

Selectivity in reductive elimination and organohalide transfer from methyl(aryl)benzylpalladium(IV) complexes of bidentate nitrogen donor ligands, PdBrMe(Ar)(CH₂Ph)(L₂)

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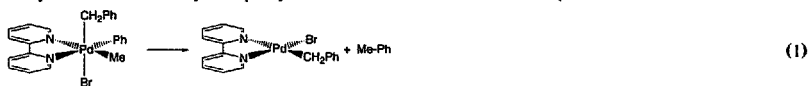
Abstract

Oxidative addition of iodoarenes to bis(dibenzylideneacetone)palladium(0) in the presence of *N,N,N',N'*-tetramethylethylenediamine (tmeda) affords PdIAr(tmeda) (Ar = 4-MeC₆H₄, 4-MeOC₆H₄, 4-Me(OCC₆H₄), 4-O₂NC₆H₄, 3-MeOC₆H₄) in high yield. Some of these complexes (Ar = 4-MeC₆H₄, 4-MeOC₆H₄, 3-MeOC₆H₄) 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(L₂); PdMePh(phen) may be obtained similarly. All of the diorganopalladium(II) complexes of bpy and phen react with benzyl bromide to form PdBrMeAr(CH₂Ph)(L₂) but a complex could not be isolated for Ar = 3-MeOC₆H₄, L₂ = bpy. The isolated palladium(IV) complexes react with PdMe₂(bpy) at –20 °C in (CD₃)₂CO to selectively transfer benzyl bromide to give PdMeAr(L₂) and PdBrMe₂(CH₂Ph)(bpy) respectively. The complexes PdBrMeAr(CH₂Ph)(bpy) (Ar = Ph, 4-MeC₆H₄, 4-MeOC₆H₄) undergo selective reductive elimination of Ar–Me in CDCl₃ to form PdBr(CH₂Ph)(L₂) but PdBrMeAr(CH₂Ph)(phen) (Ar = Ph, 4-MeC₆H₄, 4-MeOC₆H₄, 3-MeOC₆H₄) give mixtures of PdBr(CH₂Ph)(phen) and Me–Ar together with lesser amounts of PdBrMe(phen) and Ar–CH₂Ph (ca. 10–20%).

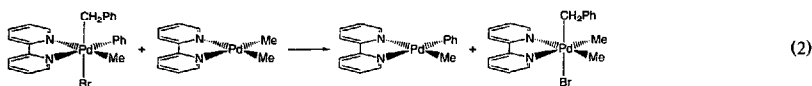
Keywords: Palladium; Oxidative addition; Reductive elimination; Redox reactions; Alkyl transfer

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(CH₂Ph)(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].



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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 $\text{PdBrMeAr}(\text{CH}_2\text{Ph})(\text{L}_2)$ [$\text{L}_2 = \text{bpy}$ 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 $\text{PdBrMe}_2(\text{CH}_2\text{Ph})(\text{L}_2)$ ($\text{L}_2 = \text{bidentate nitrogen donor ligand}$) [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 $\text{PdI}(\text{Ph})(\text{tmeda})$ (**1a**), $\text{PdMePh}(\text{tmeda})$ (**2a**) and $\text{PdMePh}(\text{bpy})$ (**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.



1a: Ar = Ph, **1b**: Ar = 4-MeC₆H₄, **1c**: Ar = 4-MeOC₆H₄

1d: Ar = 3-MeOC₆H₄, **1e**: Ar = 4-Me(O)CC₆H₄, **1f**: Ar = 4-O₂NC₆H₄



2a: Ar = Ph, **2b**: Ar = 4-MeC₆H₄

2c: Ar = 4-MeOC₆H₄, **2d**: Ar = 3-MeOC₆H₄



3a: Ar = Ph, $\text{L}_2 = \text{bpy}$

3a': Ar = Ph, $\text{L}_2 = \text{phen}$

3b: Ar = 4-MeC₆H₄, $\text{L}_2 = \text{bpy}$

3b': Ar = 4-MeC₆H₄, $\text{L}_2 = \text{phen}$

3c: Ar = 4-MeOC₆H₄, $\text{L}_2 = \text{bpy}$

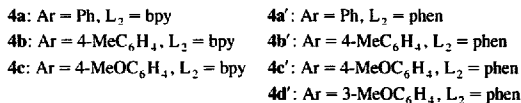
3c': Ar = 4-MeOC₆H₄, $\text{L}_2 = \text{phen}$

