Oxidative addition of a C–Se bond to a Pt^{II} centre: contrasting reactions of $[MCl_2(PhCN)_2]$ (M = Pd, Pt) with cyclohepteno-1,4-diselenin

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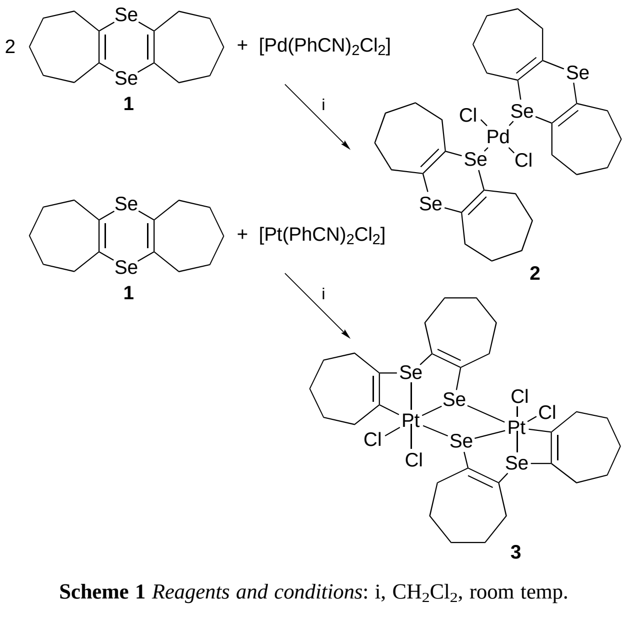
The reaction of cyclohepteno-1,4-diselenin 1 with $[PtCl_2(PhCN)_2]$ proceeds *via* unprecedented oxidative addition of a C–Se bond to yield a platinum(IV) product, whose novel dimeric structure has been determined by X-ray crystallography; by contrast, 1 reacts with $[PdCl_2(PhCN)_2]$ to form *trans*-$[PdCl_2L_2]$ (L = 1).

The chemistry of selenium-containing ligands is a subject of growing interest,[1] as a result of both their increasing accessibility, and the realisation that they may display significantly different properties from their sulfur-containing analogues. Despite their ready preparation from 1,2,3-selenadiazoles,[2] and the range of possible bonding modes (mono- or bi-dentate; terminal, bridging or chelating), the coordination chemistry of 1,4-diselenins has scarcely been investigated. Their use as precursors in the preparation of iron diselenolenes has been reported, but these reactions involved fragmentation of the ligand.[3] A number of complexes of the related selenanthrenes have also been prepared.[4,5] We have previously determined the structure of bis(cycloocteno)-1,4-diselenin,[6] and have now studied the reactions of cyclohepteno-1,4-diselenin **1** with the palladium(ii) and platinum(ii) complexes $[MCl_2(PhCN)_2]$.

Stirring 2 equiv. of **1** with $[PdCl_2(PhCN)_2]$ in dichloromethane solution at room temp. leads to rapid formation of an orange–red product **2**, with stoichiometry $[PdCl_2L_2]$ (L = **1**) (Scheme 1). Compound **2** exhibits a single band in the far IR at *ca.* 360 cm^{-1}, characteristic of dichloropalladium(ii) complexes having *trans*-geometry.[7] The structure proposed for **2** is one in which each 1,4-diselenin is acting as a monodentate ligand. Analogous complexes of dialkylselenides have been known for a long time.[8]

The corresponding platinum chemistry, however, takes a different course (Scheme 1). The reaction between $[PtCl_2(PhCN)_2]$ and **1** is somewhat slower, and if 2 equiv. of 1,4-diselenin are used then one is recovered unchanged. The NMR spectroscopic data for the product **3** show that the symmetry of the coordinated 1,4-diselenin has been broken: for example, each carbon atom of the ligand gives a separate ^{13}C resonance.†



Scheme 1 *Reagents and conditions*: i, CH_2Cl_2, room temp.

