Synthesis and structural studies of phenyl(iodo)- and methyl(phenyl)palladium(II) complexes of bidentate nitrogen donor ligands

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Abstract

Phenylpalladium(II) complexes of the type PdIPh(N-N), with N-N = N,N,N',N'-tetramethylethylenediamine (tmeda) or 2,2'-bipyridyl (bpy), can be conveniently prepared in 70–95% yield by oxidative addition of iodobenzene to bis(dibenzylideneacetone)palladium(0) in the presence of the appropriate nitrogen donor ligand. The bromo analogues were obtained in only 5–12% yield in this way. The complex PdIPh(tmeda) (1a) reacts readily with MeLi to give PdMePh(tmeda) (3) in 88% yield, whereas PdIPh(bpy) (2a) gives PdMePh(bpy) (4) and PdMe$_2$(bpy) in varying ratios. The formation of PdMe$_2$(bpy) was found to result from the synergistic action of lithium iodide and methyllithium. Pure PdMePh(bpy) (4) was obtained in 82% yield via ligand-exchange from PdMePh(tmeda) (3). The crystal structures of PdIPh(N-N) (1a, 2a) and PdMePh(N-N) (3, 4) complexes were determined by X-ray diffraction studies. The results show that the phenyl group is always oriented perpendicular to the coordination plane around palladium, with the largest deviation found for 3 (14.3(2)°). The Pd–N bond distances in the tmeda complexes (2.127(6)–2.210(3) Å) are larger than those in the bpy-coordinated complexes (2.070(8)–2.144(8) Å). Similarly, the Pd–C(Me) bond distances (2.5703(8) and 2.575(1) Å) are larger than the Pd–C(Ph) bond distances (1.985(3)–1.996(10) Å).

Key words: Palladium; Amine; Oxidative addition; Bipyridine; Crystal structure

1. Introduction

New applications of nitrogen donor ligand complexes in organopalladium chemistry are currently being developed; e.g. for organic synthesis involving systems with intramolecular coordination [1], for catalytic coupling reactions of alkyl halides with organotin reagents [2], for modelling of processes that are catalytic for phosphine complexes [3], and for the synthesis of organopalladium(IV) complexes [3a,b;4b–6]. Some of the applications have involved arylpalladium (II) complexes, but these are restricted to complexes in which the aryl group is C$_6$F$_5$ or is part of an in-

tramolecular coordination or a metallacyclic system. Early reports of isolated arylpalladium(II) complexes of nitrogen donor ligands in which the aryl group is not part of a chelating system or of a metallacycle mainly involve pentachlorophenyl and pentafluorophenyl groups [4]. Exceptions are the synthesis of PdIPh(bpy) in 17% yield from the reaction of iodobenzene with activated palladium powder in the presence of 2,2'-bipyridyl [7], and the formation of PdCl(p-tolyl)(phen) in 93% yield from the reaction of Pd$_2$(dba)$_3$ · C$_6$H$_6$ (dba = dibenzylideneacetone) with p-tolylmercuric chloride in the presence of 1,10-phenanthroline monohydrate (phen) [8]. Since the start of this work [9] a series of complexes PdClAr(bpy) has been obtained by the direct activation of toluene, xylenes and mesitylenes [10]; they were obtained in low yield (3–16%), except for PdCl(2,5-Me$_2$C$_6$H$_3$)(bpy) (64%) and PdClPh(bpy) (74%).
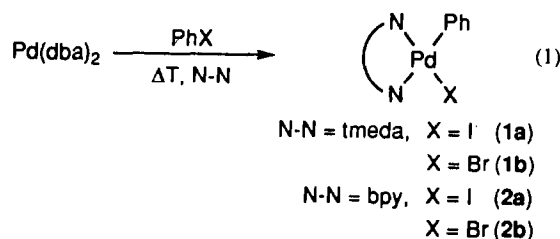
Aryl halides readily undergo oxidative addition reactions with palladium(0) phosphine complexes [11], and it has recently been demonstrated that alkyl and aryl halides undergo similar reactions with $Pd(dba)_2$ or $Pd_2(dba)_3 \cdot CHCl_3$ in the presence of nitrogen donor groups to form palladium(II) nitrogen donor complexes [6c;9;12–15]. For example, the reaction of iodomethane with $Pd(dba)_2$ in the presence of bpy gives PdIMe(bpy) in 79% yield [13]. In view of the established role of bpy and related diimines in catalysis [2;16], together with the application of bpy and N,N,N',N'-tetramethylethylenediamine (tmeda) in the development of organopalladium(II) [4–7;9;10;13;17] and palladium(IV) chemistry [4b–6], we decided to study the reactions of aryl halides with $Pd(dba)_2$ in the presence of these representative aromatic and aliphatic nitrogen donor bidentate ligands (L_2). High yield routes to simple arylpalladium(II) complexes, and synthesis of the first alkyl(aryl)palladium(II) complexes of nitrogen donor ligands are described, together with structural studies of $PdIPh(L_2)$ and $PdMePh(L_2)$.

