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Electropolymerization of a Cyclometalated Terthiophene: A Hybrid Material with a Palladium−Carbon Bond to the Backbone

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Polythiophenes have been widely investigated for their interesting and potentially useful properties, which include high conductivity and luminescence.[1,2] Many polythiophene derivatives have been prepared in order to introduce new functionalities to the material, such as side groups that allow a selective response to specific analytes for sensor applications.[3] Conjugated polymers that bear pendant metal complexes are of particular importance due to the possibility of integrating the chemical, optical, and redox properties of the metal group and the conjugated backbone to yield new hybrid materials.[3−5] Several approaches have been taken to attach metal centers to polythiophene derivatives; for example bipyridine or phenanthroline binding sites have been introduced into the backbone, and used to coordinate Cu, Zn, and Ru.[6−8] Recently, an interesting system was reported in which Ru(II) is coordinated in a bidentate fashion by a pendant phosphine group and a backbone sulfur.[9] Polythiophene may be viewed as a cis polyacetylene structure stabilized by the sulfur atom;[2] therefore, bonding a metal center to the carbon backbone is expected to directly influence the electronic properties of the polymer. We report herein the first example of such a material, in which Pd(II) is σ-bonded to a backbone carbon atom.

Electropolymerization has been widely used for the preparation of conductive polymer thin-films,[2,3] and we have elected to synthesize a metal-containing monomer for polymerization via this method. The monomer **2** was synthesized via the reaction of 3′-diphenylphosphino-2,2′:5′,2′′-terthiophene (**1**)[10] with 1 equiv of $PdCl_2$.[11] The solid-state structure of **2** was unambiguously established by determination of its X-ray crystallographic structure (Figure 1), and consists of a dimer in which Pd is square planar with bridging chlorides and **1** binding via the phosphine and C3 of the terthiophene.[12] Cyclometalation of thiophene derivatives is well-known and has been observed with nitrogen-containing chelating ligands such as 2-(2-thienyl)pyridine[13−15] and 6-(2-thienyl)-2,2′-bipyridine[16] on Pd and Pt and with diphenyl-2-thienylphosphine in a Ru cluster.[17]

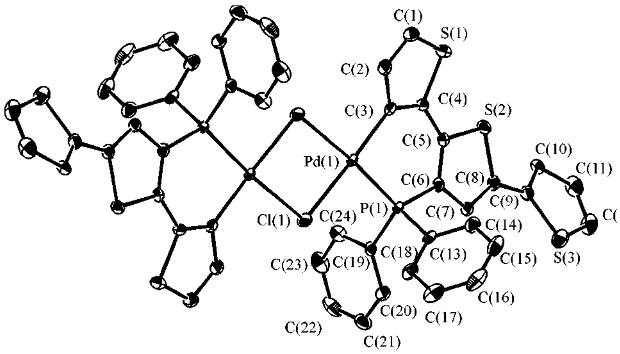
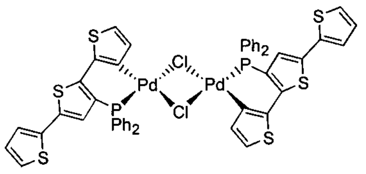


Figure 1. X-ray crystal structure of **2**. The hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at 30% probability. Selected bond lengths (Å) and angles (deg): Pd(1)−C(3) 2.002(3); Pd(1)−P(1) 2.2171(6); Pd(1)−Cl(1) 2.4184(7); P(1)−Pd(1)−C(3) 92.03(8); Cl(1)−Pd(1)−C(3) 176.55(8).



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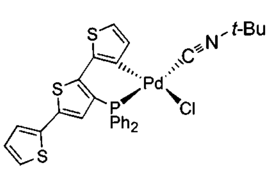

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The ^{31}P NMR spectrum of **2** in $CDCl_3$ contains two closely spaced resonances at δ 17.7 and 16.6 in a 0.7:1 ratio, likely due to the presence of both cis and trans isomers of the complex in solution as has been previously observed for other halo-bridged Pd dimers.[18,19] Reagants such as phosphines and isonitriles are known to cleave dihalo bridges in related compounds,[20] and we observe similar behavior for **2**. For example, **2** reacts with *tert*-butyl isocyanide (*t*-BuNC) at 25 °C in solution to give the monomeric complex **3**, which exhibits a characteristic terminal NC stretch at 2209 cm^{-1} in the infrared region. The isocyanide is most likely cis to the σ-bonded carbon in **3** as is typically the case in related compounds.[21] Other reagents such as PPh_3, $P(OMe)_3$, PPh_2Me, and PhNC also react with **2**, whereas no reaction occurs with MeCN.

