium(IV) chemistry. Aryl groups containing substituents exhibiting different inductive (H, Me, MeO, Me(O)C, O_2N) and mesomeric (4-MeO, 4-Me(O)C, 4-O_2N) effects were chosen, and substituents in the 2- and 6-positions were avoided in order to circumvent steric difficulties at the octahedral palladium(IV) centre. The ligand phen has been included in the study because it has been established that more rigid ligands tend to reduce selectivity in elimination of ethane from several dimethyl(benzyl)palladium(IV) complexes of the general formulation $PdBrMe_2(CH_2Ph)(L_2)$ (L_2 = bidentate nitrogen donor ligand) [2,4,8].

2. Results

2.1. Synthesis

The new palladium(II) complexes **1b–f**, **2b–d**, **3b–d** and **3a′–d′** were synthesized beginning with bis(dibenzylideneacetone)palladium(0) according to Eqs. (3)–(5), by following the reported procedures for PdIPh(tmeda) (**1a**), PdMePh(tmeda) (**2a**) and PdMePh(bpy) (**3a**) [16]. As observed for related iodoarene oxidative addition reactions [16,17], the yields for the complexes **1b–f** obtained from the reaction of Eq. (3) are high (76–100%). The reactions of Eqs. (4) and (5) proceed with yields of 87–98% and 57–93% respectively, but attempted methylation of the complexes **1e** and **1f** according to Eq. (4) was unsuccessful.

$$Pd(dba)_2 + tmeda + ArI \rightarrow \underset{\textbf{1a–f}}{PdIAr(tmeda)} + 2dba \quad (3)$$

1a: Ar = Ph, **1b**: Ar = 4-MeC_6H_4, **1c**: Ar = 4-$MeOC_6H_4$

1d: Ar = 3-$MeOC_6H_4$, **1e**: Ar = 4-Me(O)CC_6H_4, **1f**: Ar = 4-$O_2NC_6H_4$

$$PdIAr(tmeda) + LiMe \rightarrow \underset{\textbf{2a–d}}{PdMeAr(tmeda)} + LiI \quad (4)$$

2a: Ar = Ph, **2b**: Ar = 4-MeC_6H_4

2c: Ar = 4-$MeOC_6H_4$, **2d**: Ar = 3-$MeOC_6H_4$

$$PdMeAr(tmeda) + L_2 \rightarrow \underset{\textbf{3a–d, 3a′–d′}}{PdMeAr(L_2)} + tmeda \quad (5)$$

3a: Ar = Ph, L_2 = bpy — **3a′**: Ar = Ph, L_2 = phen

3b: Ar = 4-MeC_6H_4, L_2 = bpy — **3b′**: Ar = 4-MeC_6H_4, L_2 = phen

3c: Ar = 4-$MeOC_6H_4$, L_2 = bpy — **3c′**: Ar = 4-$MeOC_6H_4$, L_2 = phen

3d: Ar = 3-$MeOC_6H_4$, L_2 = bpy — **3d′**: Ar = 3-$MeOC_6H_4$, L_2 = phen

All of the new complexes exhibit microanalyses and ^1H NMR spectra in accord with the formulations presented in Eqs. (3)–(5), e.g. on comparison with reported spectra of PdIMe(tmeda) (**1a**) and $PdMe_2$(bpy) [18], PdMePh(tmeda) (**2a**) and PdMePh(bpy) (**3a**) [16].

The palladium(IV) complexes (**4b–c**, **4a′–d′**) were obtained on oxidative addition of benzyl bromide to the appropriate $PdMeAr(L_2)$ complexes at 0 °C in acetone (Eq. (6)), as reported for the synthesis of PdBrMePh(CH_2Ph)(bpy) (**4a**) [7], or at −10 °C in dichloromethane for some of the less soluble phen complexes (**3a′**,

3b'). The complexes were isolated at −60 °C, and as they are unstable their ^{1}H NMR spectra and reactivity toward decomposition and organobromide exchange were examined immediately after isolation.

