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

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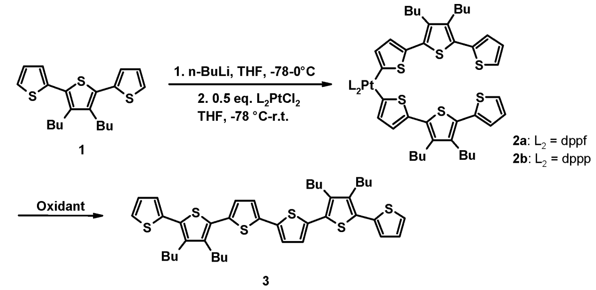
The synthesis and characterization of Pt(II) oligothienyl complexes $L_2Pt(3T)_2$ **2a**,**b** as stable models for catalytically active corresponding Ni and Pd complexes in transition metal-catalyzed cross-coupling reactions are described. Oxidatively induced reductive elimination of $L_2Pt(3T)_2$ **2a**,**b** 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 OTs[8] and more complex conjugated structures and topologies, such as macrocycles[9] or [2]catenanes[10] 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 $dppfPtCl_2$[13] or $dpppPtCl_2$[14] 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, ^{31}P 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). ^{31}P NMR spectra of **2a**,**b** exhibit a single peak with a set of ^{195}Pt satellites (**2a**: 14.33 ppm, $^1J_{Pt-P} = 2082$ Hz. **2b**: −0.48 ppm; $^1J_{Pt-P} = 1951$ 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 revealing molecular ions ($[M+H]^+$) at $m/z = 1468.2668$ (**2a**) and 1326.3158 (**2b**), respectively.

Scheme 1



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 activation[3] 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 red-shift 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 $L_2Pt(3T)_2$ 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

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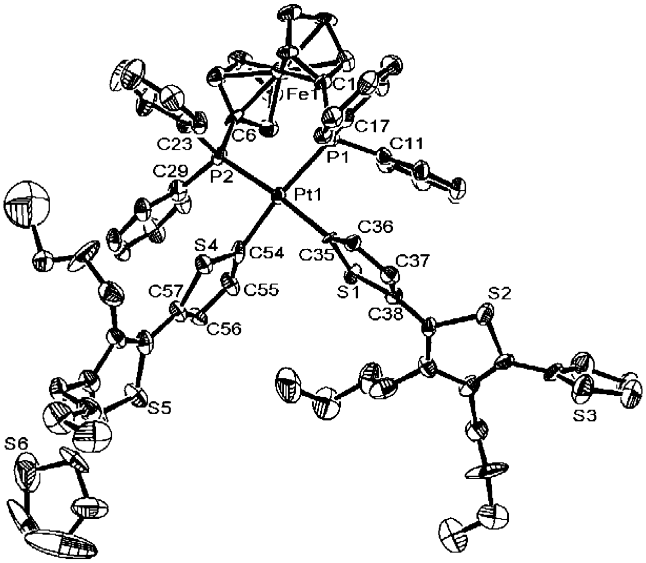

Figure 1. Molecular structure of dppfPt(3T)$_2$ complex **2a**.

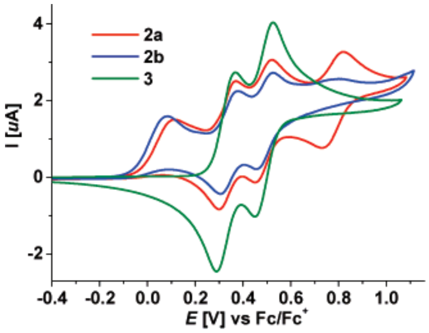

Figure 2. Cyclic voltammograms of L$_2$Pt(3T)$_2$ complexes **2a**,**b** and sexithiophene **3** (**2a**: $c = 0.87 \times 10^{-3}$ mol L^{-1}. **2b**: 1.03×10^{-3} mol L^{-1}. **3**: 1.73×10^{-3} mol L^{-1} in CH_2Cl_2/0.1 M Bu_4NPF_6, 295 K, $v = 100$ mVs^{-1}, potentials vs the ferrocene/ferrocenium (Fc/Fc$^+$) couple).

higher, identical potentials (**2a**: $E^\circ_2 = 0.34$, $E^\circ_3 = 0.49$ V. **2b**: $E^\circ_2 = 0.33$, $E^\circ_3 = 0.48$ V). A fourth reversible wave can be identified for dppfPt(3T)$_2$ complex **2a** at $E^\circ_4 = 0.77$ V. The assignment of the various redox processes can be rationalized by comparison to the CV of homocoupling product **3** which as expected shows two reversible one-electron waves ($E^\circ_1 = 0.33$, $E^\circ_2 = 0.49$ 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$_2$Pt(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 dppfPtCl$_2$ and uncoordinated dppf is anodically shifted because of Pt → 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-(σ-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−C coupling 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.

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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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