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Reversible oxidative addition of a diaryl diselenide to a diorganopalladium(II) complex, carbon–selenium bond formation at palladium(IV), and structural studies of palladium(II) and platinum(IV) selenolates

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Abstract

Methyl(4-methoxyphenyl)(2,2′-bipyridine)palladium(II) (**1**) reacts with bis(4-chlorophenyl) diselenide in dichloromethane to form an equilibrium with the Pd(IV) complex $Pd(SeC_6H_4Cl)_2Me(C_6H_4OMe)(bpy)$ (**2**) for which the forward reaction exhibits $\Delta H = -130 \pm 12$ kJ mol^{-1} and $\Delta S = -472 \pm 49$ J K^{-1} mol^{-1}, and with $K = 754 \pm 145$ at −25 °C. The Pd(IV) complex is isolable at −40 °C, and when the equilibrium mixture is kept at −25 °C, a temperature at which the Pd(II) complex is stable, selective reductive elimination of Me–SeC_6H_4Cl occurs very slowly from the Pd(IV) complex to form $Pd(SeC_6H_4Cl)(C_6H_4OMe)(bpy)$ (**3**). In contrast, $(ClC_6H_4Se)_2$ reacts with $PdMe_2(dmpe)$ (**4**) [dmpe = 1,2-bis(dimethylphosphino)ethane] to form $Pd(SeC_6H_4Cl)Me(dmpe)$ (**5**) and Me–SeC_6H_4Cl. A second equivalent of $(ClC_6H_4Se)_2$ reacts with **5** to cleave the second Pd–Me bond to give $Pd(SeC_6H_4Cl)_2(dmpe)$ (**6**) and Me–SeC_6H_4Cl. Similarly, PdMeTol(dmpe) (**7**) (Tol = 4-tolyl) forms predominantly $Pd(SeC_6H_4Cl)Tol(dmpe)$ (**8**) together with some $Pd(SeC_6H_4Cl)Me(dmpe)$ (**5**), and **8** reacts with $(ClC_6H_4Se)_2$ to form $Pd(SeC_6H_4Cl)_2(dmpe)$ (**6**) and Tol-SeC_6H_4Cl. Bis(4-chlorophenyl) diselenide reacts with $PtTol_2(bpy)$ (**9**) (Tol = 4-tolyl) to form $Pt(SeC_6H_4Cl)_2Tol_2(bpy)$ (**10**) which, together with **2**, has a trans-configuration for the selenolate ligands. X-ray structural studies of octahedral **10** as the solvate $\mathbf{10}\cdot 3CHCl_3$ and square planar **5** are reported.

1. Introduction

Formation of carbon(sp^2)-heteroatom bonds by reductive elimination from Pd(IV) centres has been proposed in catalytic processes for C–O bond formation [1–3]. Model reactions relevant to this catalysis have been reported, but coupling from a Pd(IV) intermediate containing both Pd–C and Pd–O bonds has not been detected [4]. However, related carbon–selenium bond formation from Pd(IV) species such as $Pd(SePh)_2Me_2(L_2)$ [L_2 = 2,2′-bipyridine] (Eq. (1)) has been documented, with coupling involving a C(sp^3) group [5]. We report here studies of a Pd(IV) complex containing both alkyl and aryl groups, $Pd(SeC_6H_4Cl)_2Me(C_6H_4OMe)(bpy)$ (**2**) (SeC_6H_4Cl = 4-chloroselenophenolate, C_6H_4OMe = 4-methoxyphenyl), to probe selectivity in C(sp^2)–Se and C(sp^3)–Se bond formation. This approach has led to detection of a reversible oxidative addition of $(ClC_6H_4Se)_2$ to $PdMe(C_6H_4OMe)(bpy)$ (**1**), related to a similar equilibrium reported for Pt(II) exemplified in Eq. (2) [6].

$$PdMe_2(bpy) \overset{(PhSe)_2}{\rightarrow} Pd(SePh)_2Me_2(bpy) \rightarrow Me\text{–}Me + Me\text{–}SePh \quad (1)$$

$$PtMe\{CH(CO_2Me)_2\}(4,4'\text{-}Bu^t_2bpy) + (PhSe)_2 = Pt(SePh)_2Me\{CH(CO_2Me)_2\}(4,4'\text{-}Bu^t_2\text{-}bpy) \quad (2)$$