$$\underset{\textbf{4a–c, 4a'–d'}}{PdBrMeAr(CH_2Ph)(L_2)} \quad (6)$$

4a: Ar = Ph, L_2 = bpy **4a'**: Ar = Ph, L_2 = phen

4b: Ar = 4-MeC_6H_4, L_2 = bpy **4b'**: Ar = 4-MeC_6H_4, L_2 = phen

4c: Ar = 4-$MeOC_6H_4$, L_2 = bpy **4c'**: Ar = 4-$MeOC_6H_4$, L_2 = phen

4d': Ar = 3-$MeOC_6H_4$, L_2 = phen

The new palladium(IV) complexes (**4b,c**; **4a'–d'**) exhibit ^{1}H NMR spectra that are very similar to that reported for complex **4a**, and resonances may be assigned by direct comparison.

Unlike its phenanthroline counterpart, PdMe(3-$MeOC_6H_4$)(bpy) did not yield an isolable palladium(IV) complex upon reaction with benzyl bromide. Therefore, the reaction was studied by in situ ^{1}H NMR spectroscopy. Addition of an excess of benzyl bromide to a cooled (−10 °C) solution of PdMe(3-$MeOC_6H_4$)(bpy) in $CDCl_3$ and subsequent slow warming of this solution showed that upon formation of the palladium(IV) complex (e.g. 2.30 ppm (s, Pd(IV)–Me); 6.33, 6.52, 6.67 ppm (m, 't', 't', Pd(IV)–CH_2 *Ph*); 8.24, 8.66 ppm (d (^3J = 5.2 Hz), d (^3J = 5.4 Hz), H_6–bpy)) an immediate reaction took place. The resulting very complex spectrum indicates more than one decomposition pathway, but there was no general decomposition to give palladium metal. Only 3-methylanisole and PdBrMe(bpy) could be definitely assigned. The decomposition behaviour of this complex is not compared with the other studies of reductive elimination since the excess of benzyl bromide may influence the reductive elimination.

2.2. Reductive elimination

All of the palladium(IV) complexes showed facile decomposition behaviour at ambient temperature to give C–C coupling products and monoorganopalladium(II) species that could be readily identified by ^{1}H NMR spectroscopy (Eqs. (7) and (8)). Palladium metal is not formed in any of the decomposition reactions, and the spectra indicate that $PhCH_3$ (except for **4a** and **4a'**), $PdBr_2(L_2)$, MeH and ArH are also not formed.

$$\underset{\textbf{4a–c}}{PdMeAr(CH_2Ph)(bpy)} \rightarrow PdBr(CH_2Ph)(bpy) + Ar\text{–}Me \quad (7)$$

$$PdMeAr(CH_2Ph)(phen) \rightarrow a[PdBr(CH_2Ph)(phen) + Ar\text{–}Me] + b[PdBrMe(phen) + Ar\text{–}CH_2Ph] \quad (8)$$

4a' (a = 0.83, b = 0.17), **4b'** (a = 0.91, b = 0.09)

4c' (a = 0.87, b = 0.13), **4d'** (a = 0.90, b = 0.10)

2.3. Alkyl bromide transfer from palladium(IV) to palladium(II)

All of the new palladium(IV) complexes react cleanly with $PdMe_2$(bpy) at −20 °C in $(CD_3)_2CO$ to selectively transfer benzyl bromide according to Eq. (9).

$$\underset{\textbf{4a–c, 4a'–d'}}{PdBrMeAr(CH_2Ph)(L_2)} + PdMe_2(bpy) \rightarrow \underset{\textbf{3a–c, 3a'–d'}}{PdMeAr(L_2)} + PdBrMe_2(CH_2Ph)(bpy) \quad (9)$$

3. Discussion

The synthetic methods illustrate the general applicability of the oxidative addition reaction (Eq. (3)), transmetallation (Eq. (4)) except for nitro and acetyl substituted phenyl groups, displacement of tmeda (Eq. (5)) and oxidative addition of benzyl bromide to palladium(II) (Eq. (6)). The new palladium(IV) complexes have low stability and undergo clean reductive elimination reactions (Eqs. (7) and (8)) and benzyl bromide transfer (Eq. (9)).

