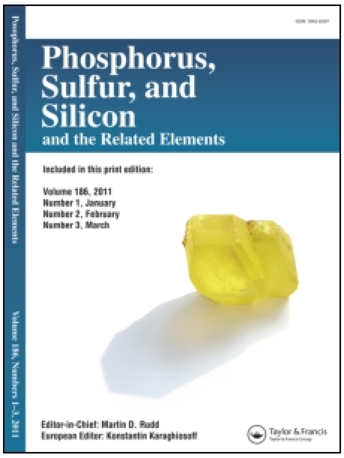

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FIRST EXAMPLES OF DISELENO TWEEZER-LIKE LIGANDS: SYNTHESIS, CHARACTERIZATION AND Pt(II) CYCLOMETALATION

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FIRST EXAMPLES OF DISELENO TWEEZER-LIKE LIGANDS: SYNTHESIS, CHARACTERIZATION AND Pt(II) CYCLOMETALATION

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The synthesis of the first examples of diseleno tweezer-like molecules is described starting from diselenocyanobenzenic or pyridinic compounds and chloronaphthyl or anthryl derivatives. The new diselenides are characterized by mass spectrometry and multinuclear NMR spectroscopy. Starting from naphthyl derivatives, it was unambigously demonstrated for the first time their cyclometalation with Pt(II) to form metalloreceptors.

Keywords: selenoligand; platinum; cyclometalation; metalloreceptor; ^{77}Se NMR

Transition metal complexes with peripheral noncovalent binding sites have been used sometimes as hosts to bind neutral, cationic or anionic guests[1]. According to these properties, many examples of polythia tweezer-like ligands have been synthetized and some of their coordination properties investigated[2]. In particular, m-thiacyclophanes can be palladated to produce organopalladium complexes containing a Pd-C bond[3].

In selenium chemistry, only some examples of selenacrown ethers have been recently described[4]. To our knowlege, there does not exist polyselena tweezer-like ligands. Owing to the soft character of the selenium ligating

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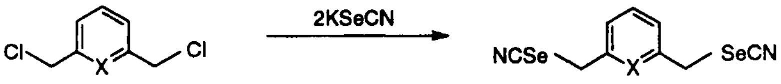
sites, the ability of such structures to form metalloreceptors and the easy detection of ^{77}Se NMR, it was of interest to developp an efficient synthetic strategy for the access to these new families.

The synthesis of this new type of diselenaligands is reported herein along with some preliminary results on their coordination properties with Pt(II).

RESULTS

Benzenic or pyridinic diselenocyanate **1** and **2** could be easily obtained (90% yield) by reacting potassium selenocyanate with dichloride derivatives in dry acetone[5] (Scheme 1):



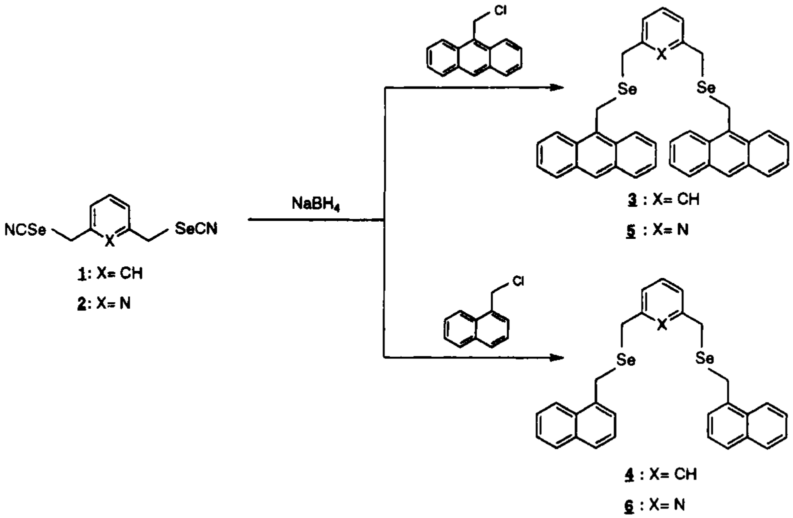
1: X= CH
2: X= N

SCHEME 1

Subsequent reduction of these derivatives **1** or **2** with natrium borohydride and treatment with the naphtyl or anthryl chloromethyl derivative led to the expected structures **3** to **6** in a pure state (Scheme 2):

The structures of the compounds **3-6** have been unambigously confirmed by analysis of their spectroscopic data.

