The condensation of *trans*-[$PdCl_2\{(C_4H_3O)SeMe\}_2$] with acetone: formation and crystal structure of [$Pd_2Cl_2(\mu\text{-}SeMe)_2\{MeSe(C_4H_2O)\}_2CMe_2$]

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The condensation of the furan rings in two *trans*-[$PdCl_2\{(C_4H_3O)SeMe\}_2$] complexes with acetone and the chlorine–selenium interactions in the coordination spheres of the two palladium atoms result in the formation of a dinuclear complex [$Pd_2Cl_2(\mu\text{-}SeMe)_2\{MeSe(C_4H_2O)\}_2CMe_2$].

Mononuclear [ML_2X_2] complexes (M = Pd, Pt; L = two organic monodentate ligands containing one selenium or tellurium donor atom each, or one didentate ligand containing two chalcogen donor atoms; X = halide) form a well explored series.[1] Most of the experimental work, however, has been carried out in solution[2] and the solid state information is sparse.[3] We have recently studied the structural and bonding trends in [$MCl_2\{(C_4H_3E)E'Me\}_2$] (M = Pd, Pt; E = S, O; E′ = Se, Te) both in solution and in the solid state.[3i] Surprisingly, it turned out that the crystallization of [$PdCl_2\{(C_4H_3O)SeMe\}_2$] **1** from acetone produced a dimer [$Pd_2Cl_2(\mu\text{-}SeMe)_2\{MeSe(C_4H_2O)\}_2CMe_2$] **2**. In this work we report the crystal structure of the dimer and discuss the route of its formation from two monomeric complexes.

The preparation of [$PdCl_2\{(C_4H_3O)SeMe\}_2$] **1**† yields orange microcrystalline material. The product was dissolved in $CDCl_3$ and $(CD_3)_2CO$ and the ^{77}Se and $^{13}C\{^1H\}$ NMR spectra of both solutions were recorded immediately upon preparation and again after a period of four weeks.‡ The spectra of both fresh and aged samples were identical.

A chloroform solution of **1** exhibits a single ^{77}Se resonance at δ 230 consistent with the chemical shift of δ 233 reported for both [$PdCl_2\{(C_4H_3S)SeMe\}_2$] **3** and [$PtCl_2\{(C_4H_3S)SeMe\}_2$] **4**.[3i] This implies the presence of only one isomer in solution. The crystal structure determinations of **3** and **4** have shown the existence of a *trans*-isomer in the solid state.[3i] The ^{77}Se resonance of **1** appears as a doublet of quartets implying that selenium is bound to the methyl group and to the furyl ring with the coupling resolvable to the nearest protons [Fig. 1(a)].§

Five signals are observed in the $^{13}C\{^1H\}$ spectrum of **1**. Four resonances at δ 146, 134, 119 and 112 are due to the furyl ring carbon atoms. These values bear a logical relationship to the $^{13}C\{^1H\}$ spectra of [$MCl_2\{(C_4H_3E)E'Me\}_2$] (M = Pd, Pt; E = S, O; E′ = Se, Te) [for detailed assignment of the resonances to individual carbon atoms, see ref. 3(*i*)]. The fifth resonance at δ 15 is assigned to the methyl carbon. NMR spectroscopy clearly shows the sole presence of monomeric *trans*-[$PdCl_2\{(C_4H_3O)SeMe\}_2$] in chloroform solution.

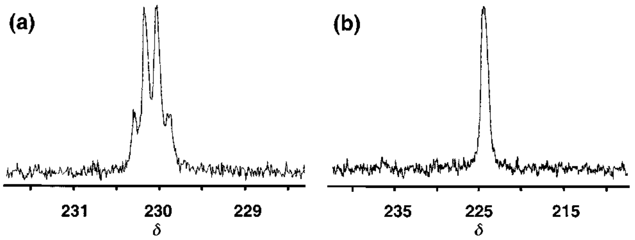

Fig. 1 The ^{77}Se NMR spectrum of [$PdCl_2\{(C_4H_3O)SeMe\}_2$] **1** in (a) $CDCl_3$ and (b) $(CD_3)_2CO$. $^2J_{HSe}$ 11, $^3J_{HSe}$ 2 Hz.

