

Published on Web 02/23/2007

A Controlled Approach to Well-Defined Oligothiophenes via Oxidatively Induced Reductive Elimination of Stable Pt(II) Oligothienyl Complexes

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The synthesis and characterization of Pt(II) oligothienyl complexes $L_2Pt(3T)_2$ **2a,b** as stable models for catalytically active corresponding Ni and Pd complexes in transition metal-catalyzed cross-coupling reactions are described. Oxidatively induced reductive elimination of $L_2Pt(3T)_2$ **2a,b** to sexithiophene (6T) **3** constitutes a novel homocoupling method which starts from terthiophene **1**.

Oligothiophenes (OT) are among the most frequently investigated conjugated systems and organic semiconductors because of their outstanding properties and their successful application in organic and molecular electronics.¹ Pd- and Ni-catalyzed cross-coupling reactions with the sequence (1) oxidative addition, (2) transmetallation, and (3) reductive elimination became most important for the synthesis of oligomers with well-defined chain and conjugation length.² Very recently, Pd-catalyzed (homo)couplings of thiophenes by C-H activation have been demonstrated.³ Corresponding Pt complexes are only useful in exceptional cases owing to their higher stability.⁴ which on the other hand allows the use of stable *cis*-Pt-(RR') complexes as models to investigate reductive elimination under formation of the C-C coupling product R-R'.⁵ In this respect, it was recently shown how electronic effects influence the kinetics of thermally activated reductive eliminations of cis-Pt (ArAr') complexes,⁶ but only a few examples through oxidative stimulation were reported.7

We recently explored *cis*-Pt-(σ -acetylide-OT)₂ complexes and their reductive elimination to OT-substituted diacetylenes which can be further transformed to thiophenes by sulfide anions. Using this "metal template approach", we synthesized linear OTs⁸ and more complex conjugated structures and topologies, such as macrocycles⁹ or [2]catenanes¹⁰ which were not accessible by other coupling methods. A much more direct approach would be realized by *cis*-Pt(II)-oligothienyl complexes which is the topic of this study. Only a very limited number of Pt(II) complexes with thienyl ligands are known.¹¹

As shown in Scheme 1, lithiation of 3',4'-dibutyl-2,2':5',2"terthiophene 1^{12} with 1 equiv of *n*-BuLi, followed by reaction with dppfPtCl213 or dpppPtCl214 in a molar ratio of 2:1 provided terthienyl-based Pt complexes 2a and 2b as yellow microcrystalline solids in 74% and 56% yield, respectively. The novel complexes have been fully characterized by ¹H, ³¹P NMR, and mass spectra which clearly confirm their structure. In the aromatic part of the ¹H NMR spectra of **2a,b** signals belonging to the phenyl protons of the dppf and dppp (7.28-7.72 ppm) and terthiophene ligands are visible, and from which the β -protons of the thiophene adjacent to the Pt are considerably upfield shifted (2a: 6.03, 6.55 ppm. 2b: 6.12, 6.56 ppm). ³¹P NMR spectra of **2a,b** exhibit a single peak with a set of ¹⁹⁵Pt satellites (**2a**: 14.33 ppm, ${}^{1}J_{Pt-P} = 2082$ Hz. **2b**: -0.48 ppm; ${}^{1}J_{Pt-P} = 1951$ Hz) confirming that the two OT-ligands are oriented trans to the dppf and dppp ligand.^{11c} Ultimate proof of the structure of 2a,b comes from high-resolution mass spectra Scheme 1



revealing molecular ions ($[M+H]^+$) at m/z = 1468.2668 (2a) and 1326.3158 (2b), respectively.

A more detailed structural characterization of dppfPt(3T)₂ complex **2a** was possible by X-ray structure analysis of single crystals which could be obtained by slow diffusion of *n*-hexane into a solution of **2a** in THF. The view of an individual molecule (Figure 1) shows a pseudo-square-planar geometry of the Pt center including a bite angle of 100.2° (P1–Pt–P2) and 87.3° for C35–Pt–C54. Bond lengths of 2.31 and 2.32 Å are found for Pt–P distances and of 2.05 and 2.02 Å for Pt-C35 and Pt-C54, respectively. Some rotational disorder is noticed for the terminal thiophene units and one butyl side chain, which is quite typical for structures of oligothiophenes.¹⁵

While *cis*-Pt(ArAr') complexes allow the thermal elimination of C–C coupling products,⁶ our $L_2Pt(3T)_2$ complexes **2a,b** form undefined polymeric products upon heating in toluene at 110 °C. However, the use of 2 equiv of a one-electron oxidant such as silver triflate at room temperature cleanly furnished the homocoupling product sexithiophene **3**¹⁶ in 66% yield from **2a** and 56% yield from **2b** (Scheme 1). These yields are comparable or superior to other homocoupling reactions of oligothiophenes, such as the Pd-catalyzed C–H activation³ or the Cu(II)-oxidative homocoupling of lithiated derivatives.^{1,17}