2. Results

2.1. Synthesis

The oxidative addition of iodobenzene to $Pd(dba)_2$ in the presence of tmeda (eqn. 1, Table 1) proceeds very smoothly at 50°C in benzene to give orange PdIPh(tmeda) (1a) in ca. 95% yield, a higher yield than that initially reported (75% [9a]) for the synthesis in THF. The analogous reaction with bromobenzene (Table 1) gave only 8% of the desired complex PdBrPh(tmeda) (1b) in benzene, but a slightly higher yield (12%) was obtained in THF. The formation of large quantities of palladium metal at the higher temperature (80°C) needed in both solvents for bromobenzene addition indicates that thermal decomposition of $Pd(dba)_2$ is faster under these conditions than oxidative addition to give 1b. The complexes PdIPh(bpy) (2a) and PdBrPh(bpy) (2b) were obtained in 70% and

TABLE 1. Halide and solvent dependence of the oxidative addition of phenyl halides

Complex	PhX	N–N	T (°C)	Solvent	Yield (%)
1a	PhI	tmeda	50	benzene	95
	PhI	tmeda	50	THF	75
2a	PhI	bpy	50	benzene	70
1b	PhBr	tmeda	80	benzene	8
	PhBr	tmeda	80	THF	12
2b	PhBr	bpy	80	benzene	5

5% yields, respectively, by a similar procedure. The complexes 1a,b and 2a,b are readily purified by recrystallization from CH_2Cl_2/Et_2O at $-20°C$. Crystals suitable for X-ray structural analysis (vide infra) of 2a were obtained by this method, while 1a was best recrystallized from hot benzene.

$$Pd(dba)_2 \xrightarrow[\Delta T, N-N]{PhX} \quad \begin{pmatrix} N \\ \\ N \end{pmatrix} Pd \begin{matrix} Ph \\ \\ X \end{matrix} \quad (1)$$

N-N = tmeda, X = I (1a)
            X = Br (1b)
N-N = bpy, X = I (2a)
            X = Br (2b)

Resonances for bpy-H6 protons adjacent to the halogen atom in PdXMe(bpy) occur downfield from bpy-H6 protons adjacent to the methyl group, by 0.69 ppm (X = Br) and 0.83 ppm (X = I) [13]. Similar effects occur for PdXPh(bpy), but the differences are greater [1.53 ppm (X = Br), 1.96 ppm (X = I)]. This effect is assumed to be due to orientation of the phenyl group approximately normal to the coordination plane (vide infra), resulting in an upfield shift for the high-field bpy-H6 protons. The chemical shifts of the phenyl protons do not depend strongly on the halide, in contrast to those for the cyclometallated complexes PdX(CNN) (I, X = Cl, Br, I and CNN = N-(2-benzyl)-N,N',N'-trimethylethylenediamine), where the phenyl group lies in the coordination plane and thus the ortho proton is closer to the halogen atom [6c].
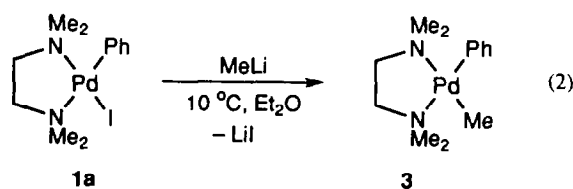

$$\begin{bmatrix} Me_2 \\ N \\ Pd \\ N \\ Me_2 \end{bmatrix} Ph \xrightarrow[-LiI]{\substack{MeLi \\ 10\,°C,\,Et_2O}} \begin{bmatrix} Me_2 \\ N \\ Pd \\ N \\ Me_2 \end{bmatrix} Ph \quad (2)$$

1a   3

Dimethylpalladium(II) complexes containing nitrogen donor ligands have been obtained either by methylation of the corresponding dihalide complexes using methylmetal reagents [6a;13;17a], or by ligand-exchange reactions [6a;13]. Reaction of 1a with methyllithium (eqn. 2) in diethyl ether gave beige PdMePh(tmeda) (3) in 88% yield. In the synthesis of the bpy analogue, PdMePh(bpy) (4), by this route both 4 and the dimethyl complex, $PdMe_2(bpy)$ were formed in varying ratios. Bright yellow 4 was however readily obtained in 82% yield from 3 by exchange of tmeda for bpy (eqn. 3).

(3)

I
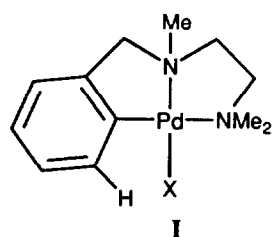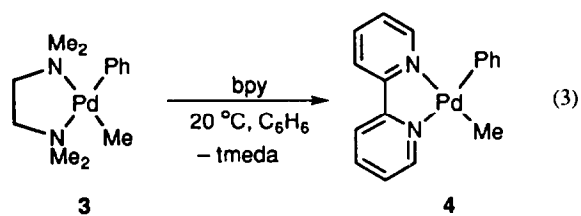
The formation of PdMe$_2$(bpy) in the reaction of PdIPh(bpy) with MeLi indicates that cleavage of the Pd–Ph bond occurs during the reaction. Formation of a palladate intermediate [18a], i.e. Li[PdMe$_2$Ph(bpy)], which would allow the loss of a phenyl group as PhLi does not appear to occur, since the reaction of PdMePh(bpy) with MeLi does not generate PdMe$_2$ (bpy). Further investigations showed that addition of lithium iodide to 4 caused rapid decomposition to palladium(0) and several organic products. However, substantial amounts of PdMe$_2$(bpy) were obtained when lithium iodide and methyl lithium were simultaneously added to PdMePh(bpy) (4). The formation of the dimethyl complex must therefore be due to the synergistic action of methyllithium and lithium iodide. Further investigations of the mechanism of both the lithium iodide induced decomposition and the exchange reaction are in progress. Complexes 3 and 4 can be handled readily in air and are thermally stable at room temperature for at least a few hours, although longer storage requires temperatures of −20°C or lower. Analytically pure samples and crystals suitable for X-ray structural
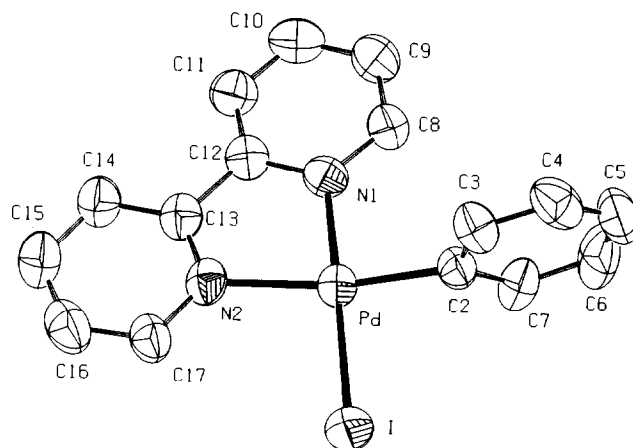