The ^{77}Se and $^{13}C\{^1H\}$ spectra of **1** in acetone resemble those in chloroform. One ^{77}Se chemical shift is found at δ 224 and five ^{13}C resonances are observed at δ 148, 135, 118, 112 and 14. The most pronounced spectroscopic difference from the sample in chloroform is the loss of coupling information in the ^{77}Se resonance [Fig. 1(b)]. This may be due to fast exchange processes taking place in acetone solution.

Upon crystallization from acetone, a small amount of red crystals appeared together with the bulk of orange microcrystalline material of **1**.¶ The crystal structure determination of the red crystals established that **1** has condensed with acetone and dimerized, as shown in Fig. 2.‖ Both palladium atoms exhibit approximately square planar coordination sharing two bridging $MeSe^-$ ligands. The coordination planes around the two palladium atoms lie at an angle of 124.50(4)° from each other. Selected bond parameters are listed in Fig. 2. They are comparable to those observed for the related complexes and follow the trends established earlier.[3a,c,i]

The probable route of formation of **2** from **1** is shown in Fig. 3. The reaction can be conceived to be initiated by the

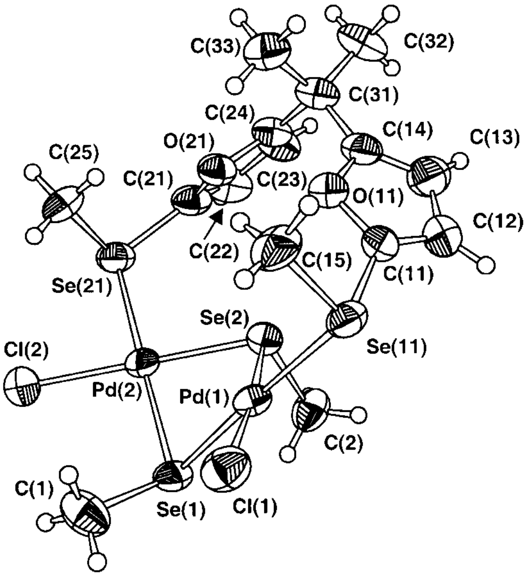

Fig. 2 The molecular structure of [$Pd_2Cl_2(\mu\text{-}SeMe)_2\{SeMe(C_4H_2O)\}_2CMe_2$] indicating the numbering of the atoms. The thermal ellipsoids have been drawn at 50% probability level. Selected bond lengths (Å) and angles (°): Pd(1)–Se(1) 2.420(2), Pd(1)–Se(2) 2.397(1), Pd(2)–Se(1) 2.408(1), Pd(2)–Se(2) 2.396(2), Pd(1)–Se(11) 2.443(2), Pd(2)–Se(21) 2.437(1), Pd(1)–Cl(1) 2.351(2), Pd(2)–Cl(2) 2.336(3), Se(1)–C(1) 1.944(9), Se(2)–C(2) 1.962(8), Se(11)–C(11) 1.893(9), Se(11)–C(15) 1.946(8), Se(21)–C(21) 1.892(10), Se(21)–C(25) 1.960(9), C(14)–C(31) 1.49(1), C(24)–C(31) 1.52(1), C(31)–C(32) 1.52(1), C(31)–C(33) 1.56(1); Pd(1)–Se(1)–Pd(2) 85.46(4), Pd(1)–Se(2)–Pd(2) 86.23(4), Se(1)–Pd(1)–Se(2) 80.53(4), Se(1)–Pd(2)–Se(2) 80.79(4), Pd(1)–Se(11)–C(11) 109.4(3), Pd(2)–Se(21)–C(21) 110.7(3), C(14)–C(31)–C(24) 107.0(7), C(14)–C(31)–C(32) 111.0(8), C(14)–C(31)–C(33) 110.5(7), C(24)–C(31)–C(32) 108.9(7), C(24)–C(31)–C(33) 109.5(8), C(32)–C(31)–C(33) 109.8(8). The angle between the least-squares planes Pd(1)–Se(1)–Se(2)–Cl(1)–Se(11) and Pd(2)–Se(1)–Se(2)–Cl(2)–Se(21) is 124.50(4)°.