The molecular structure of **3** has been determined by X-ray crystallography‡ and is shown in Fig. 1. The platinum has inserted into a carbon–selenium bond of the 1,4-diselenin, so that it has become a tridentate (C, Se, Se) ligand. The typical octahedral coordination of Pt^{IV} is achieved *via* dimerisation using bridging selenium atoms, although there is significant asymmetry in the Pt_2Se_2 unit: there are two long Pt–Se bonds of *ca.* 2.62 Å. This reflects the different *trans*-influence of the carbon and chlorine atoms bound to platinum (*vide infra*). There is no evidence that the steric effect of the alicyclic rings is preventing closer approach of the two platinum moieties: the carbon atoms in each half of the molecule are at least 3.3 Å apart. There are small differences between the distances from platinum to the two selenium atoms of a single ligand, the bonds to the disubstituted Se(2) and Se(4) being shorter by *ca.* 0.04 Å than those to Se(1) and Se(3). In fact both pairs of Pt–Se distances (av. 2.422, 2.386 Å) are considerably shorter than those previously reported for Pt^{IV}–Se bonds. For example in the complexes $[PtXMe_3(MeSeCH{=}CHSeMe)]$ average values for Pt–Se are 2.528 Å (X = Cl) and 2.533 Å (X = I):[9] this shows how sensitive the Pt–Se bond length is to the influence of the *trans*-ligand (which in these examples is a methyl group). The platinum–chlorine bonds differ in length in a similar fashion, with those to the chlorine atoms *trans* to Se(2) and Se(4) being *ca.* 0.03 Å shorter, so that overall the coordination polyhedra are

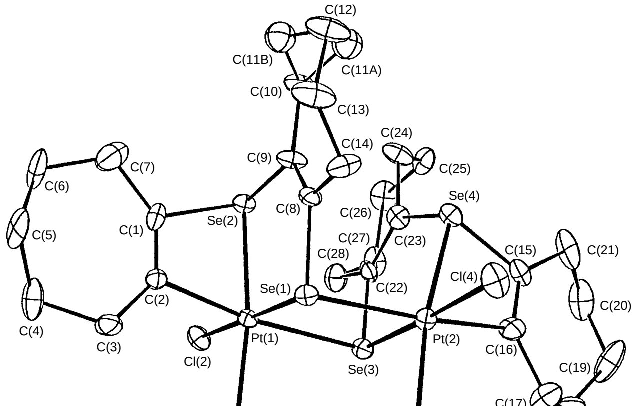


Fig. 1 Structure of **3** with H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pt(1)–Se(1) 2.421(2), Pt(2)–Se(3) 2.423(2), Pt(1)–Se(2) 2.384(2), Pt(2)–Se(4) 2.388(2), Pt(1)–Se(3) 2.620(2), Pt(2)–Se(1) 2.624(2), Pt(1)–Cl(1) 2.342(5), Pt(2)–Cl(3) 2.330(5), Pt(1)–Cl(2) 2.367(5), Pt(2)–Cl(4) 2.359(5), Pt(1)–C(2) 2.103(18), Pt(2)–C(16) 2.079(20); Se(2)–Pt(1)–Se(3) 100.9(1), Se(2)–Pt(1)–C(2) 70.9(5), Pt(1)–Se(2)–C(1) 77.8(6), Se(2)–C(1)–C(2) 103.7(1.4), Pt(1)–C(2)–C(1) 107.6(1.4).

somewhat compressed along one axis. This distortion is not chemically significant, but arises as a consequence of the geometric constraints imposed by the presence of the metal-containing four-membered ring.

The dimeric structure does not appear to be maintained in solution. The ^{77}Se NMR spectrum of **3** in CD_2Cl_2 contains two resonances, each with only one set of ^{195}Pt satellites: δ 315 [$^{1}J(^{77}Se^{195}Pt)$ 295 Hz], δ 278 [$^{1}J(^{77}Se^{195}Pt)$ 154 Hz]. There are few values in the literature for $^{1}J(^{77}Se^{195}Pt)$, but the coupling constants for **3** are similar in magnitude to those previously observed.[10]

Oxidative addition to platinum(ii) centres is common for halogens, alkyl halides, *etc.*,[11] but the reaction reported here represents the first example involving cleavage of a C–Se bond. Indeed a wide range of diorganochalcogen complexes of platinum(ii) has previously been prepared.[12] The insertion of a d^8 metal centre into a C–Se bond has only previously been observed in an iridium(i) complex of a coordinated selenophene.[13] Clearly the behaviour of the cycloalkeno-1,4-diselenins is unique, and further investigation of their coordination chemistry is in progress.

