DALTON
COMMUNICATION

Structural and complexation properties of diselenacrown ethers. Synthesis and crystal structure of a novel cationic palladium tetraselena complex

C. Bornet,[a] R. Amardeil,[a] P. Meunier *[a] and J. C. Daran[b]

[a] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques associé au CNRS (LSEO, UMR 5632), Université de Bourgogne, 6, boulevard Gabriel, 21000 Dijon, France. E-mail: Philippe.Meunier@u-bourgogne.fr*

[b] *Laboratoire de Chimie de Coordination UPR-CNRS 8241, 205, route de Narbonne, 31077 Toulouse Cedex, France*

Received 20th January 1999, Accepted 17th February 1999

The synthesis of novel cationic structures $[PdL_2][Y]_2$ [Y = NO_3, PF_6; L = diselenamacrocycle] starting from $PdLCl_2$ and L, and the first determination of the structure of such a complex by X-ray diffraction was established.

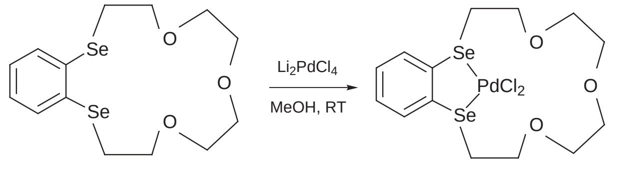
There has been much interest in the use of macrocyclic ligands for complexing transition metal ions.[1] Most of the work has concentrated on the design of selective receptors for either alkali or alkaline-earth cations. Other research has been devoted to selective complexations of transition metal cations.

Over the past 10 years, the main concern has certainly been the preparation of metallomacrocycles with hard and soft metals.[2] The major aim of these studies is the construction of supramolecular species with well defined shapes and geometries. In particular, it has been shown that complexes with hard and soft metal cations can be used for bimetallic catalysis and activation, changing in particular the redox properties of the transition metal cation. To our knowledge, similar research has not been performed in selenium chemistry.

As a preliminary result, we will show here the potential application of diselenacrown ethers whose synthesis we described earlier.[3]

Complexes of [16]aneSe_4 with Pd(II) and Pt(II) have been reported.[4] These results have shown that transition metal ions are readily inserted into the cavity of the tetraselenacrown ether [16]aneSe_4 to yield complexes with a square planar Se_4 donor set, such as $[Pd([16]aneSe_4)][PF_6]_2$. The complex, $[Pd([8]aneSe_2)_2][PF_6]_2$, constructed with two bidentate selenoether macrocycles, has been recently obtained and characterized by multinuclear NMR spectroscopy (^1H, $^{77}Se\text{-}\{^1H\}$).[5] We now report the preparation of new cationic palladium complexes binding to two selenamacrocyclic ligands and, to our knowledge, the first structure of such a complex, determined by single-crystal X-ray analyses.

The reaction (see Scheme 1) of L (95 mg, 0.24 mmol) with one equivalent of Li_2PdCl_4 (63 mg, 0.24 mmol) in methanol (10 cm^3) at room temperature (RT) caused the immediate formation of the neutral species $PdLCl_2$, in the form of an orange precipitate in high yield (80%). Recrystallisation of the product was realized by the diffusion of diethyl diether into a dimethyl sulfoxide solution of the palladium complex. As the neutral compound is insoluble in most common organic solvents, its spectroscopic characterisation was done in CD_3NO_2 or in $(CD_3)_2SO$. ^1H NMR spectroscopy (200 MHz) is an efficient probe for the differentiation of the palladium complex from the macrocyclic ligand L. The most important differences appear in the aliphatic region. In fact, the spectrum of the palladium complex was not well resolved with several signals (for the macrocyclic ligand itself, two triplets and a multiplet were observed). The high field (500 MHz) NMR spectrum showed eight signals (ABCD system). This indicated that the two faces of the complex are anisochronous and that each proton on a given carbon is not equivalent with its neighbours. Moreover, only eight signals were obtained due to the symmetry properties of the complex. However no change in morphology occurred in the aromatic region. As expected, we saw two doublets of doublets consistent with an *ortho*-disubstitued phenyl group, each resonance being shifted downfield ($\Delta\delta$ +0.5 ppm). This spectroscopic result suggests that the metal is probably not located in the cavity of the macrocyclic ligand, consistent with the metal's square planar geometry and the dimensions of the oxygenated ring. The $^{77}Se\text{-}\{^1H\}$ NMR is also evidence for complexation. The $^{77}Se\text{-}\{^1H\}$ spectra were obtained for L and $PdLCl_2$ in $(CD_3)_2SO$ solution and showed singlets at δ(Se) +273 and +522 respectively; for the palladium complex a large shift in δ(Se) to high frequency is observed.[6] This shift is typical and has been observed with many other d-block complexes with selenoether ligands.[7] Elemental analytical data are in accordance with the formulation $PdLCl_2$ (Found: C, 29.33; H, 3.47. $C_{14}H_{20}Se_2PdO_3Cl_2$ requires C, 29.42; H, 3.53%).