3d: Ar = 3-MeOC₆H₄, $\text{L}_2 = \text{bpy}$

3d': Ar = 3-MeOC₆H₄, $\text{L}_2 = \text{phen}$

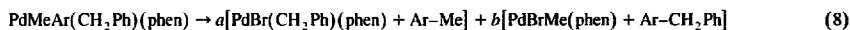
All of the new complexes exhibit microanalyses and ¹H NMR spectra in accord with the formulations presented in Eqs. (3)–(5), e.g. on comparison with reported spectra of $\text{PdI}(\text{Me})(\text{tmeda})$ (**1a**) and $\text{PdMe}_2(\text{bpy})$ [18], $\text{PdMePh}(\text{tmeda})$ (**2a**) and $\text{PdMePh}(\text{bpy})$ (**3a**) [16].

The palladium(IV) complexes (**4b–c**, **4a'–d'**) were obtained on oxidative addition of benzyl bromide to the appropriate $\text{PdMeAr}(\text{L}_2)$ complexes at 0 °C in acetone (Eq. (6)), as reported for the synthesis of $\text{PdBrMePh}(\text{CH}_2\text{Ph})(\text{bpy})$ (**4a**) [7], or at –10 °C in dichloromethane for some of the less soluble phen complexes (**3a'**,

$$\text{PdMeAr}(\text{L}_2) + \text{PhCH}_2\text{Br} \rightarrow \text{PdBrMeAr}(\text{CH}_2\text{Ph})(\text{L}_2) \quad (6)$$


Unlike its phenanthroline counterpart, $\text{PdMe(3-MeOC}_6\text{H}_4)_2(\text{bpy})$ did not yield an isolable palladium(IV) complex upon reaction with benzyl bromide. Therefore, the reaction was studied by *in situ* ^1H NMR spectroscopy. Addition of an excess of benzyl bromide to a cooled (-10°C) solution of $\text{PdMe(3-MeOC}_6\text{H}_4)_2(\text{H}_2\text{bpy})$ 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', $\text{Pd(IV)-CH}_2\text{-Ph}$); 8.24, 8.66 ppm (d ($J = 5.2\text{ Hz}$), d ($J = 5.4\text{ Hz}$), $\text{H}_6\text{-bpy}$)) 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.

All of the palladium(IV) complexes showed facile decomposition behaviour at ambient temperature to give C–C coupling products and monoorganoanypalladium(II) species that could be readily identified by ^1H 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'**), $\text{PdBr}(\text{L})$, MeH and ArH are also not formed.



4a' ($a = 0.83$, $b = 0.17$), **4b'** ($a = 0.91$, $b = 0.09$)
4c' ($a = 0.87$, $b = 0.13$), **4d'** ($a = 0.90$, $b = 0.10$)

$$\text{PdBrMeAr}(\text{CH}_2\text{Ph})(\text{L}_2) + \text{PdMe}_2(\text{bpy}) \rightarrow \text{PdMeAr}(\text{L}_2) + \text{PdBrMe}_2(\text{CH}_2\text{Ph})(\text{bpy}) \quad (9)$$

The synthetic methods illustrate the general applicability of the oxidative addition reaction (Eq. (3)), transmetalation (Eq. (4)) except for nitro and acetyl substituted phenyl groups, displacement of *tmada* (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 (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 $L_2 = \text{bpy}$ is unaffected by change of Ar, and for $L_2 = \text{phen}$ the product distributions from **4a-d'** are similar, indicating that the major determinant of selectivity is L_1 .