The cyclic voltammogram (CV) of **2** in CH_2Cl_2 containing 0.1 M $(n\text{-Bu})_4NPF_6$ shows the presence of both an oxidation wave at +1.20 V (Figure 2, first scan) and an irreversible reduction wave

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[11] Synthesis of **2**: A warm solution of **1** (108 mg, 0.25 mmol) in ethanol/acetonitrile (10/3 mL) was slowly added at 50 °C to $PdCl_2$ (50 mg, 0.28 mmol) and concentrated HCl (0.05 mL) in water (3 mL). A yellow precipitate formed immediately, and the mixture was stirred for 2 h at 50 °C, cooled, and filtered to yield a yellow powder. The solid was washed with water (2 × 10 mL), ethyl ether (1 × 5 mL), and hexanes (2 × 20 mL) and dried in air. Recrystallization from a methylene chloride/diethyl ether/hexanes mixture (1/1/1) yielded a light orange solid. Yield: 112 mg (70%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.78−7.59 (m, 4H), 7.57−7.25 (m, 17H), 7.21−6.90 (m, 9H), 6.59−6.48 (m, 2H). $^{31}P\{^{1}H\}$ NMR (81 MHz, $CDCl_3$) δ 17.72, 16.61. Anal. Calcd for $CH_{32}Cl_2P_2PdS_6$: C 50.27, H 2.79%. Found: C 50.39, H 2.85%. UV−vis: λ_{max} (nm) (ϵ ($M^{-1}cm^{-1}$)) 388 (6.64×10^4), 288 (sh) (3.84×10^4).

[12] Crystal data for 2: monoclinic, yellow block, space group $P2_1/c$, $a = 16.0489(5)$ Å, $b = 9.4521(3)$ Å, $c = 15.9728(6)$ Å, $\beta = 116.707(2)°$, $T = 173$ K, $Z = 2$, R (refined on F, $I > 3\sigma(I)$) = 0.026, $R_w = 0.036$, GOF 1.08

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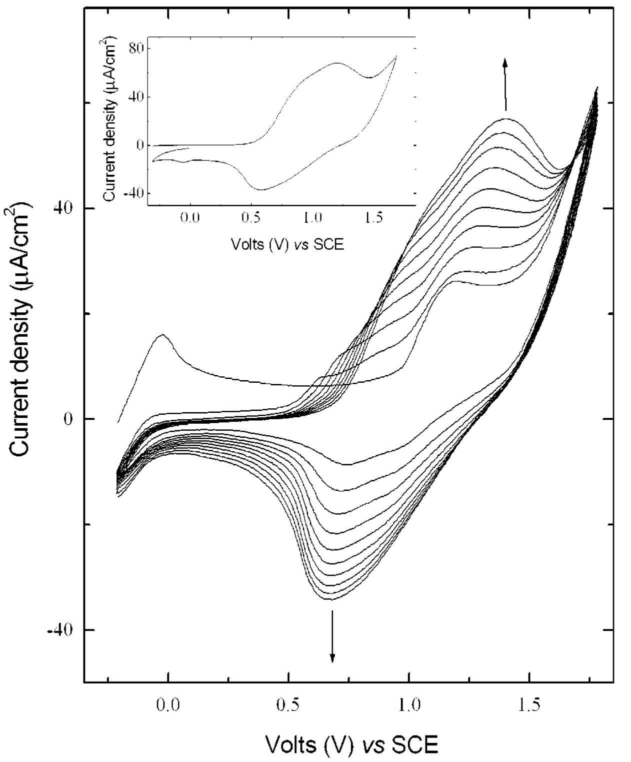

Figure 2. Cyclic voltammetry of **2** in CH_2Cl_2 containing 0.1 M (n-Bu)$_4$NPF$_6$. Multiple scans from −0.25 to +1.75 V, scan rate = 200 mV/s (the oxidation wave at 0 V in the first scan is due to added decamethylferrocene, used as an internal reference). Inset: scan of a poly-**2** film on a gold electrode in 0.1 M (n-Bu)$_4$NPF$_6$ in CH_2Cl_2 (scan rate = 200 mV/s).