Fig. 2. ORTEP drawing (50% probability level) of PdIPh(bpy) (2a).

analysis (vide infra) were obtained from acetone/pentane at −20°C.

2.2. Structures of the PdXPh(L$_2$) and PdMePh(L$_2$) complexes in the solid state

In order to determine the structural parameters of these new types of complexes, and to assess the influence of the presence of the phenyl ring on the structure compared to analogous methyl- and dimethyl complexes, the crystal structures of the complexes 1a, 2a, 3 and 4 were determined. ORTEP representations of these structures are presented in Figs. 1–4, and selected bond distances and angles are given in Table 2. The phenyl ring is, in all cases, approximately perpendicular to the coordination plane, with the largest deviation (14.3(2)°) shown by PdMePh(tmeda) (3). The Pd–N distances in both the tmeda and the bpy complexes are well within the range (2.03–2.20 Å) reported for the closely related organopalladium(II) complexes PdMe$_2$ (tmeda) [6a], [PdMe(bpy)(γ-picoline)]BF$_4$ [17p] and Pd(N$_3$)(CH$_2$Ph)(bpy) [5e].
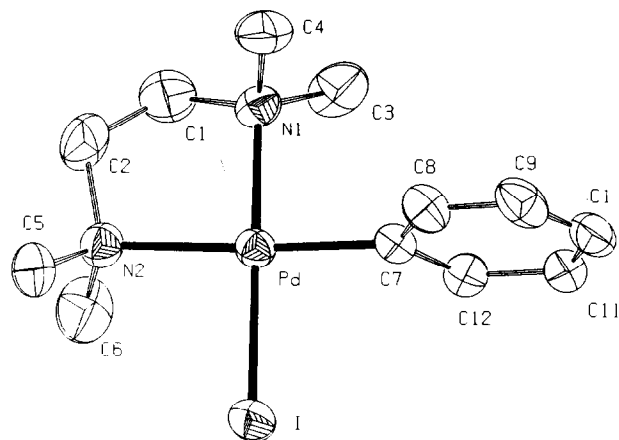

Fig. 1. ORTEP drawing (30% probability level) of PdIPh(tmeda) (1a).

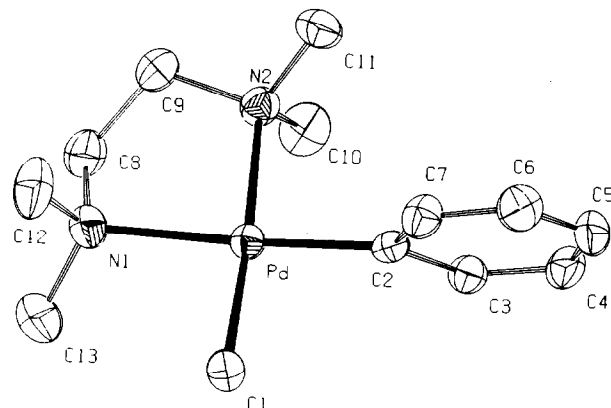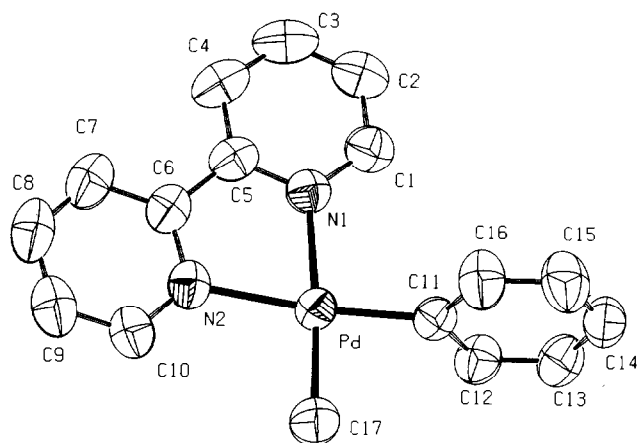Fig. 3. ORTEP drawing (30% probability level) of PdMePh(tmeda) (3).

Fig. 4. ORTEP drawing (50% probability level) of PdMePh(bpy) (4).