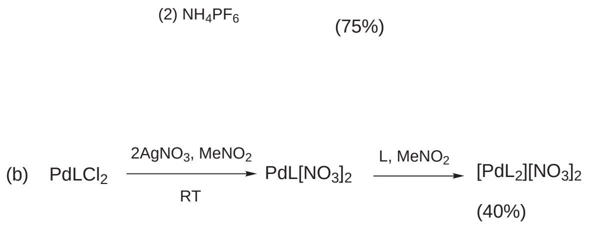


L

$PdLCl_2$

Scheme 1

We have also demonstrated that the neutral palladium complex $PdLCl_2$ is an efficient precursor for the synthesis of a selenocationic palladium complex $[PdL_2][Y]_2$ [Y = NO_3, PF_6]. Two different experimental methods were used (see Scheme 2) to provide the new selenocationic palladium complex $[PdL_2]^{2+}$: (a) displacement of Cl^- ligands from $PdLCl_2$ (110 mg, 0.189 mmol) occurs in refluxing $MeNO_2$ solution (34 cm^3) in the presence of the donor ligand L (75 mg, 0.189 mmol), followed by addition of NH_4PF_6 (62 mg, 0.378 mmol) to yield $[PdL_2][PF_6]_2$



Scheme 2

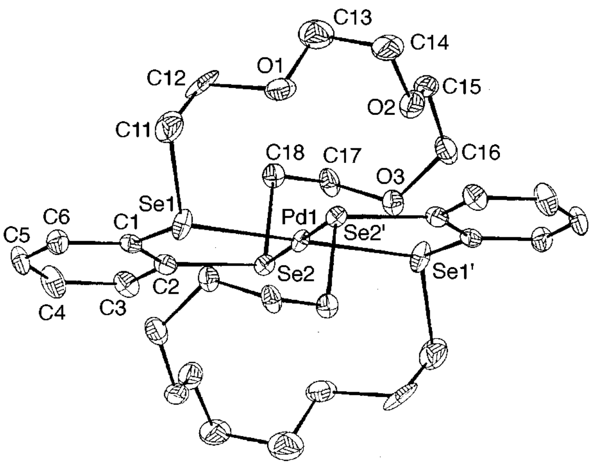


Fig. 1 A CAMERON[9] drawing of $[PdL_2][PF_6]_2$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–Se(1) 2.4191(5), Pd(1)–Se(2) 2.4183(5), Se(1)–Pd(1)–Se(2) 90.19(2), Se(1)–Pd(1)–Se(2′) 89.81(2).

