A unique mode of molecular recognition in palladium(II) metallacrown ethers

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Received (in Bloomington, IN, USA) 15th September 1998, Accepted 26th October 1998

Metallacrown ethers of the type [PdX_2{Ph_2P-($CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P′}]$_m$ (X = Cl, I) exhibit a unique and reversible mode of molecular recognition in which PdX_2 units are incorporated into the metallacrown ether ring *via* a ring-expansion reaction to form dimetallacrown ethers.

Molecular receptors are of interest as chemical sensors, catalysts and models for complex biochemical receptors.[1] Recently, molecules with multiple receptor sites have received considerable attention. The multiple receptor sites can give rise to unusual catalytic properties[2] or allow the molecules to function as highly selective sensors.[3]

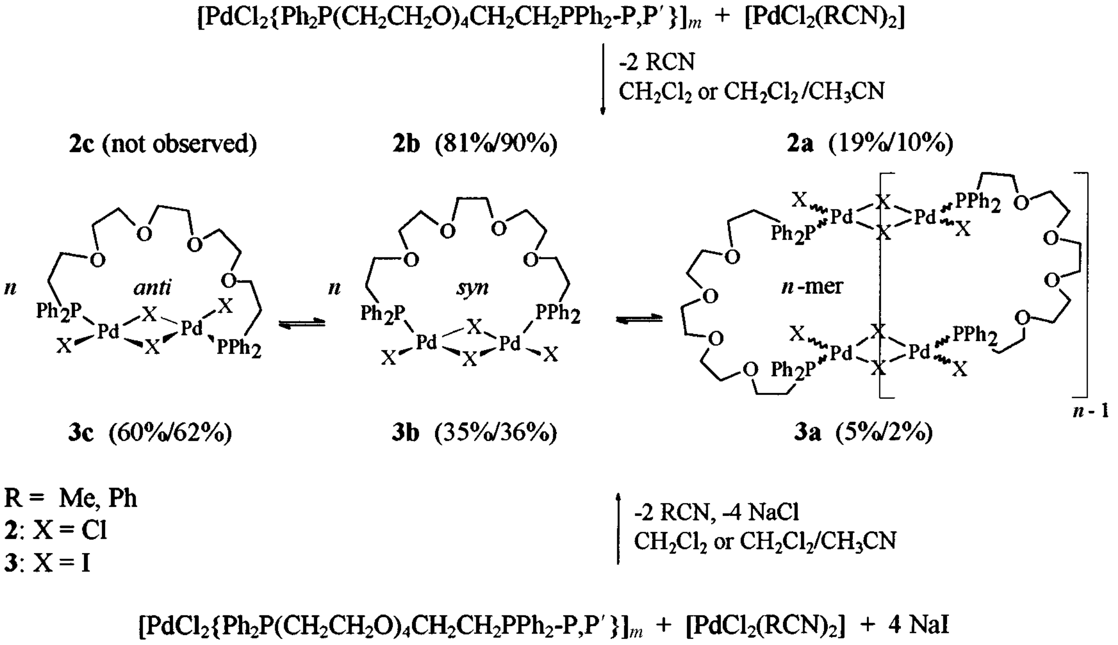
Metallacrown ethers are a class of molecular receptors with both crown ether- and transition metal-receptor sites.[4,5] We now report that the metallacrown ether [$PdCl_2${PPh_2-($CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P′}]$_m$, **1**,[6] exhibits a unique mode of molecular recognition in which the metallacrown ether ring is expanded by the incorporation of a $PdCl_2$ moiety. The product of this reaction is the first reported example of a dimetallacrown ether.

In a typical experiment, the metallacrown ether [$PdCl_2${$PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P′}]$_m$ **1**, which is mixture of *cis*- and *trans*-monomers and cyclic *n*-mers,[6] is reacted with either [$PdCl_2(PhCN)_2$] or $PdCl_2$. This reaction is rapid with soluble palladium salts, *i.e.* $PdCl_2$ in acetonitrile or [$PdCl_2(PhCN)_2$] in dichloromethane, but takes place even when the palladium salt is insoluble, *i.e.* $PdCl_2$ in chloroform. Both reactions give high yields of the dimetallacrown ether [Pd_2Cl_2(μ-Cl)$_2${$PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P′}]$_m$, **2**, (Scheme 1). A similar reaction of **1** with either [$PdCl_2(PhCN)_2$] or $PdCl_2$ and excess NaI in an acetonitrile–dichloromethane mixture gives a high yield of the dimetallacrown ether [Pd_2I_2(μ-I)$_2${$PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2$-P,P′}]$_m$, **3**. The latter reaction is of interest because it demonstrates that it is possible to exchange the anion in the dimetallacrown ether without exchanging the cation.