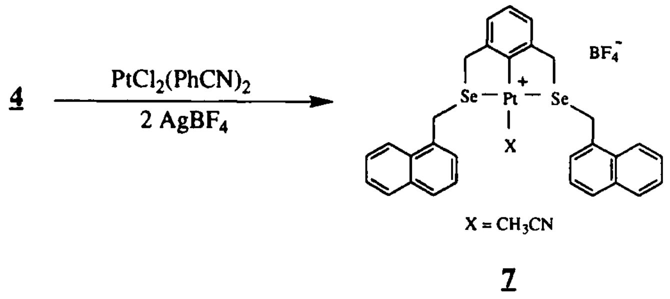
For all the compounds the mass spectra exhibit, in particular, a molecular peak with an isotopic disribution pattern typical of molecules including two selenium atoms. In the ^{1}H NMR spectra the protons of the methylene groups attached to the benzenic or pyridinic systems appear as singlets at 3.8–4.0 ppm, the chemical shift of the other methylene groups, depending of the ligand attached: at 4.2–4.3ppm for naphtalenic compounds and 4.7–4.9ppm for anthracenic ones. The $^{3}C\{^{1}H\}$ NMR spectra show the aromatic carbons and two singlets at 28.8–31.0 ppm and at 21.4–26.0 ppm corresponding to benzenic and pyridinic carbons and to carbons directly bound to naphtyl and anthryl groups, respectively. The $^{77}Se\{^{1}H\}$ NMR



SCHEME 2

spectra show well-resolved peaks at 324–326ppm and at 322–323ppm for naphtalenic and anthracenic compounds, respectively.

Metalation of **4** employing $PtCl_2(PhCN)_2$ in MeCN solution during 48 hours at 81°C, in the pressence of $AgBF_4$ yielded the metalloreceptor Pt(**4**-H)MeCN]BF_4. **7** as a mixture of two compounds (50/50%) in 91% yield (Scheme 3). The resulting complexes are bright brown, air stable, powdery solids that are highly soluble in CH_3NO_2 and considerably less soluble in MeCN.



SCHEME 3

It seems very probable that the presence of two different complexes is due to the existence of two diastereoisomers according to two asymetric selenium atoms in **7**.

The ^{1}H NMR spectrum of the complex **7** shows several resonances in the range expected for naphtalenic protons (7.3–8.2ppm), a multiplet at 7.0 ppm assigned to the benzenic ring protons, several others resonances around 4.5 ppm corresponding to the protons of methylene groups and two singlets at 2.43 and 2.24 ppm corresponding to acetonitrile protons.

The $^{13}C\{^{1}H\}$ NMR spectrum show essentially a large downfield shift, 152.04 ppm, for the C atom at 2-position on the benzenic ring attached to platinum, several signals between 122 and 138 ppm assigned to aromatic carbons, a large signal at 110.0 ppm corresponding to the quaternary carbon of acetonitrile, four singlets at 42.11, 41.05, 38.55 and 37.72 ppm corresponding to the carbons of methylene groups and two signals at 20.6 ppm and 0.06 ppm assigned to aliphatic carbon of the acetonitrile.

The structure of complex **7** is confirmed by the ^{77}Se NMR. The spectrum of **7** in CD_3NO_2 contains two signals at 355ppm and 360ppm (upfield shift of 30–35ppm relative to ligand **4**).

The FAB mass spectrum exhibits a peak with the correct isotopic distribution for Pt(**4**-H)] at m/z= 738,9 affording an unambiguous proof of the platinum-carbon bond.

Finally, we note that the ease of synthesis of the new diselenoligands coupled with the coordination potentialities of the selenium soft sites makes compounds **3-6** extremely versatile building blocks for larger and more elaborate supramolecular systems. Work in this area continues and the coordination properties of these systems will be developed in due time.

EXPERIMENTAL

All reactions were carried out under an inert atmosphere of argon. Solvants were dried and distilled prior to use. ^{1}H-NMR (200,13 MHz) and $^{13}C\{^{1}H\}$-NMR (50,3 MHz) spectra were recorded on a Brucker AC 200 spectrometer. $^{77}Se\{^{1}H\}$-NMR (95,36 MHz) spectra were recorded on a Brucker DRX 500. Mass spectra were taken on a Kratos Concept mass spectrometer by electronic ionization (70 eV) or fast atom bombardment (FAB).

General procedure for the synthesis of the ligands 3–6

Preparation of 1,3-bis[(selenomethylanthryl)methyl]benzene 3

To a solution of 1,3-bis(selenocyanatomethyl)benzene (600 mg, 1.91 mmol) in 20 ml of THF/EtOH (80/20) was added 2.1 equivalents of $NaBH_4$ (150 mg, 4 mmol). During the addition, the mixture turned yellow, and a solid began to precipitate. Stirring was continued for one hour leading to complete precipitation. A solution of chloromethylanthracene (866 mg, 3.82 mmol) in 20 ml of THF/EtOH (80/20) was added. The yellow mixture was protected from light[6] and stirred for 24 hours. After filtration, the solvants were removed in vacuo leaving a yellowish residue. The product was purified by chromatography over silica gel using CH_2Cl_2 as eluent. Yield (1.1 g, 95%). ^1H NMR ($CDCl_3$): δ(ppm) 7–8.5 (m, 22H, aromatic H), 4.72 (s, 4H, CH_2Se), 3.89 (s, 4H, benzylic). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ(ppm) 140–124 (aromatic C), 28.87 (benzylic), 20.54 (CH_2Se). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): δ(ppm) 322.1 (s). MS (EI): m/z 646 (M^+, 4%).