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Thermodynamic parameters for the Pd(II)/Pd(IV) equilibrium have been determined and the Pd(IV) species shown to decompose by C(sp^3)–Se bond formation. Carbon(sp^3)–selenium coupling is also observed on the reaction of $(ClC_6H_4Se)_2$ with $PdMe_2$(dmpe) (**4**) and Pd(SeC_6H_4Cl)Me(dmpe) (**5**) [dmpe = 1,2-bis(dimethylphosphino)ethane], both C(sp^3)–Se and C(sp^2)–Se coupling for PdMeTol(dmpe) (**7**) (Tol = 4-tolyl), and C(sp^2)–Se coupling for Pd(SeC_6H_4Cl)Tol(dmpe) (**8**). The stable Pt(IV) complex Pt$(SeC_6H_4Cl)_2Tol_2$(bpy) (**10**) has been prepared as a model for unstable Pd$(SeC_6H_4Cl)_2Me(C_6H_4OMe)$(bpy) (**2**).

2. Results and discussion

2.1. Studies of reactivity

Preliminary NMR studies at low temperature indicated the presence of the equilibrium shown in Scheme 1 with the Pd(IV) complex (**2**) dominant at low temperatures. The Pd(IV) complex (**2**) was isolated from reactions at −40 °C using an excess of diselenide, allowing confirmation of assignment of NMR spectra for the equilibrium, and allowing a study of the equilibrium over a temperature range using a pure sample of the complex. Complex **2** exhibits two pyridyl group environments and one selenolate environment, consistent with a trans orientation for the selenolate ligands as observed in crystal structure analyses of $Pd(SePh)_2Me_2$ (L_2) (L_2 = bpy, 1,10-phenanthroline) and the Pt(IV) complex Pt$(SeC_6H_4Cl)_2Tol_2$(bpy) (**10**) (see below). Equilibrium constants for the forward reaction of Scheme 1 were estimated from ^{1}H NMR integrations, and a plot of $\ln K$ versus T^{-1}, leading to estimation of $\Delta H = -130 \pm 12$ kJ mol^{-1} and $\Delta S = -472 \pm 49$ J K^{-1} mol^{-1}. At higher temperatures (−25 to −20 °C) very small amounts of reductive elimination products were apparent and, although the decomposition may have minimal impact on the determination of equilibrium constants, the values determined are not considered sufficiently reliable to allow detailed comparison with related data for platinum chemistry referred to above [6].

The palladium(II) reagent is stable at −25 °C, allowing determination of the decomposition behaviour of **2** to be as shown in Eq. (3), together with a small quantity (<5%) of Me–C_6H_4OMe. Complex **3** was identified by ^{1}H NMR spectroscopy (two pyridyl ring environments, one selenolate and 4-methoxyphenyl environment) and Me–SeC_6H_4Cl by NMR and GC–MS.

$$Pd(SeC_6H_4Cl)_2Me(C_6H_4OMe)(bpy)\ (\mathbf{2}) \rightarrow Pd(SeC_6H_4Cl)(C_6H_4OMe)(bpy)\ (\mathbf{3}) + Me\text{–}SeC_6H_4Cl \quad (3)$$

An extension of this approach to include a complex containing a bidentate phosphine, $PdMe_2$(dmpe) (**4**) led to the formation of Me–SeC_6H_4Cl at −15 °C and the isolation of Pd(SeC_6H_4Cl)Me(dmpe) (**5**) without detection of a potential Pd(IV) intermediate (Eq. (4)). Complex **5** was identified by ^{1}H and ^{31}P{^{1}H}NMR spectroscopy and a crystal structure analysis (see below) and, on addition of a second equivalent of $(ClC_6H_4Se)_2$, it forms $Pd(SeC_6H_4Cl)_2$(dmpe) (**6**) and Me–SeC_6H_4Cl (Eq. (5)). In similar reactions, PdMeTol(dmpe) (**7**) forms predominantly Pd(SeC_6H_4Cl)Tol(dmpe) (**8**) and Me–SeC_6H_4Cl (Eq. (6)); addition of a second equivalent of $(ClC_6H_4Se)_2$ results in cleavage of Pd–Me and Pd–Tol bonds of **5** and **8** according to Eqs. (5) and (7), respectively.