The Pd–Me bond distance in PdMePh(bpy) (4, 2.020(5) Å) is normal for a methyl group *trans* to a pyridine nitrogen, as illustrated by the value for the related complex [PdMe(bpy)(γ-picoline)]BF$_4$ (2.036(6) Å). The Pd–Me bond distance in PdMePh(tmeda) (3, 2.107(3) Å) is *ca.* 0.08 Å longer than that in PdMe$_2$(tmeda) (2.026(3) Å) [6a], although the Pd–N(*trans* to Me) bond distance (2.210(3) Å) and N–Pd–N (82.5(1)°) and C–Pd–C (88.3(1)°) bond angles of 3 are comparable to those in PdMe$_2$(tmeda) (2.200(2) Å, 82.7(8)° and 87.4(1)°, respectively). The Pd–C(phenyl) bonds in 3 and 4 are significantly shorter than the Pd–C(methyl) bonds, although this effect is more pro-

TABLE 2. Selected bond distances (Å) and bond angles (°)

	Complexes			
	1a	2a	3	4
Bond distances				
Pd–N(a)[a]	2.127(6)	2.070(8)	2.210(3)	2.117(3)
Pd–N(b)[a]	2.193(6)	2.144(8)	2.195(3)	2.138(3)
Pd–C(Ph)	1.992(7)	1.996(10)	1.985(3)	1.985(3)
Pd–C(Me)			2.107(3)	2.020(5)
Pd–I	2.5703(8)	2.575(1)		
Bond angles				
N(a)–Pd–N(b)	84.0(2)	78.2(3)	82.5(1)	77.2(1)
N(a)–Pd–C(Ph)	92.8(3)	93.5(4)	95.5(1)	98.3(1)
N(b)–Pd–C(Me)			93.8(1)	99.0(2)
N(b)–Pd–I	95.8(2)	100.1(2)		
C(Ph)–Pd–C(Me)			88.3(1)	85.7(2)
C(Ph)–Pd–I	87.4(2)	88.7(3)		
N(a)–Pd–C(Me)			176.3(1)	175.5(2)
N(a)–Pd–I	178.3(1)	173.9(3)		
N(b)–Pd–C(Ph)	176.8(3)	170.1(4)	176.4(1)	173.4(1)
θ[b]	87.5(3)	88.7(5)	75.7(2)	78.7(2)

[a] N(a): *trans* to I or Me; N(b): *trans* to Ph. [b] Calculated angle between the plane of the phenyl ring and the coordination plane defined by N1, N2, C1, C2 or N1, N2, C1, I.

nounced for the tmeda coordinated complex (3). This is consistent with the general trend that Pd–C(sp^2) bond distances (1.89–2.00 Å [19]) are shorter than Pd–C(sp^3) (2.08–2.13 Å [20]). Similarly, the Pd–N(sp^2) bond distances (2.070(8)–2.144(8) Å) in the bpy complexes are shorter than the Pd–N(sp^3) bond distances in the tmeda complexes (2.127(6)–2.210(3) Å). Surprisingly, the Pd–I bond lengths in PdIPh(tmeda) (1a) and PdIPh(bpy) (2a) are similar, while the Pd–Me bond lengths in the analogous PdMePh(N–N) complexes (3, 4) differ by *ca.* 0.08 Å. The Pd–I bonds of 1a and 2a are *ca.* 0.3 Å shorter than those in the palladium(IV) complex PdIMe$_3$(bpy) [5b]. This is probably a result of the stronger *trans* influence of the methyl group in PdIMe$_3$(bpy) compared with that of the nitrogen donors in 1a and 2a.

3. Discussion

Recently there has been significant progress in the development of suitable reagents for the synthesis of methyl(halogeno)- and dimethyl-palladium(II) complexes with nitrogen, phosphorus or mixed nitrogen/phosphorus donor ligands; in particular the applications of PdIMe(tmeda) [21], PdClMe(cod) [22], [PdMe(SMe$_2$)X]$_2$ (X = Cl, Br, I) [13;17p;23;24], [PdMe$_2$(pyridazine)]$_n$ [13;23b] and PdMe$_2$(tmeda) [6a] have been explored. These reactions all proceed under ambient conditions in common organic solvents in moderate to high yield. The facile oxidative addition of iodobenzene to Pd(dba)$_2$ in the presence of bidentate nitrogen donor ligands now allows the synthesis of PdIPh(L$_2$) complexes (L$_2$ = tmeda or bpy) in high yield. These complexes are thermally very stable, like their methyl analogues. The complex PdIPh(tmeda) (1a) has also been shown to be a very good reagent for the synthesis of other PdIPh(L$_2$) complexes, *e.g.* L$_2$ = (R,R)-diop (75%) or 2 PPh$_3$ (90%) [9a]. The yields of the bromo complexes, *i.e.* 8–12% (1b) and 5% (2b), are very low compared with those from oxidative addition of aryl bromides that contain potentially intramolecular coordinating substituents; *e.g.*, 1-bromo-2,6-bis[(dimethylamino)methyl]benzene (NCN–Br) reacts with Pd(dba)$_2$ to give PdBr(NCN) in 88% yield [15]. Whether this is due to the aryl moiety being kept near the palladium centre or to the fact that the substituent lowers the oxidation potential of the metal is not known.

Complexes of the type M(alkyl)(aryl)(N–N) do not appear to have been reported for the other nickel triad elements. The availability of PdMePh(tmeda) as a suitable substrate for the synthesis of related complexes enables the development of new organopalladium(II) and -(IV) chemistry; *e.g.* comparisons of the reactivity

of Pd–alkyl and Pd–aryl bonds. In a separate study we have reported on the oxidative addition of alkyl halides to PdMePh(N-N) (N-N = tmeda, bpy) to give the first examples of mono-arylpalladium(IV) compounds [25]. Finally it must be noted that the molecular structures of the complexes PdIPh(N-N) (1a,2a) and PdMePh(N-N) (3,4) in the solid state now provide important structural data for arylpalladium complexes in which the aryl group is not part of a metallacycle or a cyclometallation system. The availability of these structural details is of great importance for numerical studies.