Comparison of the rates of $PdCl_2$ binding by **1** and [$PdCl_2(PPh_2Et)_2$] **4**[7] in chloroform-*d* solutions clearly demonstrates the importance of the metallacrown ether receptor in **1**. After 20 h at ambient temperature, **1** is completely converted into **2**. In contrast, after 20 h at ambient temperature, only 10.5% of **4** is converted into the corresponding dinuclear palladium complex, [$Pd_2Cl_4(PPh_2Et)_2$].

The binding of $PdCl_2$ by the metallacrown ether, **1**, is strong and reversible. It is not possible to remove the $PdCl_2$ from **2** by extracting chloroform-*d* solutions of **2** with 0.5 M aqueous HCl solutions. However, the $PdCl_2$ can be completely removed from **2** *via* chromatography, with the $PdCl_2$ remaining on the silica and **1** eluting from the column.

Chloroform-*d* solutions of **2** and **3** contain multiple resonances in their $^{31}P\{^1H\}$ NMR spectra (Fig. 1) indicating that these complexes, like **1**, exhibit both geometrical and monomer/*n*-mer equilibria in solution.[6] The major resonance in the $^{31}P\{^1H\}$ NMR spectrum of **2** is assigned to the monomeric *syn*-dimetallacrown ether **2b** while the minor resonances are assigned to *n*-meric dimetallacrown ethers **2a**. This assignment is supported by the decrease in ratio of the major resonance **2b** to the minor resonance **2a** both as the concentration increases (8.0/1 at 0.0175 M *versus* 4.3/1 at 0.0350 M) and as the



Scheme 1 Proposed equilibria for the dimetallacrown ethers. The relative species percentages were determined by integration of the quantitative $^{31}P\{^1H\}$ NMR spectra and are given for both 0.0350 M and 0.0175 M solutions of **2** in chloroform-*d* and for both 0.0350 M and 0.0175 M solutions of **3** in (1 : 1) dichloromethane/chloroform-*d* at 295 K.

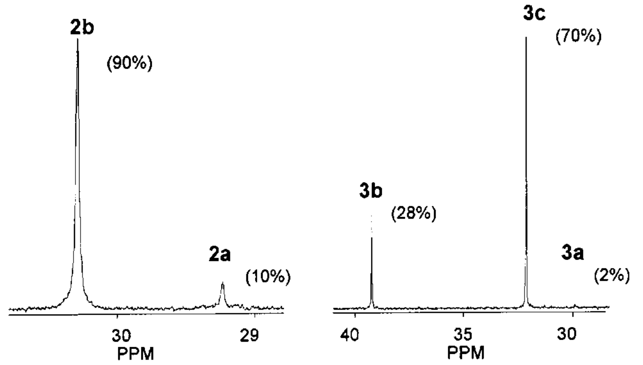


Fig. 1 $^{31}P\{^1H\}$ NMR spectra of 0.0175 M solutions of the dimetallacrown ethers, **2** and **3**, in chloroform-*d* at 295 K. {Spectral parameters: $^{31}P\{^1H\}$, 121.498 MHz, number of scans 256, line broadening 1.0 Hz, sweep width 2439.02 Hz, 30° inverse gated pulse, pulse delay 30 sec}.

temperature decreases (11.3/1 for a 0.0175 M solution at 331 K *versus* 8.0/1 for a 0.0175 M solution at 295 K).[8] The assignment of **2b** as the *syn* isomer is based on the similarity of the chemical shift of its $^{31}P\{^1H\}$ NMR resonance to those of *syn*-$Pd_2Cl_4L_2$ (L = monodentate phosphine) complexes.[9]

The major resonance in the $^{31}P\{^1H\}$ NMR spectrum of **3** is assigned to the monomeric *anti*-dimetallacrown ether **3c**, and the minor resonance is assigned to the *syn*-dimetallacrown ether **3b** (Fig. 1). This assignment is supported by the increase in the ratio of the major resonance **3c** to the minor resonance **3b** as the polarity of the solvent decreases (1.8/1 in a 1 : 1 dichloromethane–chloroform mixture *versus* 2.4/1 in chloroform). The very small, upfield resonances **3a** appear to be due to *n*-meric dimetallacrown ethers. The very different behavior of **2** and **3** in solution demonstrates that the halide ligand has a surprising effect on both the isomerization and *n*-merization equilibria in dimetallacrown ethers.