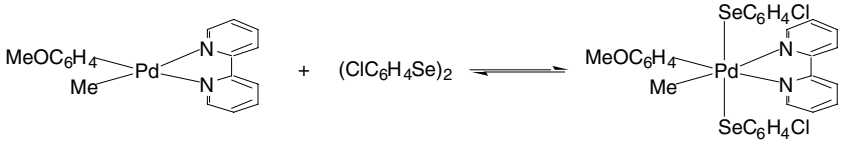
$$PdMe_2(dmpe)\ (\mathbf{4}) + (ClC_6H_4Se)_2 \rightarrow Pd(SeC_6H_4Cl)Me(dmpe)\ (\mathbf{5}) + Me\text{–}SeC_6H_4Cl \quad (4)$$

$$Pd(SeC_6H_4Cl)Me(dmpe)\ (\mathbf{5}) + (ClC_6H_4Se)_2 \rightarrow Pd(SeC_6H_4Cl)_2(dmpe)\ (\mathbf{6}) + Me\text{–}SeC_6H_4Cl \quad (5)$$

$$PdMeTol(dmpe)\ (\mathbf{7}) + (ClC_6H_4Se)_2 \rightarrow \sim 0.8[Pd(SeC_6H_4Cl)Tol(dmpe)\ (\mathbf{8}) + Me\text{–}SeC_6H_4Cl] + \sim 0.2[Pd(SeC_6H_4Cl)Me(dmpe)\ (\mathbf{5}) + Tol\text{-}SeC_6H_4Cl] \quad (6)$$

$$Pd(SeC_6H_4Cl)Tol(dmpe)\ (\mathbf{8}) + (ClC_6H_4Se)_2 \rightarrow Pd(SeC_6H_4Cl)_2(dmpe)\ (\mathbf{6}) + Tol\text{-}SeC_6H_4Cl \quad (7)$$

The reaction of Eq. (2) indicates that C(sp^3)–Se rather than C(sp^2)–Se coupling occurs from Pd(IV) centres containing nitrogen donor ligands. Palladium(IV) intermediates may occur in the reactions of Eqs. (4)–(7), and if so, the reaction of Eq. (6) is consistent with the preference for C(sp^3)–Se coupling. In related studies, Steinborn and coworkers [11] found that $PdMe_2$(dppe) [dppe = 1,2-bis(diphenylphosphino)ethane] reacts with $(PhSe)_2$ to form Pd(SePh)Me(dppe) (91%) and Pd(SePh)2(dppe) (9%). Although the palladium(IV) complex **2**



1 **2**

Scheme 1.

proved to be too unstable to allow successful attempts to obtain crystals suitable for X-ray diffraction, a related arylplatinum(IV) complex $Pt(SeC_6H_4Cl)_2Tol_2(bpy)$ (**10**) was readily obtained on reaction of $PtTol_2(bpy)$ (**9**) with $(ClC_6H_4Se)_2$ in acetone and crystals obtained from CH_2Cl_2/diethyl ether.

2.2. Structural studies of *5* and *10*

The results of the single crystal X-ray structure determinations are consistent with the above stoichiometries and connectivities, despite, in the case of **10**, difficulties associated with the material and solvent disorder which somewhat adversely affected the precision of the study (Fig. 1(a), Tables 1 and 2). Also, for this complex, one-half of the formula unit comprises the asymmetric unit, the substrate molecule and one of the solvent molecules being disposed about crystallographic 2-axes, which, in the case of the substrate, pass through the metal atom and the mid-point of the bpy ligand. Displacement parameter amplitudes are rather high, particularly at the molecular peripheries, possibly indicating minor unresolved disorder, and thus geometries should be treated with caution. Disorder is also resolvable in one of the bridging methylene groups of the dmpe ligand of **5**, apparently impacting on the displacement parameters of the nearby methyl groups of the ligand, disorder not being resolvable in the latter.