4. Experimental section

All operations were conducted under dry nitrogen by use of Schlenk techniques. 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 (tmeda), 2,2'-bipyridine (bpy), iodobenzene, bromobenzene and acetone (p.a.) were obtained from Janssen Chimica and used without purification. Bis(dibenzylideneacetone) palladium(0) was prepared by a published procedure [26]. ^{1}H NMR spectra were recorded on a Bruker AC300 (300 MHz) spectrometer. Chemical shifts are given in ppm relative to tetramethylsilane. Microanalyses were performed by the Institute for Applied Chemistry (TNO), Zeist, Netherlands.

4.1. Preparation of PdIPh(tmeda) (1a)

To a purple solution of 4.0 g (7 mmol) of Pd(dba)$_2$ in 100 ml of benzene were added 1.3 ml (9 mmol) of tmeda and 1.1 ml (10 mmol) of iodobenzene. The mixture was slowly heated to 50°C during which the colour changed to green. After filtration of the solution through filter-aid the volatiles were evaporated and the residue washed with diethyl ether (4 × 50 ml). Yield: 2.8 g (95%). Recrystallization was from boiling benzene or methylene chloride/diethyl ether. Anal. Found: C, 43.2; H, 4.8; N, 6.1. C$_{12}$H$_{21}$IN$_2$Pd calcd. C, 33.8; H, 5.0; N, 6.6%. ^{1}H NMR (CDCl$_3$) δ: 2.26 (6H, s, NMe$_2$), 2.58 (4 H, AA'BB', 2 CH$_2$), 2.62 (6H, s, NMe$_2$), 6.75 (1H, t, $2\times^3J = 7.1$ Hz, p-Ph), 6.88 (2H, dd, $^3J = 7.1$ and 7.7 Hz, m-Ph), 7.20 (2H, d, $^3J = 7.7$ Hz, o-Ph). Complexes 1b, 2a and 2b were prepared similarly.

4.2. PdBrPh(tmeda) (1b)

Yield: 8% (C$_6$H$_6$) or 12% (THF). Anal. Found: C, 37.5; H, 5.45; N, 7.3. C$_{12}$H$_{21}$BrN$_2$Pd calcd. C, 34.0; H, 5.6; N, 7.4%. ^{1}H NMR (CDCl$_3$) δ: 2.39 (6H, s, NMe$_2$), 2.62 (6H, s, NMe$_2$), 2.63 (4H, AA'BB', 2 CH$_2$), 6.82 (1H, t, $2\times^3J = 7.2$ Hz, p-Ph), 6.92 (2H, dd, $^3J = 7.2$ and 7.3 Hz, m-Ph), 7.25 (2H, d, $^3J = 7.3$ Hz, o-Ph).

4.3. PdIPh(bpy) (2a)

Yield: 70%. Anal. Found: C: C, 40.5; H, 2.85; N, 5.8. C$_{15}$H$_{13}$IN$_2$Pd calcd. C, 41.2; H, 2.8; N, 6.0%. ^{1}H NMR (CDCl$_3$) δ: 6.94 (1H, t, $2\times^3J = 7.2$ Hz, p-Ph), 7.06 (2H, dd, $^3J = 6.9$ and 7.2 Hz, m-Ph), 7.35 (1H, m, H$_{5'}$-bpy), 7.40 (2H, d, $^3J = 6.9$ Hz, o-Ph), 7.54 (1H, m, H$_5$-bpy), 7.69 (1H, d, $^3J = 3.9$ Hz, H$_{6'}$-bpy), 8.00 (2H, m, H$_{4,4'}$-bpy), 8.09 (2H, m, H$_{3,3'}$-bpy), 9.65 (1H, d, $^3J = 5.2$ Hz, H$_6$-bpy).

4.4. PdBrPh(bpy) (2b)

Yield: 5%. Anal. Found: C, 45.3; H, 3.2; N, 6.6. C$_{15}$H$_{13}$BrN$_2$Pd calcd. C, 45.8; H, 3.1; N, 6.7%. ^{1}H NMR (CDCl$_3$) δ: 6.97 (1H, t, $2\times^3J = 7.2$ Hz, p-Ph), 7.07 (2H, dd, $^3J = 7.2$ and 7.9 Hz, m-Ph), 7.33 (1H, m, H$_{5'}$-bpy), 7.42 (2H, d, $^3J = 7.9$ Hz, o-Ph), 7.56 (1H, m, H$_5$-bpy), 7.91 (1H, d $^3J = 4.5$ Hz, H$_{6'}$-bpy), 8.10 (4H, m, H$_{3,3'}$- and H$_{4,4'}$-bpy), 9.44 (1H, d, $^3J = 5.1$ Hz, H$_6$-bpy).

4.5. Preparation of PdMePh(tmeda) (3)

A suspension of 1a (2.39 g, 5.6 mmol) in 100 ml of diethyl ether was cooled to $-40°C$ and treated with 3.8 ml of MeLi (1.6 M in diethyl ether). The mixture was allowed to warm up slowly, and the solution became clear at ca. $+10°C$. The solution was then cooled to 0°C and treated with water (10 ml). The mixture was cooled to $-40°C$ and the ether layer decanted from the frozen aqueous layer. Subsequently, the volatiles were evaporated in vacuo, after which the greyish residue was dissolved in 10 ml of benzene and the solution filtered through filter-aid. Evaporation of the solvent gave a beige solid, from which traces of benzene were removed by washing with pentane (4 × 20 ml). Yield: 88%. Crystals suitable for the X-ray structure determination were obtained from acetone/pentane at $-20°C$. Anal. Found: C, 49.3; H, 7.4; N, 8.9. C$_{13}$H$_{24}$N$_2$Pd calcd. C, 49.6; H, 7.7; N, 8.9%. ^{1}H NMR (CD$_3$COCD$_3$) δ: -0.21 (3H, s, PdMe), 2.26 (6H, s, NMe$_2$), 2.49 (6H, s, NMe$_2$), 2.64 (4H, AA'BB', 2 CH$_2$), 6.68 (1H, t, $2\times^3J = 7.2$ Hz, p-Ph), 6.81 (2H, dd, $^3J = 7.2$ and 7.9 Hz, m-Ph), 7.37 (2H, d, $^3J = 7.9$ Hz, o-Ph).