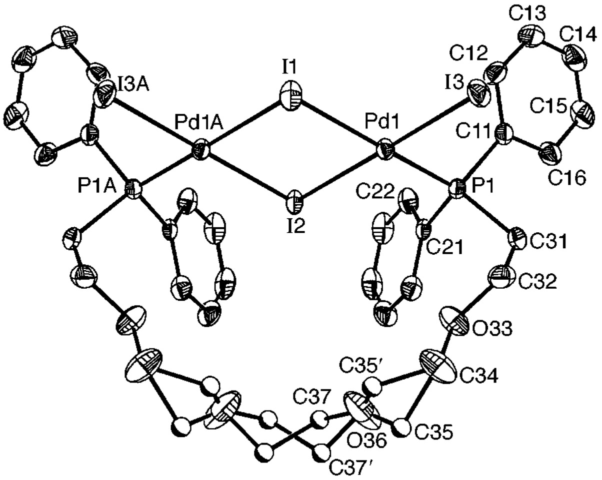


Fig. 2 Molecular structure of **3c**. For clarity the hydrogen atoms are removed, and the complete molecule (two asymmetric units) is shown. Selected bond lengths [Å] and angles [°]: Pd1–I1 2.667(1), Pd1–I2 2.602(1), Pd1–I3 2.598(1), Pd1–P1 2.264(2), P1–C11 1.822(7), P1–C21 1.819(6), P1–C31 1.815(7); I1–Pd1–I2 84.0(1), I1–Pd1–I3 91.3(1), I2–Pd1–I3 173.9(1), I1–Pd1–P1 177.4(1), I2–Pd1–P1 94.7(1), I3–Pd1–P1 90.1(1), Pd1–I1–Pd1A 94.3(1), Pd1–I2–Pd1A 97.4(1), Pd1–P1–C11 115.1(2), Pd1–P1–C21 113.6(2).

The X-ray crystal structure of **3c**,[10] shown in Fig. 2, suggests that this dimetallacrown ether could have quite different receptor properties from those of the previously reported metallacrown ethers, *cis*-$[PtCl_2\{PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]$, **5**, and *trans*-$[Mo(CO)_4\{PPh_2(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}]$, **6**.[4d,4e] The average cross-ring oxygen–oxygen distance in **3c** (O33–O36A and O33A–O36, 5.27 Å), which provides a measure of the ring size, is intermediate between that in **5** (4.66 Å) and that in **6** (5.87 Å).[4d,4e] The angle of intercept between the least squares planes through the ether oxygens (O33, O36, O33A, O36A) and that containing the Pd_2I_2 fragment is 42° in **3c**. In contrast, the angle between the least squares planes through the ether oxygens and the $PtCl_2$ center in **5** is 60°. The smaller angle means that an alkali metal cation in the dimetallacrown ether receptor site would be in closer proximity to the transition metal center in **3c** (the distance from the centroid of the four ether oxygens to Pd1 is 4.984 Å). A bifunctional molecule, such as CO, could easily coordinate to both the Pd and the alkali metal cation in the dimetallacrown ether.

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10 Crystallograpic data: Formula, $C_{34}H_{28}O_4I_4P_2Pd_2$; M = 1282.9; orthorhombic, a = 17.2007(28), b = 24.7961(40), c = 9.5467(20) Å, V = 4072(2) Å^3; T = 297 K; *Pnma*, Z = 4; μ = 4.028 mm^{-1}; refl. meas. = 7278, ind. refl. = 2734 (R_{int} = 3.09%); R = 4.16, R_w = 5.33 (all data). Crystallographic data for **3c** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-101344. CCDC 182/1070.

Communication 8/07170E