With these reservations, the Pt–Se bond distance [2.519(1) Å] in **10** is similar to those reported for $Pt(SePh)_2Me_2(L_2)$ [L_2 = bpy (2.498(1) Å), 1,10-phenanthroline (2.491(1), 2.486(1) Å], the Pt–N distance [2.140(9) Å] is similar to that in the latter complexes [2.162(5); 2.150(5), 2.168(6) Å], and the Pt–C distance [2.02(1) Å] is also similar [2.055(8); 2.058 (9), 2.049(8) Å]. The Pd–Se distance in **5** [2.4483(8) Å] compares well with $Pd(SePh)_2(dppe)$ [2.444(1), 2.480(1) Å] which also has the selenolate group trans to a phosphine donor [12].

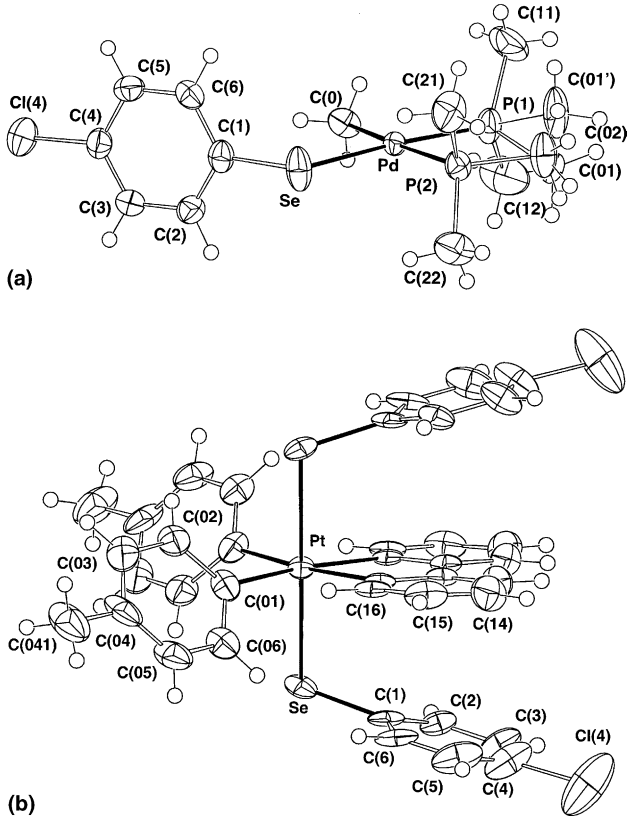


Fig. 1. Projections of molecules of (a) $Pd(SeC_6H_4Cl)Me(dmpe)$ (**5**) and (b) $Pt(SeC_6H_4Cl)_2Tol_2(bpy)$ (**10**) in its chloroform solvate **10** · $3CHCl_3$.

Table 1
Selected geometries for $Pd(SeC_6H_4Cl)Me(dmpe)$ (**5**)

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Pd–P(1)	2.230(1)	Pd–C(0)	2.116(6)
Pd–P(2)	2.305(2)	Pd–Se	2.4483(8)
C(4)–Cl(4)	1.746(6)	Se–C(1)	1.916(6)
Angles (°)			
P(1)–Pd–P(2)	85.79(8)	P(2)–Pd–C(0)	175.2(2)
P(1)–Pd–C(0)	89.4(2)	P(2)–Pd–Se	88.20(4)
P(1)–Pd–Se	173.78(6)	C(0)–Pd–Se	96.6(2)
Pd–P(1)–C(11)	118.5(2)	Pd–P(2)–C(21)	117.9(3)
Pd–P(1)–C(12)	117.1(4)	Pd–P(2)–C(22)	117.5(2)
Pd–P(1)–C(01)	107.1(5)	Pd–P(2)–C(02)	107.5(2)
Pd–P(1)–C(01′)	105.9(5)	Pd–Se–C(1)	110.7(2)
Torsion angles (carbon atoms denoted by number only)			
P(2)–Pd–P(1)–C(01)	20.8(5)	P(1)–Pd–P(2)–C(02)	0.2(3)
P(2)–Pd–P(1)–C(01′)	−17.5(5)	Pd–P(2)–C(02)–C(01)	−26.6(8)
Pd–P(1)–C(01)–C(02)	−43.5(9)	Pd–P(2)–C(02)–C(01′)	28.3(10)
Pd–P(1)–C(01′)–C(02)	39.7(11)	P(2)–C(02)–C(01)–P(1)	45.0(10)
Pd–Se–C(1)–C(2)	97.2(5)	P(2)–C(02)–C(01′)–P(1)	−43.1(11)

Pd lies 0.031(2) out of the P_2SeC donor plane ($\chi^2 = 36$); the P_2SeC/phenyl C_6 interplanar dihedral angle is 88.3(2).