The bpy complexes exhibit high selectivity for aryl–methyl coupling, but with phen as the bidentate ligand ca. 10–20% of the decomposition proceeds to give aryl–benzyl coupling (Eq. (8)). The selectivity in coupling for L_2 = bpy is unaffected by change of Ar, and for L_2 = phen the product distributions from **4a'–d'** are similar, indicating that the major determinant of selectivity is L_2.

The lower selectivity observed for the phen complexes suggests that the preference for aryl–methyl over

aryl–benzyl coupling is not very great, since the change in ligand environment is minor. Selectivity in coupling may be expected to result from a combination of thermodynamic and kinetic factors. It has been suggested that Me–Me and Me–CH_2Ph bond energies are the main factors that determine selectivity in reductive elimination from $PdBrMe_2(CH_2Ph)(L_2)$ [19], and the selectivity for Ar–Me coupling exhibited by $PdBrMeAr(CH_2Ph)(bpy)$ (Eq. (7)) is consistent with this in view of the bond energy sequence Ar–Me > Ar–CH_2Ph > Me–CH_2Ph. Thus, kinetic factors are assumed to account for the differences in selectivity exhibited in Eqs. (7) and (8). These factors could include the requirement for preliminary halide loss from $PdBrMeAr(CH_2Ph)(L_2)$ to facilitate the lowest energy pathway for reductive elimination, suggested from kinetic studies of reductive elimination by $PdIMe_3(bpy)$ [19,20], and (re)orientation of the organic groups to positions appropriate for reductive elimination by methyl, aryl, or benzyl groups at an (expected) octahedral centre $[PdMeAr(CH_2Ph)(L_2)(acetone)]^+$. This latter step appears to be the one at which a change of L_2 from bpy to phen would have greatest effect, since phen is more rigid than bpy, and thus the transition state(s) leading to the thermodynamically preferred Ar–Me coupling may be less accessible. For example, coupling from $[PdMe_3(L_2)(acetone)]^+$ is believed to involve an equatorial and an axial methyl group rather than the two equatorial methyl groups [19]; a similar elimination pathway from $[PdMeAr(CH_2Ph)(L_2)(acetone)]^+$ to give Ar–Me coupling requires isomerisation since both Me and Ar groups are *trans* to L_2 in $PdBrMeAr(CH_2Ph)(L_2)$.

The high selectivity for benzyl bromide transfer from palladium(IV) to palladium(II) (Eq. (9)) is consistent with the proposed mechanism for this type of reaction. It has been suggested that preliminary bromide loss from $PdBrMeAr(CH_2Ph)(L_2)$ to form $[PdMeAr(CH_2Ph)(L_2)]^+$ (probably solvated as $[PdMeAr(CH_2Ph)(L_2)(acetone)]^+$) is followed by nucleophilic attack by $PdMe_2(bpy)$ on the alkyl group(s) at the cationic palladium(IV) centre [2,7]. Normally, nucleophilic attack on $PhCH_2-X$ occurs faster than on CH_3-X by factors as high as 500 [21], and thus selective benzyl halide transfer is expected.

4. Experimental details

All syntheses were conducted in an atmosphere of dry nitrogen with the use of Schlenk techniques. ^1H NMR spectra were recorded at 200 MHz on a Bruker AC200 spectrometer. Spectra of palladium(II) complexes were measured at room temperature, whereas spectra of palladium(IV) complexes were measured at −10 °C. Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane. Microanalyses were performed by the Institute for Applied Chemistry (TNO), Zeist, Netherlands, and Dornis und Kolbe Microanalytical Laboratories, Mulheim a.d. Ruhr, Germany. Benzene, pentane, and diethyl ether were all freshly distilled from sodium/benzophenone ketyl. Methyllithium (1.6 M in diethyl ether), *N,N,N',N'*-tetramethylethylenediamine, 2,2'-bipyridine, iodobenzene, iodo(4-methyl)benzene, iodo(3-methoxy)benzene, iodo(4-methoxy)benzene, iodo(4-nitro)benzene and 4-iodoacetophenone benzyl bromide and acetone (p.a.) were obtained from Janssen Chimica and used without purification.