4.6. Preparation of PdMePh(bpy) (4)

A yellow solution of 3 (1.86 g, 5.9 mmol) and bpy (1.65 g, 10.6 mmol) in 30 ml of benzene was stirred for 1 h at room temperature. Addition of pentane (20 ml) precipitated the bright yellow product, which was collected on a sintered glass filter and subsequently washed with 3 × 20 ml of pentane. Yield: 82%. Crystals suitable for X-ray structure determination were obtained from acetone/pentane at $-20°C$. Anal. Found: C, 57.2; H, 4.6; N, 7.65. C$_{17}$H$_{16}$N$_2$Pd calcd. C, 57.6; H, 4.55; N, 7.9%. ^{1}H NMR (CD$_3$COCD$_3$) δ: 0.38 (3H, s,

TABLE 3. Crystal data and details of the structure determination

	C₁₂H₂₁IN₂Pd (1a)	C₁₆H₁₃IN₂Pd (2a)	C₁₃H₂₄N₂Pd (3)	C₁₇H₁₆N₂Pd (4)
Empirical formula	$C_{12}H_{21}IN_2Pd$ (1a)	$C_{16}H_{13}IN_2Pd$ (2a)	$C_{13}H_{24}N_2Pd$ (3)	$C_{17}H_{16}N_2Pd$ (4)
Formula weight	426.64	466.62	314.77	354.75
Crystal system	tetragonal	monoclinic	monoclinic	monoclinic
Space group	$P4_2/n$	$P2_1/n$	$C2/c$	$P2_1/n$
a, b, c [Å]	19.082(1), 19.082(1), 8.5367(5)	8.886(2), 16.788(4), 10.586(5)	23.3019(16), 8.2587(8), 16.8712(18)	8.570(1), 19.486(1), 9.449(1)
α, β, γ [deg]	90; 90; 90	90; 106.87(3); 90	90; 115.70(1); 90	90; 111.36(1); 90
V [Å³]	3108.4(3)	1511.2(9)	2925.6(5)	1469.6(3)
Z	8	4	8	4
D_{calc} [g/cm³]	1.823	2.051	1.429	1.603
$F(000)$ [Electrons]	1648	888	1296	712
μ(Mo Kα) [/cm]	31.3	32.2	12.3	12.4
Crystal size [mm]	0.25 × 0.25 × 0.30	0.05 × 0.05 × 1.20	0.25 × 0.33 × 0.63	0.03 × 0.40 × 0.68
Temperature (K)	295	300	300	300
Radiation (Å)	Mo Kα(Zr) 0.71073	Mo Kα(mon) 0.71073	MoKα(mon) 0.71073	MoKα(mon) 0.71073
Theta min-max (deg)	1.0; 27.5	1.21; 27.5	1.34; 25.3	0.1; 27.5
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Scan, (deg)	0.55 + 0.35 tg θ	0.74 + 0.35 tg θ	0.73 + 0.35 tg θ	0.74 + 0.35 tg θ
Reference reflection (s)	1 2 2; 1 $\bar{2}$ $\bar{2}$ (no decay)	4 2 1; 2 1 $\bar{4}$; 1 2 2 (no decay)	$\bar{2}$ 0 $\bar{6}$; 6 2 $\bar{3}$; 9 1 2 (small decay)	2 7 $\bar{1}$; 2 2 $\bar{5}$; 2 0 2 (6% decay)
Dataset	0:24; 0:24; −11:11	−11:11; −21:0; 0:13	−26:0; −9:0; −17:19	−11:11; −25:0; −12:12
Tot. uniq. data	7561; 3566	6378; 3472	2645; 2387	7392; 3361
Observed data [$I > 2.5\,\sigma(I)$]	2315	1999	2089	2750
N_{ref}, N_{par}	2315, 160	1999; 182	2089; 205	2750; 245
R, R_w, S	0.050; 0.042; 2.56	0.055; 0.053; 2.36	0.025; 0.034; 1.64	0.033; 0.043; 0.71
Weighting scheme, w^{-1}	$\sigma^2(F)$	$\sigma^2(F)$	$\sigma^2(F)$	$\sigma^2(F) + 0.0003\,F^2$
Max. and av. shift/error	0.3; 0.05	0.03; 0.006	0.36; 0.05	0.4; 0.03
Min. and max. resd. dens. [e/Å³]	−0.86; 0.91	−1.19; 0.80	−0.27; 0.49	−0.50; 1.11

PdMe), 6.83 (1H, t, $2 \times {}^3J = 7.2$ Hz, p-Ph), 6.97 (2H, dd, ${}^3J = 7.2$ and 7.9 Hz, m-Ph), 7.48 (2H, d, ${}^3J = 7.9$ Hz, o-Ph), 7.52 (1H, m, $H_{5'}$-bpy), 7.74 (1H, m, H_5-bpy), 8.20 (3H, m, $H_{6'}$- and $H_{4,4'}$-bpy), 8.49 (2H, m, $H_{3,3'}$-bpy), 8.80 (1H, d, ${}^3J = 5.2$ Hz, H_6-bpy).