Table 2
Selected geometries for $Pt(SeC_6H_4Cl)_2Tol_2(bpy)$ (**10**) in ($\mathbf{10}\cdot 3CHCl_3$) primed atoms are related by the intramolecular 2-axis

Atoms	Parameter	Atoms	Parameter
Distances (Å)			
Pt–C(01)	2.02(1)	Se–C	1.93(1)
Pt–N(1)	2.140(9)	C(4)–Cl(4)	1.77(2)
Pt–Se	2.519(1)		
Angles (°)			
Se–Pt–N(1)	95.2(2)	N(1)–Pt–N(1′)	76.4(4)
Se–Pt–N(1′)	85.0(2)	N(1)–Pt–C(01)	97.8(5)
Se–Pt–C(01)	92.0(3)	N(1)–Pt–C(01′)	173.2(4)
Se–Pt–C(01′)	87.8(3)	C(01)–Pt–C(01′)	88.1(6)
Se–Pt–Se′	179.7(2)	Pt–Se–C(11)	102.0(3)

Interplanar dihedral angles: N(1, 1′) C(01, 01′)/C(1–6), C(01–06) 14.0(4), 53.1(5); C(1–6)/C(01–06) is 44.0(5).

3. Experimental

The reagents $PdMe(C_6H_4OMe)(bpy)$ [7], $PdMe_2$(dmpe) [8] PdMeTol(bpy) [7] and $PtTol_2(bpy)$ [9] were prepared as described. Solvents were dried and distilled, stored under nitrogen, and all procedures were carried out under nitrogen. NMR spectra were recorded on a Varian Unity Inova 400 MHz wide bore instrument, at 399.7 MHz for ^1H and 161.8 MHz for ^{31}P, at room temperature unless indicated otherwise. Chemical shifts are given in ppm relative to $SiMe_4$ and external H_3PO_4. Microanalyses were performed by the Central Science Laboratory, University of Tasmania. GC–MS analyses were performed using an HP5890 gas chromatograph equipped with an HP5790 MSD and a 25 m × 0.32 mm HP1 column (0.52 m film thickness, He at 10 psi).

3.1. Synthesis of $Pd(SeC_6H_4Cl)_2Me(C_6H_4OMe)(bpy)$ (**2**)

A solution of $(ClC_6H_4Se)_2$ (0.060 g, 0.157 mmol) in CH_2Cl_2 (2 ml) was added to solid $PdMe(C_6H_4OMe)$(bpy) (0.038 g, 0.098 mmol) precooled to −40 °C. The solution quickly became dark red and stirring was continued for 2 h at −40 °C. The volume was reduced to near dryness, and pentane added to precipitate a red solid which was collected by filtration, rinsed with pentane (2 × 3 ml) and diethyl ether (2 ml) and dried under a vacuum. The product was stored at −20 °C. Yield: 0.070 g (93%). ^1H NMR ($CDCl_3$, −50 °C): δ 8.97 (d, 1H, $^3J = 5.2$ Hz, H6), 8.25 (d, 1H, $^3J = 5.2$ Hz, H6′), 7.93(t, $^3J = 7.6$ Hz, H4), 7.79 (t, $^3J = 7.6$ Hz, H4′), 7.69 (d, 1H, $^3J = 8.0$ Hz, H3), 7.53 (m, 4H, H3′, H5 and *ortho*-C_6H_4), 7.25 m, H5′), 6.90 (d, 2H, $^3J = 8.4$ Hz, *meta*-C_6H_4), 6.48 (d, 4H, $^3J = 8.0$ Hz, SeC_6H_4Cl), 6.42 (d, 4H, $^3J = 8.0$ Hz, SeC_6H_4Cl), 3.84 (s, 3H, OMe), 2.58 (s, 3H, PdMe). Anal. Calcd.: C, 47.05; H, 3.42; N, 3.66. Found: C, 46.98; H, 3.36; N, 3.58%.