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–CH₂Ph bond energies are the main factors that determine selectivity in reductive elimination from PdBrMe₂(CH₂Ph)(L₂) [19], and the selectivity for Ar–Me coupling exhibited by PdBrMeAr(CH₂Ph)(bpy) (Eq. (7)) is consistent with this in view of the bond energy sequence Ar–Me > Ar–CH₂Ph > Me–CH₂Ph. 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(CH₂Ph)(L₂) to facilitate the lowest energy pathway for reductive elimination, suggested from kinetic studies of reductive elimination by PdIme₃(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(CH₂Ph)(L₂)(acetone)]⁺. This latter step appears to be the one at which a change of L₂ 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 [PdMe₃(L₂)(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(CH₂Ph)(L₂)(acetone)]⁺ to give Ar–Me coupling requires isomerisation since both Me and Ar groups are *trans* to L₂ in PdBrMeAr(CH₂Ph)(L₂).

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(CH₂Ph)(L₂) to form [PdMeAr(CH₂Ph)(L₂)]⁺ (probably solvated as [PdMeAr(CH₂Ph)(L₂)(acetone)]⁺) is followed by nucleophilic attack by PdMe₂(bpy) on the alkyl group(s) at the cationic palladium(IV) centre [2,7]. Normally, nucleophilic attack on PhCH₂–X occurs faster than on CH₃–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. Methylolithium (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], PdMe₃(bpy) [18], PdMePh(tmeda) [16], PdBrMe₂(CH₂Ph)(bpy) [4] and PdBrMePh(CH₂Ph)(bpy) [7] were prepared according to reported procedures. The new complexes Pd(4-RC₆H₄)(tmeda) (R = Me, MeO, Me(O)C, O₂N), Pd(3-MeOC₆H₄)(tmeda), PdMePh(phen), PdMe(4-RC₆H₄)(L₂) (L₂ = phen, bpy, R = Me, MeO), PdMe(3-MeOC₆H₄)(L₂) (L₂ = bpy, phen), PdBrMePh(CH₂Ph)(phen), PdBrMe(4-RC₆H₄)(CH₂Ph)(L₂) (L₂ = bpy, phen, R = Me, MeO) and PdBrMe(3-MeOC₆H₄)(CH₂Ph)(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)₃ in the presence of tmeda, transmetalation with LiMe, exchange of tmeda by bpy or phen, and oxidative addition of PhCH₂Br.

4.1. Pd(4-MeC₆H₄)(tmeda) (1b)

Yield: 90%. Anal. Found: C, 35.5; H, 5.3; N, 6.3. C₁₃H₂₃N₂IPd Calc.: C, 35.4; H, 5.3; N, 6.4%. ¹H NMR (CDCl₃): δ 2.22 (3H, s, Me), 2.34 (6H, s, NMe₂), 2.58 (2H, m, CH₂), 2.67 (6H, s, NMe₂) and 2.72 (2H, m, CH₂) overlapping, 6.75 (2H, d, H_{3,5}–C₆H₄, ³J = 7.9 Hz), 7.11 (2H, d, H_{2,6}–C₆H₄, ³J = 7.9 Hz).

4.2. Pd(4-MeOC₆H₄)(tmeda) (1c)

Yield: 96%. Anal. Found: C, 34.1; H, 5.0; N, 6.1. C₁₃H₂₃N₂IPdO Calc.: C, 34.2; H, 5.1; N, 6.1%. ¹H NMR (CDCl₃): δ 2.29 (6H, s, NMe₂), 2.60 (4H, m, 2 CH₂) and 2.64 (6H, s, NMe₂) overlapping, 3.69 (3H, s, MeO), 6.59 (2H, d, H_{3,5}–C₆H₄, ³J = 8.3 Hz), 7.07 (2H, d, H_{2,6}–C₆H₄, ³J = 8.3 Hz).