4.7. X-ray structural analyses

General: Scattering factors were taken from Cromer and Mann and corrected for anomalous dispersion [27]. All calculations were carried out on a DEC 5000 system. Geometrical calculations and illustrations were done with PLATON [28]. Crystal data and details of the structure determinations are presented in Table 3. Fractional atomic coordinates are given in Tables 4–7.

4.7.1. PdIPh(tmeda) (1a) [9a]

For a yellow crystal glued on top of a glass fibre, a total of 7561 reflections were scanned on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were derived from the 25 SET4 setting angles in the range $12° < \theta < 20°$. Data were corrected for Lp and absorption (DIFABS [29]). The structure was solved by Patterson techniques (SHELXS86 [30]) and refined by full matrix least squares on F (SHELX76 [31]) to a final

$R = 0.050$. Hydrogen atoms were refined, riding on their carrier atoms, with three common isotropic thermal parameters.

TABLE 4. Fractional coordinates and equivalent isotropic thermal parameters for PdIPh(tmeda) (1a)

	x	y	z	U_{eq} (Å²) [a]
I	0.20966(3)	0.55604(3)	0.55597(7)	0.0835(2)
Pd	0.28117(3)	0.50921(3)	0.32328(6)	0.0534(2)
N(1)	0.3377(3)	0.4685(3)	0.1288(7)	0.064(2)
N(2)	0.2342(3)	0.5788(3)	0.1479(7)	0.067(2)
C(1)	0.3035(5)	0.4967(6)	−0.010(1)	0.108(4)
C(2)	0.2799(6)	0.5686(5)	0.008(1)	0.106(5)
C(3)	0.3356(6)	0.3921(4)	0.117(1)	0.113(5)
C(4)	0.4125(4)	0.4901(5)	0.132(1)	0.098(4)
C(5)	0.2383(5)	0.6535(4)	0.188(1)	0.093(4)
C(6)	0.1606(5)	0.5607(6)	0.121(1)	0.120(5)
C(7)	0.3269(4)	0.4435(4)	0.4731(8)	0.061(3)
C(8)	0.3889(4)	0.4599(4)	0.5477(9)	0.075(3)
C(9)	0.4216(5)	0.4147(6)	0.647(1)	0.086(4)
C(10)	0.3919(6)	0.3504(6)	0.680(1)	0.092(4)
C(11)	0.3301(5)	0.3328(5)	0.611(1)	0.085(4)
C(12)	0.2975(4)	0.3799(4)	0.5064(9)	0.075(4)

[a] $U_{eq} = 1/3$ trace of the orthogonalized U tensor.

TABLE 5. Final coordinates and equivalent isotropic thermal parameters for PdIPh(bpy) (2a)

	x	y	z	U_{eq} (Å²) [a]
I	0.25343(10)	0.14349(5)	0.67802(7)	0.0671(3)
Pd	0.20710(10)	0.12830(4)	0.90592(8)	0.0474(3)
N(1)	0.1485(10)	0.1092(5)	1.0790(8)	0.051(3)
N(2)	0.2693(10)	0.0056(5)	0.9453(9)	0.050(3)
C(2)	0.1605(13)	0.2446(6)	0.9032(10)	0.052(3)
C(3)	0.2857(14)	0.2949(6)	0.9653(12)	0.060(4)
C(4)	0.2583(17)	0.3743(7)	0.9835(12)	0.074(5)
C(5)	0.1125(18)	0.4057(7)	0.9444(14)	0.079(6)
C(6)	-0.0114(17)	0.3555(9)	0.8827(15)	0.087(6)
C(7)	0.0128(14)	0.2752(7)	0.8593(12)	0.066(4)
C(8)	0.0823(13)	0.1628(7)	1.1407(11)	0.058(4)
C(9)	0.0330(13)	0.1426(7)	1.2484(11)	0.061(4)
C(10)	0.0547(14)	0.0658(8)	1.2965(12)	0.067(4)
C(11)	0.1216(13)	0.0119(7)	1.2323(11)	0.060(4)
C(12)	0.1722(12)	0.0336(6)	1.1284(10)	0.048(3)
C(13)	0.2440(12)	-0.0228(6)	1.0531(11)	0.050(3)
C(14)	0.2860(15)	-0.0982(6)	1.0976(13)	0.066(4)
C(15)	0.3525(15)	-0.1488(7)	1.0227(13)	0.075(5)
C(16)	0.3752(15)	-0.1183(7)	0.9103(13)	0.074(5)
C(17)	0.3329(13)	-0.0422(6)	0.8710(12)	0.058(4)

[a] $U_{eq} = 1/3$ trace of the orthogonalized U tensor.