3.2. Synthesis of $Pd(SeC_6H_4Cl)Me(dmpe)$ (**5**)

A solution of $(ClC_6H_4Se)_2$ (0.014 g, 0.038 mmol) in CH_2Cl_2 (2 ml) was added to a stirred solution of $PdMe_2$(dmpe) (0.011 g, 0.037 mmol) in CH_2Cl_2 (2 ml) at −50 °C. The solution was allowed to warm slowly to ambient temperature with stirring. The volume was reduced to near dryness under a vacuum, and pentane added to precipitate the product as an orange solid which was collected by filtration, rinsed with pentane (3 × 5 ml) and dried under a vacuum. Yield: 0.016 g (95%). ^1H NMR ($CDCl_3$): δ 7.60 (d, 2H, $^3J = 8.4$ Hz, C_6H_4), 7.01 (d, 2H, $^3J = 8.4$ Hz, C_6H_4), 1.88–1.58 (m, 4H, PCH_2), 1.48 (s, 6H, $^2J_{PH} = 10.0$ Hz, PMe_2), 1.13 (s, 6H, $^2J_{PH} = 8.4$ Hz, PMe_2), 0.15 (t, 3H, $^3J_{PH} = 6.8$ Hz and 6.0 Hz, PdMe). $^{31}P\{^1H\}$($CDCl_3$): δ 21.4. Anal. Calcd.: C, 33.79; H, 5.02. Found: C, 33.78; H, 5.08%.

3.3. Synthesis of $Pd(SeC_6H_4Cl)_2(dmpe)$ (**6**)

A solution of $PdMe_2$(dmpe) (0.010 g, 0.036 mmol) and $(ClC_6H_4Se)_2$ (0.035 g, 0.091 mmol) in CH_2Cl_2 (0.8 ml) was allowed to react at ambient temperature for 2 h to give an orange solution. Pentane was added to precipitate the product, the suspension was centrifuged and the yellow supernatant removed. The orange product was rinsed with pentane (2 × 1 ml) and diethyl ether (2 ml), and dried under a vacuum. Yield: 0.010 g (44%). ^1H NMR (CD_2Cl_2): δ 7.51 (d, 4H, $^3J = 8.0$ Hz, C_6H_4), 6.97(d, 4H, $^3J = 8.0$ Hz, C_6H_4), 1.80 (d(br), 4H, $^2J_{PH} = 20.0$ Hz, PCH_2), 1.42 (d, 12H, $^2J_{PH} = 10.8$ Hz, PMe_2). $^{31}P\{^1H\}$(CD_2Cl_2): δ 37.6. Anal. Calcd.: C, 33.91; H, 3.79. Found: C, 33.77; H, 3.98%.

3.4. Synthesis of PdMeTol(dmpe) (**7**)

1,2-Bis(dimethylphosphino)ethane (52 μl, 0.31 mmol) was added to a solution of PdMeTol(tmeda) (0.100 g, 0.300 mmol) in benzene (1 ml). After several minutes of stirring a white precipitate formed. Pentane (2 ml) was added and the solution decanted. The white solid was rinsed with pentane (2 × 5 ml) and diethyl ether (2 × 2 ml) and dried under a vacuum. Yield: 0.110 g (100%). ^1H NMR (acetone-d_6): δ 7.21 (t, 2H, $J = 7.0$ Hz, *ortho*-Tol), 6.73 (d, 2H, $^3J = 6.0$ Hz, *meta*-Tol), 2.14 (s, 3H, Me), 1.38 (d, 6H, $^2J_{PH} = 8.0$ Hz, PMe_2), 1.17 (d, 6H, $^2J_{PH} = 8.0$ Hz, PMe_2), 0.01 (dd, 3H, $J_{PH} = 7.2$ Hz, $J_{PH} = 8.8$ Hz, PdMe). $^{31}P\{^1H\}$ (acetone-d_6): δ 25.5 (d, $J_{PP} = 24.0$ Hz), 22.3 (d, $J_{PP} = 24.4$ Hz).