Bis(dibenzylideneacetone)palladium(0) [22], $PdMe_2(bpy)$ [18], $PdMePh(tmeda)$ [16], $PdBrMe_2(CH_2Ph)(bpy)$ [4] and $PdBrMePh(CH_2Ph)(bpy)$ [7] were prepared according to reported procedures. The new complexes $PdI(4\text{-}RC_6H_4)(tmeda)$ (R = Me, MeO, Me(O)C, O_2N), $PdI(3\text{-}MeOC_6H_4)(tmeda)$, $PdMePh(phen)$, $PdMe(4\text{-}RC_6H_4)(L_2)$ (L_2 = phen, bpy, R = Me, MeO), $PdMe(3\text{-}MeOC_6H_4)(L_2)$ (L_2 = bpy, phen), $PdBrMePh(CH_2Ph)(phen)$, $PdBrMe(4\text{-}RC_6H_4)(CH_2Ph)(L_2)$ (L_2 = bpy, phen, R = Me, MeO) and $PdBrMe(3\text{-}MeOC_6H_4)(CH_2Ph)(phen)$ were prepared by procedures exactly as reported for the PhPd(II) [16] and PhPd(IV) [7] analogues except where indicated below, involving oxidative addition of iodoarene to $Pd(dba)_2$ in the presence of tmeda, transmetallation with LiMe, exchange of tmeda by bpy or phen, and oxidative addition of $PhCH_2Br$.

4.1. *PdI(4-MeC$_6$H$_4$)(tmeda) (1b)*

Yield: 90%. Anal. Found: C, 35.5; H, 5.3; N, 6.3. $C_{13}H_{23}N_2IPd$ Calc.: C, 35.4; H, 5.3; N, 6.4%. ^1H NMR ($CDCl_3$): δ 2.22 (3H, s, Me), 2.34 (6H, s, NMe_2), 2.58 (2H, m, CH_2), 2.67 (6H, s, NMe_2) and 2.72 (2H, m, CH_2) overlapping, 6.75 (2H, d, $H_{3,5}$–C_6H_4, ^3J = 7.9 Hz), 7.11 (2H, d, $H_{2,6}$–C_6H_4, ^3J = 7.9 Hz).

4.2. *PdI(4-MeOC$_6$H$_4$)(tmeda) (1c)*

Yield: 96%. Anal. Found: C, 34.1; H, 5.0; N, 6.1. $C_{13}H_{23}N_2IPdO$ Calc.: C, 34.2; H, 5.1; N, 6.1%. ^1H NMR ($CDCl_3$): δ 2.29 (6H, s, NMe_2), 2.60 (4H, m, 2 CH_2) and 2.64 (6H, s, NMe_2) overlapping, 3.69 (3H, s, MeO), 6.59 (2H, d, $H_{3,5}$–C_6H_4, ^3J = 8.3 Hz), 7.07 (2H, d, $H_{2,6}$–C_6H_4, ^3J = 8.3 Hz).

4.3. PdI(3-MeOC$_6$H$_4$)(tmeda) (1d)

Yield: 92%. Anal. Found: C, 34.3; H, 5.0; N, 6.1. $C_{13}H_{23}N_2IPdO$ Calc.: C, 34.2; H, 5.1; N, 6.1%. ^{1}H NMR ($CDCl_3$): δ 2.34 (6H, s, NMe_2), 2.55 (2H, m, CH_2), 2.67 (6H, s, NMe_2) and 2.73 (2H, m, CH_2) overlapping, 3.74 (3H, s, MeO), 6.38 (1H, m, H_4–C_6H_4), 6.83 (3H, m, $H_{2,5,6}$–C_6H_4 overlapping).

4.4. PdI(4-Me(O)CC$_6$H$_4$)(tmeda) (1e)

Yield: 100%. Anal. Found: C, 35.8; H, 5.0; N, 6.0. $C_{14}H_{23}N_2IPdO$ Calc.: C, 35.9; H, 5.0; N, 6.0%. ^{1}H NMR ($CDCl_3$): δ 2.31 (6H, s, NMe_2), 2.48 (3H, s, COMe), 2.64 (4H, m, 2 CH_2) and 2.67 (6H, s, NMe_2) overlapping, 7.46 (4H, m, C_6H_4).