4.3. *PdI(3-MeOC₆H₄)(tmeda) (1d)*

Yield: 92%. Anal. Found: C, 34.3; H, 5.0; N, 6.1. C₁₃H₂₃N₂IPdO Calc.: C, 34.2; H, 5.1; N, 6.1%. ¹H NMR (CDCl₃): δ 2.34 (6H, s, NMe₂), 2.55 (2H, m, CH₂), 2.67 (6H, s, NMe₂) and 2.73 (2H, m, CH₂) overlapping, 3.74 (3H, s, MeO), 6.38 (1H, m, H₄-C₆H₄), 6.83 (3H, m, H_{2,5,6}-C₆H₄ overlapping).

4.4. *PdI(4-Me(O)CC₆H₄)(tmeda) (1e)*

Yield: 100%. Anal. Found: C, 35.8; H, 5.0; N, 6.0. C₁₄H₂₃N₂IPdO Calc.: C, 35.9; H, 5.0; N, 6.0%. ¹H NMR (CDCl₃): δ 2.31 (6H, s, NMe₂), 2.48 (3H, s, COMe), 2.64 (4H, m, 2 CH₂) and 2.67 (6H, s, NMe₂) overlapping, 7.46 (4H, m, C₆H₄).

4.5. *PdI(4-O₂NC₆H₄)(tmeda) (1f)*

Yield: 100%. Anal. Found: C, 29.9; H, 4.2; N, 8.8. C₁₃H₂₀N₃IPdO Calc.: C, 30.6; H, 4.3; N, 8.9%. ¹H NMR (CDCl₃): δ 2.35 (6H, s, NMe₂), 2.63 (2H, m, CH₂), 2.71 (6H, s, NMe₂) and 2.75 (2H, m, CH₂) overlapping, 7.55 (2H, d, H_{3,5}-C₆H₄, ³J = 8.7 Hz), 7.77 (2H, d, H_{2,6}-C₆H₄, ³J = 8.7 Hz).

4.6. *PdMe(4-MeC₆H₄)(tmeda) (2b)*

Yield: 97%. Anal. Found: C, 50.4; H, 8.1; N, 8.1. C₁₄H₂₆N₂Pd Calc.: C, 51.1; H, 8.0; N, 8.5%. ¹H NMR (CDCl₃): δ -0.86 (3H, s, PdMe), 2.21 (3H, s, Me), 2.30 (6H, s, NMe₂), 2.51 (6H, s, NMe₂) and 2.53 (4H, m, 2 CH₂) overlapping, 6.80 (2H, d, H_{3,5}-C₆H₄, ³J = 7.6 Hz), 7.33 (2H, d, H_{2,6}-C₆H₄, ³J = 7.6 Hz).

4.7. *PdMe(4-MeOC₆H₄)(tmeda) (2c)*

Yield: 87%. Anal. Found: C, 48.7; H, 7.7; N, 8.2. C₁₄H₂₆N₂PdO Calc.: C, 48.8; H, 7.6; N, 8.1%. ¹H NMR (CDCl₃): δ -0.23 (3H, s, PdMe), 2.25 (6H, s, NMe₂), 2.48 (6H, s, NMe₂), 2.61 (4H, AA'BB', 2 CH₂), 3.64 (3H, s, MeO), 6.51 (2H, d, H_{3,5}-C₆H₄, ³J = 8.4 Hz), 7.23 (2H, d, H_{2,6}-C₆H₄, ³J = 8.4 Hz).

4.8. *PdMe(3-MeOC₆H₄)(tmeda) (2d)*

Yield: 98%. Anal. Found: C, 48.9; H, 7.5; N, 7.9. C₁₄H₂₆N₂PdO Calc.: C, 48.8; H, 7.6; N, 8.1%. ¹H NMR (CDCl₃): δ -0.07 (3H, s, PdMe), 2.31 (6H, s, NMe₂), 2.52 (6H, s, NMe₂) and 2.57 (4H, m, 2 CH₂) overlapping, 3.77 (3H, s, MeO), 6.42 (1H, m, H₄-C₆H₄), 6.89 (1H, dd, H₅-C₆H₄, ³J = 7.9 and 7.5 Hz), 7.06 (2H, m, H_{2,6}-C₆H₄).