3.5. Synthesis of $Pt(SeC_6H_4Cl)_2(Tol)_2(bpy)$ (**10**)

A solution of $(ClC_6H_4Se)_2$ (0.030 g, 0.080 mmol) in acetone (1 ml) was added to a stirred solution of

$Pt(Tol)_2(bpy)$ (0.0398 g, 0.080 mmol) in acetone (5 ml). The solution was stirred at ambient temperature for 12 h, the solvent removed in a vacuum, and the solid washed with diethyl ether (3×1 ml). The solid was recrystallised from CH_2Cl_2/diethyl ether to give orange –red crystals of the product. Yield: 0.030 g (41%). ^1H NMR ($CDCl_3$): δ 8.95 (d, 2H, $^3J = 5.5$ Hz, $J_{PtH} \sim 18$ Hz, H6), 7.77 (td, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, H4), 7.47 (m, 6H, H3 and *ortho*-Tol), 7.36 (t, $^3J = 6.2$ Hz, H5), 6.92 (d, 4H, $^3J = 8.4$ Hz, *meta*-Tol), 6.63 (d, 4H, $^3J = 8.0$ Hz, SeC_6H_4Cl), 6.36 (d, 4H, $^3J = 8.4$ Hz, SeC_6H_4Cl), 2.35 (s, 6H, Me). Anal. Calcd.: C, 47.28; H, 3.31. Found: C, 47.26; H, 3.38%.

3.6. NMR studies

In a typical experiment for the determination of equilibrium constants for the reaction of Scheme 1, a sample of $Pd(SeC_6H_4Cl)_2Me(C_6H_4OMe)(bpy)$ (**2**) (0.0040 g, 0.0052 mmol) was cooled to the required temperature then dissolved in CD_2Cl_2 (600 μl). The sample was kept at the required temperature for several hours until equilibrium was reached. The concentration of each compound was determined by integration, and 5% tolerance in integration was assumed ($K = 35408 \pm 7750$ at −40 °C, 4628 ± 950 at −35 °C, 2010 ± 400 at −30 °C, 754 ± 145 at −25 °C, 116 ± 20 at −20 °C). In a typical experiment relating to the reactions of Eqs. (4)–(7), a solution of $(ClC_6H_4Se)_2$ (0.0040 g, 0.0105 mmol) in CD_2Cl_2 (0.4 ml) was added to a solution of PdMeR(dmpe) (R = Me, Tol) (0.0105 mmol) in CD_2Cl_2 (0.2 ml). The sample was monitored by ^1H and/or ^{31}P NMR spectroscopy to the completion of the reaction. To this was added a second equivalent of $(ClC_6H_4Se)_2$ (0.0040 g, 0.0105 mmol) and the reaction monitored to its completion. NMR spectra (in CD_2Cl_2) of products are listed above for complexes **5** and **6**; Me–SeC_6H_4Cl: δ 7.35 (d, 2H, $^3J = 8.4$ Hz), 7.23 (d, 2H, $^3J = 8.8$ Hz), 2.34 (s, 3H, Me); Tol-SeC_6H_4Cl: δ 7.40 (d, 2H, $^3J = 8.0$ Hz), 7.31 (m) and 7.21 (m) overlapping, 7.13 (d, 2H, $^3J = 7.8$ Hz), 2.33 (s, 3H, Me); $Pd(SeC_6H_4Cl)(C_6H_4OMe)(bpy)$ (**3**): δ 9.06 (d, 1H, $^3J = 4.0$ Hz, bpy), 8.10 (m, 2H, bpy), 8.00 (m, 2H, bpy), 7.92 (d, ^1H, $^3J = 5.2$ Hz, bpy), 7.69 (d, 2H, $^3J = 8.4$ Hz, SeC_6H_4Cl or C_6H_4OMe), 7.45 (m, 1H, bpy), 7.35 (m, 1H, bpy overlapping with other resonances), 7.21 (d, 2H, $^3J =$ 8.4 Hz, SeC_6H_4Cl or C_6H_4OMe), 6.86 (d, 2H, $^3J = 8.4$ Hz, SeC_6H_4Cl or C_6H_4OMe), 6.67 (d, 2H, $^3J = 8.0$ Hz, SeC_6H_4Cl or C_6H_4OMe), 3.74 (s, 3H, OMe); $Pd(SeC_6H_4Cl)Tol(dmpe)$ (**8**): δ 7.13 (m, 2H, Tol or SeC_6H_4Cl), 6.89 (d(b), 2H, $^3J = 7.8$ Hz, Tol or SeC_6H_4Cl), 6.82 (d(b), 2H, $^3J = 6.8$ Hz, Tol or SeC_6H_4Cl), 2.20 (s, 3H, PdTol), 1.70 (m, 4H, CH_2), 1.22 (d, 6H, $J_{PH} = 10.4$ Hz, PMe_2), 1.05 (d, 6H, $J_{PH} = 8.8$ Hz, PMe_2), $^{31}P\{^1H\}$ δ 28.2 (d, $J_{PP} = 20.9$ Hz), 22.5 (d, $J_{PP} = 20.6$ Hz).