condensation of two furan rings from two separate *trans*-[$PdCl_2\{(C_4H_3O)SeMe\}_2$] complexes by acetone. This type of condensation reaction between furan and ketones is well known.[6] Furan and acetone produce tetrametric $\{(C_4H_2O)CMe_2\}_4$ the crystal structure of which[7] shows a similar –CMe_2– link between the two furan rings as **2**.

We have established[3i] that the packing in [$MCl_2\{(C_4H_3E)TeMe\}_2$] and other related telluroether-containing palladium and platinum complexes[3d,g,h] involves close tellurium–halogen contacts. The strength of this interaction is directly proportional to the electron-withdrawing nature of the aromatic substituents bound to the tellurium atom. In the case of monomeric selenoether complexes no such halogen–chalcogen interaction is observed.[3a,c,i] The furan ring, however, may be sufficiently electrophilic to induce a chlorine–selenium interaction and form the intermediate **A**, as shown in Fig. 3. The formation of **A** is sterically very facile despite the constraint generated by the link between the two furan rings. In fact, the solid state packing of the dimer **2** involves two short intermolecular selenium–chlorine contacts of 3.505 Å and lends credibility to the intermediate **A**. Only slight rearrangement of the ligands around the two palladium atoms is needed to cleave two molecules of 2-furyl chloride and form **B**. The reaction is completed by the two $MeSe^-$ fragments that bridge the palladium atoms and thus regenerate the square-planar coordination around each.

Diorganoselenides generally act as neutral monodentate ligands without C–Se bond fission during the complexation.[1c,d] The presence of bridging $MeSe^-$ ligands in **2**, however, must be a consequence of the cleavage of the Se–C_{aryl} bond. This behaviour is consistent with the oxidative addition of organic tellurides to Pt(0) that results in the cleavage of the Te–C_{aryl} bond in preference to the Te–C_{alkyl} bond.[8]

It can be concluded that **2** is probably formed from **1** upon crystallization from acetone. Spectroscopic and compositional data indicate that the orange product obtained upon precipitation with hexane is pure monomer **1**. Upon crystallization from acetone, the solid monomer itself appears only as microcrystalline material, but small amounts of **2** build up as well formed red crystals. A systematic study on the factors affecting the formation of dimeric complex from [$MCl_2\{(C_4H_3E)SeMe\}_2$] (M = Pd, Pt, E = O, S) and the optimization of the condensation reactions are currently in progress.

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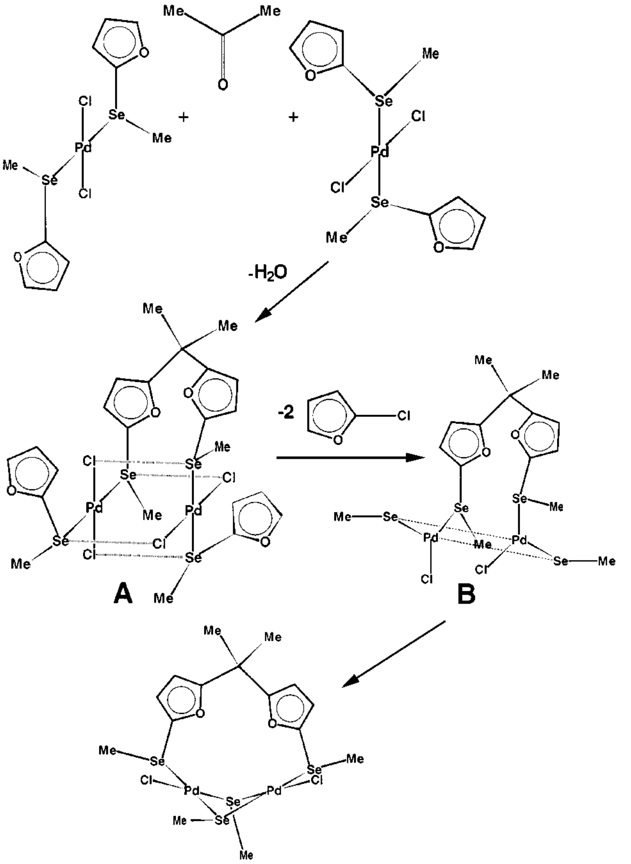

Fig. 3 Pathway of the dimerization of **1**.