Investigation of the optical and redox properties of the Pt complexes **2a,b** provides insight into their electronic structure and the interplay of conjugated π -system and metal fragment. The absorption spectra of the complexes show one prominent band with a maximum at 367 nm which is shifted to significantly lower energy and double intensity in comparison to ligand 1 ($\lambda_{max} = 335$ nm). The absorption of the complexes is dominated by the $\pi - \pi^*$ transition of the 3T ligands. The degree of π conjugation is increased by additional charge transfer from the Pt center to the ligands via $d\pi \rightarrow p\pi$ interaction. However, this backbonding effect does not lead to full conjugation as can be seen by the further redshift of absorption maximum of product 3 ($\lambda_{max} = 413$ nm).

Cyclic voltammograms (CV) of Pt complexes **2a**,**b** are shown in Figure 2. For the L₂Pt(3T)₂ complexes we find one irreversible oxidation wave at relatively low potential (**2a**: $E_{p1} = 0.12$ V. **2b**: $E_{p1} = 0.09$ V) and two reversible one-electron redox processes at



Figure 1. Molecular structure of dppfPt(3T)₂ complex 2a.



Figure 2. Cyclic voltammograms of L2Pt(3T)2 complexes 2a,b and sexithiophene 3 (2a: $c = 0.87 \times 10^{-3} \text{ mol } \text{L}^{-1}$. 2b: $1.03 \times 10^{-3} \text{ mol } \text{L}^{-1}$ **3**: 1.73×10^{-3} mol L⁻¹ in CH₂Cl₂/0.1 M Bu₄NPF₆, 295 K, v = 100 mVs⁻¹, potentials vs the ferrocene/ferrocenium (Fc/Fc⁺) couple).

higher, identical potentials (**2a**: $E_2^\circ = 0.34$, $E_3^\circ = 0.49$ V. **2b**: $E_2^\circ = 0.33$, $E_3^\circ = 0.48$ V). A fourth reversible wave can be identified for dppfPt(3T)₂ complex 2a at $E_4^\circ = 0.77$ V. The assignment of the various redox processes can be rationalized by comparison to the CV of homocoupling product $\mathbf{3}$ which as expected shows two reversible one-electron waves ($E_1^\circ = 0.33$, $E_2^\circ =$ 0.49 V) concomitant with the formation of stable radical cations and dications.1b Both waves perfectly coincide with the second and third redox wave obtained for the $L_2Pt(3T)_2$ complexes. Therefore, we ascribe the first irreversible oxidation wave in the CVs of the complexes to the two-electron oxidation of the central Pt(II) to Pt-(IV).¹⁸ As for the chemical oxidation of complexes **2a**,**b**, the CV reductive elimination is initiated by the increase of the oxidation state of the central Pt(II) moiety which then releases homocoupling product 3 and reflects a typical ECE electrode mechanism.¹⁹ The fourth reversible wave of $dppfPt(3T)_2$ complex 2a is ascribed to the oxidation of the dppf-ligand which compared to dppfPtCl2 and uncoordinated dppf is anodically shifted because of $Pt \rightarrow P$ backbonding.20

In the same line, potentiostatic electrolysis of complexes 2a or 2b at 0.67 V versus Ag/AgCl (~0.2 V vs Fc/Fc⁺) gave sexithiophene 3 in 67% and 63% yield, respectively, after workup, which are in the same range as those from alternative chemical oxidation. This electrochemical behavior is in full accordance with various cis-Pt- $(\sigma$ -acetylide-OT)₂ complexes which we already investigated.⁸⁻¹⁰

In conclusion, we were able to synthesize Pt(II) oligothienyl complexes 2a,b as stable models of corresponding catalytically active Ni- or Pd-intermediates and to investigate their geometric and electronic structure. Chemical or electrochemical oxidation of the central Pt(II) to Pt(IV) induces reductive elimination under C-Ccoupling and formation of the homocoupling product, sexithiophene 3. The two-step reaction constitutes a novel homocoupling method of oligothiophenes. Studies aiming at the template-directed synthesis of more complicated linear and cyclic structures are in progress.

Acknowledgment. We acknowledge financial support by the German Research Foundation (DFG, SFB 569), help in X-ray crystallography (B. Müller, Univ. Ulm; Dr. J. W. Bats, Univ. Frankfurt), and HR mass spectra (Prof. C.A. Schalley, FU Berlin; A. Rang, Univ. Bonn).

Supporting Information Available: Experimental details, analytical data absorption spectra, and X-ray structure analysis; crystallographic information (CIF) for complex 2a. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA070083K