4.5. PdI(4-O$_2$NC$_6$H$_4$)(tmeda) (1f)

Yield: 100%. Anal. Found: C, 29.9; H, 4.2; N, 8.8. $C_{12}H_{20}N_3IPdO$ Calc.: C, 30.6; H, 4.3; N, 8.9%. ^{1}H NMR ($CDCl_3$): δ 2.35 (6H, s, NMe_2), 2.63 (2H, m, CH_2), 2.71 (6H, s, NMe_2) and 2.75 (2H, m, CH_2) overlapping, 7.55 (2H, d, $H_{3,5}$–C_6H_4, ^3J = 8.7 Hz), 7.77 (2H, d, $H_{2,6}$–C_6H_4, ^3J = 8.7 Hz).

4.6. PdMe(4-MeC$_6$H$_4$)(tmeda) (2b)

Yield: 97%. Anal. Found: C, 50.4; H, 8.1; N, 8.1. $C_{14}H_{26}N_2Pd$ Calc.: C, 51.1; H, 8.0; N, 8.5%. ^{1}H NMR ($CDCl_3$): δ −0.86 (3H, s, PdMe), 2.21 (3H, s, Me), 2.30 (6H, s, NMe_2), 2.51 (6H, s, NMe_2) and 2.53 (4H, m, 2 CH_2) overlapping, 6.80 (2H, d, $H_{3,5}$–C_6H_4, ^3J = 7.6 Hz), 7.33 (2H, d, $H_{2,6}$–C_6H_4, ^3J = 7.6 Hz).

4.7. PdMe(4-MeOC$_6$H$_4$)(tmeda) (2c)

Yield: 87%. Anal. Found: C, 48.7; H, 7.7; N, 8.2. $C_{14}H_{26}N_2PdO$ Calc.: C, 48.8; H, 7.6; N, 8.1%. ^{1}H NMR ($CDCl_3$): δ −0.23 (3H, s, PdMe), 2.25 (6H, s, NMe_2), 2.48 (6H, s, NMe_2), 2.61 (4H, AA'BB', 2 CH_2), 3.64 (3H, s, MeO), 6.51 (2H, d, $H_{3,5}$–C_6H_4, ^3J = 8.4 Hz), 7.23 (2H, d, $H_{2,6}$–C_6H_4, ^3J = 8.4 Hz).

4.8. PdMe(3-MeOC$_6$H$_4$)(tmeda) (2d)

Yield: 98%. Anal. Found: C, 48.9; H, 7.5; N, 7.9. $C_{14}H_{26}N_2PdO$ Calc.: C, 48.8; H, 7.6; N, 8.1%. ^{1}H NMR ($CDCl_3$): δ −0.07 (3H, s, PdMe), 2.31 (6H, s, NMe_2), 2.52 (6H, s, NMe_2) and 2.57 (4H, m, 2 CH_2) overlapping, 3.77 (3H, s, MeO), 6.42 (1H, m, H_4–C_6H_4), 6.89 (1H, dd, H_5–C_6H_4, ^3J = 7.9 and 7.5 Hz), 7.06 (2H, m, $H_{2,6}$–C_6H_4).

4.9. PdMe(4-MeC$_6$H$_4$)(bpy) (3b)

Yield: 88%. Anal. Found: C, 58.5; H, 4.9; N, 7.5. $C_{16}H_{18}N_2Pd$ Calc.: C, 58.6; H, 4.9; N, 7.6%. ^{1}H NMR ($CDCl_3$): δ 0.59 (3H, s, PdMe), 2.31 (3H, s, Me), 6.98 (2H, d, $H_{3,5}$–C_6H_4, ^3J = 7.6 Hz), 7.37 (1H, m, bpy), 7.52 (3H, d, $H_{2,6}$–C_6H_4 and 1 bpy overlapping), 7.90–8.11 (4H, m, bpy), 8.41 (1H, d, bpy, ^3J = 5.1 Hz), 8.88 (1H, d, bpy, ^3J = 5.1 Hz).