3.7. X-ray data collection and structure determination, and refinement for complexes 5 and 10

Crystals of **5** and **10**·$CHCl_3$ were obtained by recrystallisation from $CHCl_3$/diethyl ether and CH_2Cl_2/diethyl ether, respectively, and full spheres of CCD area-detector diffractometer data were measured (Bruker AXS instrument, $2\theta_{max} = 58°$, ω-scans, monochromatic Mo $K\alpha$ radiation, $\lambda = 0.7107_3$ Å; T ca. 153 K) yielding $N_{(total)}$ reflections, merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ considered 'observed' and used in the full-matrix least squares refinements, refining anisotropic displacement parameter forms for the non-hydrogen atoms, $(x, y, zU_{iso})_H$ being included and constrained at estimated values. Conventional residuals R, R_w (weights: $(\sigma^2(F) + 0.0004F^2)^{-1}$) on $|F|$ are cited at convergence. Neutral atom complex scattering factors were employed within the Xtal 3.7 program system [10]. Pertinent results are given in Tables 1 and 2 and Fig. 1(b), the latter showing 50% probability displacement amplitudes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Individual variations in procedure and difficulties are cited as 'variata'.

4. Crystal/refinement data

4.1. Pd(SeC6H4Cl)Me(dmpe) (5)

$C_{13}H_{23}ClP_2PdSe$, $M = 462.1$. Orthorhombic, space group $Pna2_1$ (C_{2v}^9, No. 33), $a = 16.919(3)$, $b = 6.1734(9)$, $c = 16.906(3)$ Å, $V = 1766$ Å^3. D_c ($Z = 4$) $= 1.73_8$ g cm^{-3}. $\mu_{Mo} = 34$ cm^{-1}; specimen: $0.20 \times 0.17 \times 0.14$ mm; $T_{min/max} = 0.88$. $2\theta_{max} = 75°$; $N_t = 36023$, $N = 4731$ ($R_{int} = 0.051$), N_o 2953; $R = 0.034$, $R_w = 0.037$.

Variata: Within the present space group, one of the bidentate methylene groups is modelled as disordered over a pair of sites, occupancies set at 0.5 after trial refinement. 'Friedel' data were preserved distinct, x_{abs} refining to 0.02(1).

4.2. Pt(SeC6H4Cl)2(Tol)2(bpy)·3CHCl3

(**10**·$3CHCl_3$) ≡ $C_{39}H_{33}Cl_{11}N_2PtSe_2$, $M = 1272.7$. Monoclinic, space group C/c (C_{2h}^6, No.15), $a = 24.345$ (3), $b = 14.405(2)$, $c = 15.848(2)$ Å, $\beta = 127.032(2)°$, $V = 4437$ Å^3. D_c ($Z = 4$ f.u.) $= 1.90_5$ g cm^{-3}. $\mu_{Mo} = 55$ cm^{-1}; specimen: $0.35 \times 0.12 \times 0.12$ mm; $T_{min/max} = 0.57$. $2\theta_{max} = 50°$; $N_t = 51575$, $N = 3905$ ($R_{int} = 0.11$), $N_o = 3260$; $R = 0.059$, $R_w = 0.072$.

Variata: One of the solvent molecules was modelled as disordered about a crystallographic 2-axis in the present space group. The material presented as substantial, readily desolvating specimens, from which a

transparent fragment was excised and transferred to the diffractometer low temperature system.

5. Supporting material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Cente (Deposition Nos. CCDC 222409 and 222410). Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc,cam.ac.uk).

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