(yield: 168 mg, 75%) (Found: C, 28.81; H, 3.61. $C_{28}H_{40}Se_4O_6$-PdP_2F_6 require C, 28.39; H, 3.40%) and (b) by treatment of $PdLCl_2$ (44 mg, 7.75×10^{-2} mmol) with two equivalents of $AgNO_3$ (22 mg, 0.15 mmol) in nitromethane (10 cm^3), followed by removal of AgCl and addition of one equivalent of L (31 mg, 7.75×10^{-2} mmol) (yield: 31.5 mg, 40%). The ^{77}Se and ^{1}H NMR spectra were obtained as previously in $(CD_3)_2SO$ or CD_3NO_2 solution. Important differences could be observed in the ^{1}H NMR spectra of the neutral and cationic complexes. In particular, in cationic species, only five separate broad bands were observed in the range δ 3.17–4.21 integrating each for 1, 2, 3, 1 and 1 protons respectively. We also notice that the resonances of the aromatic protons are shifted downfield (0.1–0.2 ppm) in changing from $PdLCl_2$ to $[PdL_2][Y]_2$. The ^{77}Se-$\{^{1}H\}$ spectra (CD_3NO_2) also showed significant differences: δ +510 for $PdLCl_2$ (δ +476 for $PdL[NO_3]_2$); δ +456 for $[PdL_2][NO_3]_2$ and δ +453 for $[PdL_2][PF_6]_2$. These compare favorably with similar data observed for $Pd([8]aneSe_2)Cl_2$ and $[Pd([8]$-$aneSe_2)_2][PF_6]_2$ whose signals appear at δ +199 and δ +164 respectively.[5] Here again, we note that these compounds show shifts to high frequency on co-ordination to palladium [free L: δ (^{77}Se) +268]. In order to confirm the formulation $[PdL_2][Y]_2$ and establish the geometry of the complex formed, a single crystal structure determination was carried out. Orange single crystals were obtained by slow diffusion of Et_2O vapour into a solution of $[PdL_2][PF_6]_2$ in CH_3NO_2.† The single crystal X-ray structure determination showed a square planar arrangement of the four selenium atom donors around the central metal ion. The Pd–Se bond distances (see Fig. 1) were comparable with previous values [*cf.* Pd–Se, 2.423(1) and 2.432(1) Å in $[Pd([16]aneSe_4)][BF_4]_2$;[8] 2.428(1) and 2.435(1) Å in $\{Pd([16]$-$aneSe_4)][PF_6]_2\}$.[4] The two oxygenated cavities in the cationic complex $[PdL_2][PF_6]_2$ adopted a *trans* configuration compared to the plane defined by the two benzene rings and the four selenium atoms.

With a view to obtaining the *cis* configuration for the oxygen cavities, we are currently investigating similar chemistry starting from tetraselenacrown ethers.

Notes and references

† Crystal data: $C_{14}H_{20}O_3Pd_{0.5}Se_2F_6PC_2H_5O_{0.5}$, $M = 629.45$, monoclinic, space group $C2/c$ (no. 15), $a = 13.848(1)$, $b = 15.917(2)$, $c = 19.785(1)$ Å, $\beta = 95.49(1)°$, $U = 4340.0(6)$ Å^3, $Z = 4$, $\mu = 39.071$ cm^{-1}, $T = 180(2)$ K, $R = 0.0414$ and $Rw = 0.0489$ for 2589 reflections [$I > 2\sigma(I)$]. CCDC reference number 186/1358. See http://www.rsc.org/suppdata/dt/1999/1039/ for crystallographic files in .cif format.

1 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, New York, 1989; P. K. Baker, M. C. Durrant, S. D. Harris, D. L. Hughes and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1997, 509; S. J. A. Pope, N. R. Champness and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 1639; W. Levason, J. J. Quirk and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 3719.
2 A. Varshney and G. M. Gray, *Inorg. Chem.*, 1991, **30**, 1748; A. Varshney, M. L. Webster and G. M. Gray, *Inorg. Chem.*, 1992, **31**, 2580; J. Powell, A. Lough and F. Wang, *Organometallics*, 1992, **11**, 2289; G. M. Gray and C. H. Duffey, *Organometallics*, 1995, **14**, 245; F. C. J. M. Van Veggel, W. Verboom and D. N. Reinhoudt, *Chem. Rev.*, 1994, **94**, 279; A. Mazouz, P. Meunier, M. M. Kubicki, B. Hanquet, R. Amardeil, C. Bornet and A. Zahidi, *J. Chem. Soc., Dalton Trans.*, 1997, 1043.
3 A. Mazouz, J. Bodiguel, P. Meunier and B. Gautheron, *Phosphorus Sulfur Silicon Rel. Elem.*, 1991, **61**, 247.
4 N. R. Champness, P. F. Kelly, W. Levason, G. Reid, A. M. Z. Slawin and D. J. Williams, *Inorg. Chem.*, 1995, **34**, 651.
5 N. R. Champness, W. Levason, J. J. Quirk and G. Reid, *Polyhedron*, 1995, **14**, 2753.
6 D. G. Booth, W. Levason, J. J. Quirk, G. Reid and S. M. Smith, *J. Chem. Soc., Dalton Trans.*, 1997, 3493.
7 E. G. Hope and W. Levason, *Coord. Chem. Rev.*, 1993, **122**, 109.
8 R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J. Gu, B. M. Pinto and X. Zhou, *Inorg. Chem.*, 1996, **35**, 3667.
9 D. J. Watkin, C. K. Prout and L. J. Pearce, CAMERON, Chemical Crystallography Laboratory, University of Oxford, 1996.

Communication 9/00545E