4.9. *PdMe(4-MeC₆H₄)(bpy) (3b)*

Yield: 88%. Anal. Found: C, 58.5; H, 4.9; N, 7.5. C₁₆H₁₈N₂Pd Calc.: C, 58.6; H, 4.9; N, 7.6%. ¹H NMR (CDCl₃): δ 0.59 (3H, s, PdMe), 2.31 (3H, s, Me), 6.98 (2H, d, H_{3,5}-C₆H₄, ³J = 7.6 Hz), 7.37 (1H, m, bpy), 7.52 (3H, d, H_{2,6}-C₆H₄ 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-MeOC₆H₄)(bpy) (3c)*

Yield: 75%. Anal. Found: C, 56.0; H, 4.7; N, 7.3. C₁₈H₂₆N₂PdO Calc.: C, 56.2; H, 4.7; N, 7.3%. ¹H NMR (CDCl₃): δ 0.57 (3H, s, PdMe), 3.80 (3H, s, MeO), 6.81 (2H, d, H_{3,5}-C₆H₄, ³J = 8.3 Hz), 7.33 (1H, m, bpy), 7.47 (2H, d, H_{2,6}-C₆H₄, 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-MeOC₆H₄)(bpy) (3d)*

Yield: 57%. Anal. Found: C, 56.1; H, 4.8; N, 7.3. C₁₈H₂₆N₂PdO Calc.: C, 56.2; H, 4.7; N, 7.3%. ¹H NMR (CDCl₃): δ 0.59 (3H, s, PdMe), 3.81 (3H, s, MeO), 6.57 (1H, m, H₄-C₆H₄), 7.06 (1H, dd, H₅-C₆H₄, ³J = 7.8 and 7.6 Hz), 7.32 (2H, m, H_{2,6}-C₆H₄), 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, $H_{1-2}-C_6H_4$), 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-MeC₆H₄)(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-MeOC₆H₄)(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 0.72 (3H, s, PdMe), 3.82 (3H, s, MeO), 6.62 (1H, dd, $H_{1-2}-C_6H_4$, $^3J = 7.9$ 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, $^3J = 4.9$ Hz, $^4J = 1.4$ Hz), 9.17 (1H, dd, phen, $^3J = 4.9$ Hz, $^4J = 1.3$ Hz).

4.15. *PdMe(3-MeOC₆H₄)(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, $H_{1-2}-C_6H_4$, $^3J = 7.9$ 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-MeC₆H₄)(CH₂Ph)(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 + $H_{2,6}-C_6H_4$), 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-MeOC₆H₄)(CH₂Ph)(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(CH₂Ph)(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-MeC₆H₄)(CH₂Ph)(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. $\text{PdBrMe}(4\text{-MeOC}_6\text{H}_4)(\text{CH}_2\text{Ph})(\text{phen})$ (**4c'**)

Yield: 50%. ^1H 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, *o*-benzyl), 6.27 (2H, 't', *m*-benzyl), 6.54 (1H, 't', *p*-benzyl), 6.95 (2H, d, $\text{H}_{3,5}\text{-C}_6\text{H}_4$, $^3J = 8.1$ Hz), 7.60 (1H, m, phen), 7.74–7.87 (5H, m, 3 phen and $\text{H}_{2,6}\text{-C}_6\text{H}_4$), 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. $\text{PdBrMe}(3\text{-MeOC}_6\text{H}_4)(\text{CH}_2\text{Ph})(\text{phen})$ (**4d'**)

Yield: 30%. ^1H 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, *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. ^1H 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 $\text{PdBrMe}(\text{L}_2)$ ($\text{L}_2 = \text{bpy}$, phen), $\text{PdMe}_2(\text{L}_2)$, $\text{PdBr}(\text{CH}_2\text{Ph})(\text{bpy})$, $\text{PdMeAr}(\text{L}_2)$, $\text{PdBrMe}_2(\text{CH}_2\text{Ph})(\text{L}_2)$, 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 $\text{PdMe}_2(\text{bpy})$ to a solution of the palladium(IV) complex and following the reaction until completion.

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