4.10. PdMe(4-MeOC$_6$H$_4$)(bpy) (3c)

Yield: 75%. Anal. Found: C, 56.0; H, 4.7; N, 7.3. $C_{18}H_{26}N_2PdO$ Calc.: C, 56.2; H, 4.7; N, 7.3%. ^{1}H NMR ($CDCl_3$): δ 0.57 (3H, s, PdMe), 3.80 (3H, s, MeO), 6.81 (2H, d, $H_{3,5}$–C_6H_4, ^3J = 8.3 Hz), 7.33 (1H, m, bpy), 7.47 (2H, d, $H_{2,6}$–C_6H_4, ^3J = 8.3 Hz), 7.51 (1H, m, bpy), 7.91 (1H, m, bpy), 8.03 (2H, d, bpy, ^3J = 4.7 Hz), 8.34 (2H, m, bpy), 8.84 (1H, d, bpy, ^3J = 5.3 Hz).

4.11. PdMe(3-MeOC$_6$H$_4$)(bpy) (3d)

Yield: 57%. Anal. Found: C, 56.1; H, 4.8; N, 7.3. $C_{18}H_{26}N_2PdO$ Calc.: C, 56.2; H, 4.7; N, 7.3%. ^{1}H NMR ($CDCl_3$): δ 0.59 (3H, s, PdMe), 3.81 (3H, s, MeO), 6.57 (1H, m, H_4–C_6H_4), 7.06 (1H, dd, H_5–C_6H_4, ^3J = 7.8 and 7.6 Hz), 7.32 (2H, m, $H_{2,6}$–C_6H_4), 7.54 (1H, m, bpy), 7.86–8.11 (5H, m, bpy), 8.35 (1H, d, bpy, ^3J = 5.1 Hz), 8.86 (1H, d, bpy, ^3J = 5.1 Hz).

4.12. PdMePh(phen) (3a')

Yield: 81%. Anal. Found: C, 60.1; H, 4.2; N, 7.5. $C_{19}H_{16}N_2Pd$ Calc.: C, 60.3; H, 4.3; N, 7.4%. ^1H NMR ($CDCl_3$): δ 0.74 (3H, s, PdMe), 7.04 (1H, m, H_4–C_6H_4), 7.15 (2H, m, $H_{3,5}$–C_6H_4), 7.78 (3H, m, $H_{2,6}$–C_6H_4 and 1 phen overlapping), 7.89 (3H, m, phen), 8.40 (2H, m, phen), 8.68 (1H, d, phen, $^3J = 4.9$ Hz), 9.18 (1H, d, phen, $^3J = 4.9$ Hz).

4.13. PdMe(4-MeC$_6$H$_4$)(phen) (3b')

Yield: 83%. No satisfactory microanalysis could be obtained for this compound. The ^1H NMR spectrum of the corresponding Pd(IV) compound has been added as Supplementary Material. ^1H NMR ($CDCl_3$): δ 0.73 (3H, s, PdMe), 2.33 (3H, s, Me), 7.02 (2H, d, $H_{3,5}$–C_6H_4, $^3J = 7.6$ Hz), 7.58 (2H, d, $H_{2,6}$–C_6H_4, $^3J = 7.6$ Hz), 7.67 (1H, m, phen), 7.78–7.93 (3H, m, phen), 8.71 (1H, d, phen, $^3J = 4.9$ Hz), 9.15 (1H, d, phen, $^3J = 4.9$ Hz).

4.14. PdMe(4-MeOC$_6$H$_4$)(phen) (3c')

Yield: 62%. Anal. Found: C, 58.6; H, 4.4; N, 6.8. $C_{20}H_{18}N_2PdO$ Calc.: C, 58.8; H, 4.4; N, 6.9%. ^1H NMR ($CDCl_3$): δ 0.74 (3H, s, PdMe), 3.83 (3H, s, MeO), 6.86 (2H, d, $H_{3,5}$–C_6H_4, $^3J = 8.5$ Hz), 7.57 (2H, d, $H_{2,6}$–C_6H_4, $^3J = 8.5$ Hz), 7.68 (1H, m, phen), 7.85 (1H, m, phen), 7.92 (2H, s, phen), 8.35–8.49 (2H, m, phen), 8.69 (1H, dd, phen, $^3J = 4.9$ Hz, $^4J = 1.4$ Hz), 9.17 (1H, dd, phen, $^3J = 4.9$ Hz, $^4J = 1.3$ Hz).