Preparation of 1,3-bis[(selenomethyl-1-naphtyl)methyl]benzene 4

The product was prepared according to a procedure similar to that described above for **3**, using,3-bis(selenocyanatomethyl)benzene and 1-chloromethylnaphtalene as starting material. The product was purified by chromatography over silica gel using pentane/ether (10/90) as eluent. Yield: 35%.

^1H NMR ($CDCl_3$): δ(ppm) 7–8.5 (m, 18H, aromatic H), 4.23 (s, 4H, CH_2Se), 3.80 (s, 4H, benzylic). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ(ppm) 141–124 (aromatic C), 29.10 (benzylic), 26.00 (CH_2Se). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): δ(ppm) 324.6 (s). MS (EI): m/z 546 (M^+, 18%).

Preparation of 2,6-bis[(selenomethylanthryl)methyl]pyridine 5

To a mixture of chloromethylanthracene (493 mg, 2.17 mmol) and $NaBH_4$ (90.5 mg, 2.39 mmol) in 20 ml of THF/EtOH (75/25) was added a solution of 2,6-bis(selenocyanatomethyl)pyridine (600 mg, 1.91 mmol) in 13 ml of THF/EtOH 75/25%. The yellow mixture was protected from light[5] and stirred for 24 hours. After filtration, the solvants were removed in vacuo leaving a yellowish residue. The product was purified by chromatography over silica gel using CH_2Cl_2 as eluent. Yield (650 mg, 93%).

^1H NMR ($CDCl_3$): δ(ppm) 7–8.4 (m, 21H, aromatic H), 4.95 (s, 4H, CH_2Se), 4.08 (s, 4H, $PyCH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ(ppm) 160.4 (quaternary pyridinic C), 139–121 (aromatic C), 31.04 ($PyCH_2$), 21.42 (CH_2Se). $^{77}Se\{^1H\}$ NMR $CDCl_3$): δ(ppm) 322.4 (s). MS (EI): m/z 647 (M^+, 7%).

Preparation of 2,6-bis[(selenomethyl-1-naphtyl)methyl]pyridine 6

The product was prepared according to a procedure similar to that described above for **5**, using 2,6-bis(selenocyanatomethyl)pyridine and 1-chloromethylnaphtalene as starting material. The product was purified by chromatography over silica gel using pentane/ether (10/90) as eluent. Yield: 30%.

^1H NMR ($CDCl_3$): δ(ppm) 7–8.5 (m, 17H, aromatic H), 4.36 (s, 4H, CH_2Se), 3.92 (s, 4H, $PyCH_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ(ppm) 160.2 (quaternary pyridinic C), 138–121 (aromatic C), 30.51 ($PyCH_2$), 25.85 (CH_2Se). $^{77}Se\{^1H\}$ NMR ($CDCl_3$): δ(ppm) 325.4 (s). MS (EI): m/z 547 (M^+, 6%).

Preparation of [(Pt(4-H)MeCN]BF_4 7

$PtCl_2(PhCN)_2$ (0.346g, 0.73 mmol), $AgBF_4$ (0.292g, 1.5 mmol) and the ligand **4** (0.4g, 0.73 mmol) were combined in dry MeCN (40 ml). The solution was protected from light and refluxed for 48h. The resulting mixture was filtered to remove AgCl. The solution was concentrated to 3–5 ml and the complex precipitated by the addition of diethyl ether to the solution. Yield of bright brown solid: 0.57 g (91%).

^1H NMR (CD_3NO_2): δ(ppm) 7.3–8.2 (m, 14H, naphtalenic H), 7.0 (m, 3H, benzenic H), 3.70–4.80 (m, 8H, CH_2Se), 2.43 and 2.24 (s, 3H, CH_3CN). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ(ppm) 152.04 (quaternary C-Pt), 145–123 (aromatic C), 110.0 (quaternary C of CH_3CN) 42.11, 41.05, 38.55, 37.72 (CH_2Se), 20.60 and 20.06 (primary C of CH_3CN). $Se\{^1H\}$ NMR (CD_3NO_2): δ(ppm) 360 and 355 (s). MS (FAB): m/z 738.9 (M^+-CH_3CN-BF_4, 9%).

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