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Footnotes

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† *Synthesis of* **3**: A mixture of $[PtCl_2(PhCN)_2]$ (0.100 g, 0.21 mmol) and **1** (0.073 g, 0.21 mmol) in CH_2Cl_2 (10 cm^3) was stirred overnight. The solvent was removed by evaporation under reduced pressure and the residue washed with light petroleum, to leave the product as an orange–brown powder. This was purified by recrystallisation from dichloromethane–toluene. Yield: 0.080 g (62%); mp 205 °C (decomp.); ^{1}H NMR (400 MHz, CD_2Cl_2, $SiMe_4$), δ 3.19 (m, 1 H), 2.85–2.65 (m, 3 H), 2.65–2.35 (m, 11 H), 1.45 (m, 1 H); ^{13}C NMR (100 MHz, CD_2Cl_2, $SiMe_4$), δ 149.1, 133.5, 131.9, 126.1, 39.4, 37.0, 35.9, 34.5, 31.8, 29.2, 29.0, 28.1, 27.6, 25.2; ^{77}Se NMR (47.7 MHz, CD_2Cl_2, external $SeMe_2$), δ 315 [$J(^{77}Se^{195}Pt)$ 295 Hz], 278 [$J(^{77}Se^{195}Pt)$ 154 Hz]; IR (KBr disk), 2921vs, 2849s, 1443s, 1385m, 1359m, 1267m, 1215m, 1071m, 967m cm^{-1}; Far IR (Nujol mull, CsI plates): 330m, 310m cm^{-1}; UV–VIS (CH_2Cl_2): λ_{max}/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$) = 490 (≈ 200, vbr), 330 (9000), 285 (15000), 260 (17000), 230 (22000); MS (FAB): *m/z* (%), 1187 (≈ 1) [$M^+ - Cl$], 348 (45) [$\mathbf{1}^+$], 267 (100) [$\mathbf{1}^+ - SeH$]; C, H analysis ($C_{28}H_{40}Cl_4Pt_2Se_4$, 1224.46): calc. C 27.45, H 3.27; found C 27.78, H 3.41 %.

‡ *Crystal data for* **3**: $C_{28}H_{40}Cl_4Pt_2Se_4$; $M_r = 1224.46$; crystal size 0.07 × 0.13 × 0.27 mm; orthorhombic, space group *Pcab*; $a = 15.203(2)$, $b = 17.301(4)$, $c = 25.935(4)$ Å, $U = 6821(2)$ Å^3, $Z = 8$, $F(000) = 4544$, $D_c = 2.384$ g cm^{-3}, $\mu(Cu\text{-}K\alpha) = 234.4$ cm^{-1}. Data collection (Enraf-Nonius CAD4, graphite-monochromated Cu-Kα radiation, $\lambda = 1.5418$ Å, $T = 295$ K), ω—2θ scans, $3 < \theta < 60°$. 4831 measured reflections ($+h$, $+k$, $+l$), 3875 unique, 2887 with $I > 3\sigma_I$ used in final refinement. Structure solution and refinement: direct methods, with SIR,[14] and heavy-atom procedures with SHELX-76. A series of Fourier syntheses provided the positions of all non-hydrogen atoms. An empirical absorption correction (min., max. correction factors 0.92, 1.11) was applied at isotropic convergence.[15] In the final refinement cycles, performed against *F* by full-matrix least squares, all non-hydrogen atoms were assigned anisotropic temperature factors, except for a methylene carbon atom which was found to occupy two positions, in a disordered fashion. Its two fractions were assigned an overall isotropic temperature factor and the complementary occupancy factors of the two sites were refined. The four C–C bond distances formed by the two fractions of the disordered C atom with the other atoms of the ring were linked, allowing for a 0.01 Å σ, to a unique value, which was refined. The hydrogen atoms were introduced in calculated positions, with C–H = 0.96 Å and $U_H = 1.2\ U_C$, where U_C is the equivalent isotropic temperature factor of the carrier C atom, and were not refined. With 343 parameters refined the data : parameter ratio was 8.4. Final *R* values: $R = 0.045$, $R_w = 0.053$. Max., min. values of residual electron density: +0.82, −0.87 e Å^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/422.

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