4.15. PdMe(3-MeOC$_6$H$_4$)(phen) (3d')

Yield: 93%. Anal. Found: C, 58.9; H, 4.5; N, 6.7. $C_{20}H_{18}N_2OPd$ Calc.: C, 58.8; H, 4.4; N, 6.9%. ^1H NMR ($CDCl_3$): δ 0.72 (3H, s, PdMe), 3.82 (3H, s, MeO), 6.62 (1H, dd, H_4–C_6H_4, $^3J = 7.9$ Hz, $^4J = 1.7$ Hz), 7.13 (1H, m, H_5–C_6H_4), 7.30 (1H, m, $H_{2,6}$–C_6H_4), 7.65 (1H, m, phen), 7.82 (1H, m, phen), 7.89 (2H, s, phen) 8.35–8.47 (2H, m, phen), 8.65 (1H, dd, phen, $^3J = 4.8$ Hz, $^4J = 1.2$ Hz), 9.08 (1H, dd, phen, $^3J = 4.2$ Hz, $^4J = 1.0$ Hz).

4.16. PdBrMe(4-MeC$_6$H$_4$)(CH$_2$Ph)(bpy) (4b)

Yield: 78%. ^1H NMR ($CDCl_3$): δ 2.37 (3H, s, Me), 2.38 (3H, s, PdMe), 3.77 (2H, AB, CH_2), 6.42 (2H, m, b, *o*-benzyl), 6.60 (2H, 't', *m*-benzyl), 6.79 (1H, 't', *p*-benzyl), 7.14 (2H, d, $H_{3,5}$–C_6H_4, $^3J = 8.0$ Hz), 7.24 (1H, m, bpy), 7.44 (1H, m, bpy), 7.68–7.98 (5H, m, 4 bpy + H_2–C_6H_4), 8.08 (1H, d, H_6–C_6H_4, $^3J = 8.0$ Hz), 8.32 (1H, d, H_6–bpy, $^3J = 4.6$ Hz), 8.75 (1H, d, H_6–bpy, $^3J = 4.6$ Hz).

4.17. PdBrMe(4-MeOC$_6$H$_4$)(CH$_2$Ph)(bpy) (4c)

Yield: 61%. ^1H NMR ($CDCl_3$): δ 2.35 (3H, s, PdMe), 3.74 (2H, AB, CH_2), 3.85 (3H, s, MeO), 6.40 (2H, d, *o*-benzyl, $^3J = 7.1$ Hz), 6.57 (2H, 't', *m*-benzyl), 6.76 (1H, 't', b, *p*-benzyl), 6.90 (2H, d, $H_{3,5}$–C_6H_4, $^3J = 8.6$ Hz), 7.23 (1H, m, bpy), 7.37 (1H, m, bpy), 7.65–8.04 (6H, m, bpy + $H_{2,6}$–C_6H_4, (d, $^3J = 8.6$ Hz)), 8.36 (1H, d, H_6–bpy, $^3J = 4.9$ Hz), 8.64 (1H, d, H_6–bpy, $^3J = 5.0$ Hz).

4.18. PdBrMePh(CH$_2$Ph)(phen) (4a')

This complex was prepared using CH_2Cl_2 as a solvent.

Yield: 51%. ^1H NMR ($CDCl_3$): δ 2.55 (3H, s, PdMe), 3.84 (2H, AB, CH_2), 6.11 (2H, m, b, *o*-benzyl), 6.28 (2H, 't', *m*-benzyl), 6.55 (1H, 't', *p*-benzyl), 7.24–7.39 (3H, m, $H_{3,5}$–C_6H_4), 7.61 (1H, m, phen), 7.77 (1H, m, phen), 7.81 (1H, s, phen), 7.85 (1H, s, phen), 7.98 (2H, d, $H_{2,6}$–C_6H_4, $^3J = 7.1$ Hz), 8.29 (1H, d, phen, $^3J = 8.1$ Hz), 8.44 (1H, d, phen, $^3J = 8.1$ Hz), 8.75 (1H, d, phen, $^3J = 4.7$ Hz), 9.10 (1H, d, phen, $^3J = 4.7$ Hz).