TABLE 7. Fractional coordinates and equivalent isotropic thermal parameters for PdMePh(bpy) (4)

	x	y	z	U_{eq} (Å²) [a]
Pd	0.74577(3)	-0.08695(1)	0.84386(3)	0.0511(1)
N(1)	0.8141(3)	0.00975(13)	0.7822(3)	0.0541(8)
N(2)	0.7390(3)	-0.02165(14)	1.0233(3)	0.0563(8)
C(1)	0.8623(5)	0.0219(2)	0.6645(4)	0.0666(12)
C(2)	0.9119(6)	0.0849(2)	0.6344(6)	0.0773(17)
C(3)	0.9123(6)	0.1382(2)	0.7262(6)	0.0844(16)
C(4)	0.8652(5)	0.12760(18)	0.8493(6)	0.0757(14)
C(5)	0.8161(4)	0.06212(17)	0.8751(4)	0.0569(9)
C(6)	0.7645(4)	0.04567(17)	1.0035(4)	0.0569(10)
C(7)	0.7399(5)	0.0946(2)	1.1003(6)	0.0743(12)
C(8)	0.6887(6)	0.0751(3)	1.2156(5)	0.0834(17)
C(9)	0.6657(5)	0.0079(3)	1.2356(5)	0.0793(16)
C(10)	0.6917(5)	-0.0395(2)	1.1388(4)	0.0679(11)
C(11)	0.7373(4)	-0.13926(16)	0.6610(3)	0.0535(9)
C(12)	0.8676(5)	-0.1807(2)	0.6568(5)	0.0659(11)
C(13)	0.8672(5)	-0.2123(2)	0.5277(5)	0.0720(14)
C(14)	0.7330(6)	-0.2054(2)	0.3953(5)	0.0706(14)
C(15)	0.6012(6)	-0.1667(3)	0.3946(5)	0.0856(16)
C(16)	0.6038(5)	-0.1338(2)	0.5251(4)	0.0777(14)
C(17)	0.6901(8)	-0.1771(2)	0.9200(7)	0.0819(18)

[a] $U_{eq} = 1/3$ trace of the orthogonalized U tensor.

4.7.2. PdIPh(bpy) (2a)

Data were collected on an Enraf-Nonius CAD4T/ rotating anode system from an orange, needle-shaped crystal glued on top of a glass fibre. Cell parameters were derived from the setting angles of 25 reflections (SET4) in the range $9° < \theta < 14°$. A total of 6378 reflections was scanned, corrected for Lp and absorption/extinction (DIFABS [29]) and merged ($R_{int} = 0.052$) into a unique set of 1999 reflections with $I > 2.5 \, \sigma(I)$. The structure was solved by direct methods (SHELXS86

TABLE 6. Fractional coordinates and equivalent isotropic thermal parameters for PdMePh(tmeda) (3)

	x	y	z	U_{eq} (Å²) [a]
Pd	0.13299(1)	0.12710(3)	0.12574(1)	0.0398(1)
N(1)	0.14366(15)	-0.0465(4)	0.22975(18)	0.0563(10)
N(2)	0.13015(15)	-0.0965(3)	0.05213(19)	0.0499(9)
C(1)	0.13683(19)	0.3307(4)	0.2031(2)	0.0483(11)
C(2)	0.11831(15)	0.2768(3)	0.0267(2)	0.0414(10)
C(3)	0.16352(18)	0.3137(5)	-0.0040(2)	0.0499(11)
C(4)	0.1490(2)	0.4061(5)	-0.0779(3)	0.0609(14)
C(5)	0.0898(2)	0.4651(5)	-0.1246(3)	0.0689(16)
C(6)	0.0442(2)	0.4367(5)	-0.0960(3)	0.0662(14)
C(7)	0.05857(17)	0.3482(4)	-0.0213(2)	0.0538(12)
C(8)	0.1593(2)	-0.2041(4)	0.2000(3)	0.0690(4)
C(9)	0.1206(2)	-0.2281(4)	0.1030(3)	0.0669(14)
C(10)	0.1895(3)	-0.1188(6)	0.0439(4)	0.0762(19)
C(11)	0.0771(3)	-0.0978(6)	-0.0365(3)	0.0700(14)
C(12)	0.0825(3)	-0.0576(8)	0.2364(4)	0.085(2)
C(13)	0.1955(3)	-0.0110(7)	0.3171(3)	0.0852(18)

[a] $U_{eq} = 1/3$ trace of the orthogonalized U tensor.

[30]) and refined by full matrix least-squares on F (SHELX76 [31]) to a final $R = 0.055$. Hydrogen atoms were taken into account at calculated positions with one common U_{iso}.

4.7.3. PdMePh(tmeda) (3)

A transparent, block shaped crystal was mounted on top of a glass fibre and transferred to an Enraf-Nonius CAD4T/ rotating anode diffractometer. Precise lattice parameters and their standard deviations were derived from the angular setting of 25 reflections in the range $11° < \theta < 16°$. The net intensities of the data were corrected for Lorentz and polarization effects and a small linear decay. An absorption correction was applied using standard Patterson methods (SHELXS86 [30]) and subsequent difference Fourier syntheses, and refined by full-matrix least-squares techniques on F (SHELX76 [31]). All hydrogen atoms were introduced on calculated positions (C–H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. An empirical isotropic extinction coefficient (final value = 0.00019(2)) was refined. Refinement converged at $R = 0.0249$ ($R_w = 0.0339$).

4.7.4. PdMePh(bpy) (4) [9b]

A yellow crystal was glued on top of a glass fibre and transferred for data collection to an Enraf-Nonius CAD4T/rotating anode system. Unit cell parameters were derived from the 25 SET4 setting angles in the

range $11° < \theta < 14°$. A redundant set of 7392 reflections was scanned, corrected for Lp, and merged into a unique set of 2750 reflections with $I > 2.5 \ \sigma(I)$. The structure was solved with the PATT option of SHELXS86 [30] and refined with SHELX76 [31] by full-matrix least-squares techniques. Convergence was reached at $R = 0.033$. Hydrogen atoms were located from a difference density map, and their positions and isotropic thermal parameters refined.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and a complete list of bond lengths and angles.

Acknowledgments

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