Notes and references

† The general procedure for the preparation of (C_4H_3E)E′Me and [$MCl_2\{(C_4H_3E)E'Me\}_2$] (M = Pd, Pt; E = S, O; E′ = Se, Te) has been described earlier.[3i] Methyl(2-furyl)selane (0.20 g, 1.3 mmol) in 5 ml acetone was added into 20 ml of acetone solution of [$PdCl_2(PhCN)_2$] (0.17 g, 0.44 mmol) and stirred for 3 h. The solution was concentrated and hexane added. The precipitate was filtered off, washed with hexane, and dried. Yield 0.18 g, 82%. Anal. Calc. for $C_{10}H_{12}Cl_2PdO_2Se_2$: C, 24.05: H, 2.42. Found: C, 24.10: H, 2.50%. δ_H($CDCl_3$) 2.62 (6H, s), 6.46 (2H, dd, $^2J_{HH}$ 1.7, 3.4 Hz), 6.95 (2H, d, $^2J_{HH}$ 3.4 Hz), 7.66 (2H, d, $^2J_{HH}$ 1.7 Hz); [$(CD_3)_2CO$] 2.85 (6H, s), 6.60 (2H, dd, $^2J_{HH}$ 2.1, 3.4 Hz), 7.05 (2H, br), 7.86 (2H, br).

‡ The ^{77}Se and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DPX 400 spectrometer operating at 76.31 and 100.61 MHz for ^{77}Se and ^{13}C, respectively. The solvent, $CDCl_3$ or $(CD_3)_2CO$, served as an internal ^{2}H lock. Saturated solution of SeO_2(aq) was used as an external standard for the ^{77}Se chemical shifts and $SiMe_4$ as an internal standard for the ^{13}C chemical shifts. The ^{77}Se chemical shifts are reported relative to neat Me_2Se, [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$] and the ^{13}C shifts relative to TMS.

§ The coupling patterns of the ^{77}Se resonances in *trans*-[$PdCl_2\{(C_4H_3S)SeMe\}_2$] **3** and *trans*-[$PtCl_2\{(C_4H_3S)SeMe\}_2$] **4** are identical to that of **1** indicating that the structures of all three complexes **1**, **3** and **4** are similar.

¶ We were unable to obtain crystals from chloroform solution.

‖ *Crystal data* for $C_{15}H_{22}O_2Cl_2Pd_2Se_4$: $M = 833.87$, triclinic, $P\bar{1}$, $a = 9.640(2)$, $b = 11.557(2)$, $c = 12.535(3)$ Å, $\alpha = 100.17(3)$, $\beta = 105.38(3)$, $\gamma = 113.52(3)°$, $U = 1170.0(4)$ Å^3, $Z = 2$, $D_c = 2.367$ g cm^{-3}, $F(000) = 780$, $\mu = 7.995$ mm^{-1}, $T = 293$ K, crystal dimensions 0.1 × 0.2 × 0.2 mm. Reflections (14164 total, 4310 unique, $R_{int} = 0.0854$) were collected on a Nonius Kappa CCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption correction was applied to the net intensities.[4] The structure was solved by direct methods[5a] and refined on F^2.[5b] $R_1 = 0.0481$ and $wR_2 = 0.1148$ [for 2993 reflections with $F_o > 4\sigma(F_o)$] [$R_1 = 0.0815$ and $wR_2 = 0.1302$ (all data)]. CCDC 182/1175. See http://www.rsc.org/suppdata/cc/1999/585/ for crystallographic files in .cif format.

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