4.19. PdBrMe(4-MeC$_6$H$_4$)(CH$_2$Ph)(phen) (4b')

Yield: 46%. ^1H NMR ($CDCl_3$): δ 2.42 (3H, s, Me), 2.53 (3H, s, PdMe), 3.82 (2H, AB, CH_2), 6.10 (2H, m, b, *o*-benzyl), 6.28 (2H, 't', *m*-benzyl), 6.54 (1H, 't', *p*-benzyl), 7.19 (2H, d, $H_{3,5}$–C_6H_4, $^3J = 7.9$ Hz), 7.57 (1H, m, phen), 7.72–7.89 (5H, m, 3 phen and $H_{2,6}$–C_6H_4), 8.26 (1H, d, phen, $^3J = 7.4$ Hz), 8.42 (1H, d, phen, $^3J = 7.3$ Hz), 8.71 (1H, d, phen, $^3J = 4.0$ Hz), 9.10 (1H, d, phen, $^3J = 4.0$ Hz).

4.20. PdBrMe(4-MeOC$_6$H$_4$)(CH$_2$Ph)(phen) (4e')

Yield: 50%. ^{1}H NMR ($CDCl_3$): δ 2.51 (3H, s, PdMe), 3.80 (2H, AB, CH_2) and 3.87 (3H, s, MeO) overlapping, 6.09 (2H, m, b, *o*-benzyl), 6.27 (2H, 't', *m*-benzyl), 6.54 (1H, 't', *p*-benzyl), 6.95 (2H, d, $H_{3,5}$–C_6H_4, ^3J = 8.1 Hz), 7.60 (1H, m, phen), 7.74–7.87 (5H, m, 3 phen and $H_{2,6}$–C_6H_4), 8.28 (1H, d, phen, ^3J = 8.1 Hz), 8.43 (1H, d, phen, ^3J = 8.1 Hz), 8.74 (1H, d, phen, ^3J = 4.8 Hz), 9.06 (1H, d, phen, ^3J = 4.8 Hz).

4.21. PdBrMe(3-MeOC$_6$H$_4$)(CH$_2$Ph)(phen) (4d')

Yield: 30%. ^{1}H NMR (CD_3COCD_3): δ 2.43 (3H, s, PdMe), 3.81 (2H, AB, CH_2), 3.82 (3H, s, MeO), 6.17 (2H, m, b, *o*-benzyl), 6.27 (2H, 't', *m*-benzyl), 6.51 (1H, 't', *p*-benzyl), 6.76 (1H, d, PdAr, ^3J = 8.4 Hz), 7.19 (1H, 't', PdAr), 7.52 (1H, m, PdAr), 7.89 (1H, m, phen), 8.02–8.21 (5H, m, 3 phen and PdAr), 8.64 (1H, d, phen, ^3J = 8.2 Hz), 8.80 (1H, d, phen, ^3J = 8.1 Hz), 8.93 (1H, d, phen, ^3J = 4.7 Hz), 9.09 (1H, d, phen, ^3J = 4.7 Hz).

4.22. ^{1}H NMR studies of decomposition and alkyl bromide transfer reactions

All of the complexes decomposed in chloroform very slowly at 0–10 °C, and thus the studies of decomposition were conducted at 25 °C after obtaining spectra of the complexes at −10 °C and warming of solutions with checking of decomposition behaviour at 10 °C intervals. Spectra were compared with those of PdBrMe(L_2) (L_2 = bpy, phen), $PdMe_2(L_2)$, PdBr(CH_2Ph)(bpy), PdMeAr(L_2), $PdBrMe_2(CH_2Ph)(L_2)$, toluene, methane, ethane, benzene, bibenzyl, ethylbenzene and diphenylmethane.

The alkyl bromide transfer reactions were performed in acetone at −10 °C by adding an excess of $PdMe_2$(bpy) to a solution of the palladium(IV) complex and following the reaction until completion.

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