at −1.31 V vs SCE (not shown). The wave at −1.31 V is assigned to a Pd-based reduction as **1** does not exhibit any reduction waves between 0 and −1.5 V. The anodic wave has two associated cathodic features which appear on the return scan. The wave at 0.73 V results from the reduction of surface-confined material formed upon oxidation, and the shoulder to higher potential is likely due to reduction of shorter oligomers. Repeated scanning from −0.25 to +1.75 V results in the deposition of a red film of poly-**2** on the electrode surface, along with an increase in the current in the CV (Figure 2). The CV of the film after removal of the electrode from the polymerization solution shows broad oxidation and reduction waves between −0.25 and +1.75 V vs SCE (Figure 2, inset), similar to CV scans observed for other polythiophene derivatives.[2] The conductivity of the film when oxidized is 10^{-3} S cm^{-1}.

Poly-**2** films were characterized by several methods. The elemental composition of the films was determined by energy-dispersive X-ray (EDX) analysis to be the same as that of the monomer within experimental error. X-ray photoelectron spectroscopy (XPS) analysis shows a Pd ($3d_{5/2}$) peak at 337.3 eV, consistent with Pd(II) (no Pd(0) or (IV) was detected). The P 2p peak in the XPS appears at 131 eV, as expected for a coordinated phosphine.[22] Careful inspection of the surface reflectance IR spectrum of poly-**2** reveals that many of the same bands are present as in a solid-state transmission spectrum of **2**; however, other bands are subdued or absent. The structural differences between poly-**2** and the monomer are expected to cause some changes in the infrared spectrum, as has been previously observed for other thiophene oligomers and polymers.[23]

The reactivity of poly-**2** films is very similar to that of **2**. Exposure of a poly-**2** film to a solution of t-BuNC in hexanes at 25 °C resulted in a rapid reaction. The surface reflectance IR spectrum of the reacted film shows a new, strong band at 2208 cm^{-1} similar to the −NC stretch in **3** and the region between 1500 and 600 cm^{-1} also shows good correlation with the transmission spectrum of **3**. When a film of poly-**2** is treated with a solution of phenyl isocyanide (PhNC) in hexanes at 25 °C, the IR spectrum of the resulting film also contains a new band at 2188 cm^{-1} due to a terminal isocyanide group. After reaction of the poly-**2** films with either isocyanide, the resulting films are insoluble in hexanes but highly soluble in CH_2Cl_2, in marked contrast to poly-**2** which is completely insoluble in this solvent. Reaction of poly-**2** films with PPh_3, $P(OMe)_3$, or PPh_2Me also resulted in an increase in the solubility in CH_2Cl_2, whereas MeCN did not react.

The characterization and reactivity of poly-**2** all support the conclusion that the coordination at the Pd center is retained upon polymerization. Thiophene oligomers polymerize primarily by C−C coupling at the α position,[2] and we therefore propose that the films consist primarily of α,α-coupled **2**, although α,*β*- or *β*,*β*-coupled material may also be present. Reaction of poly-**2** with isocyanides and phosphines cleaves the dichloro bridges, thus eliminating intrachain cross-linking in the material and adding solubilizing groups to the backbone. These factors together are responsible for the increase in solubility.

The UV−vis spectrum of a neutral film of poly-**2** shows a strong absorption band with λ_{max} at 522 nm, which shifts to 808 nm upon oxidation. The positions of these bands are comparable to those observed in substituted polythiophenes,[24] and the red-shift of the absorption band relative to **2** is consistent with a significant increase in conjugation length upon polymerization. Upon reaction of the film with t-BuNC or PhNC, the absorption band red-shifts to λ_{max} = 528 nm for poly-**2**/t-BuNC and 542 nm for poly-**2**/PhNC. These shifts are indicative of the electronic effect on the backbone caused by the reaction at the pendant metal, and the differences in λ_{max} observed for reactions with two similar isonitriles indicates how sensitive the electronic structure of the conjugated backbone is to the ligands at the Pd center.

In conclusion, we have prepared, by electropolymerization of the cyclometalated Pd dimer **2**, the first conductive polythiophene derivative in which a metal is σ-bonded to the conjugated backbone. The Pd moiety is stable under the electropolymerization conditions; however, it undergoes subsequent reactions with isocyanides and phosphines. The proximity of the Pd to the conjugated backbone in this new binding mode, combined with the reactivity of the Pd center, suggests that these materials may be useful in transition-metal based conductive polymer sensors.

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Supporting Information Available: Preparative details for **3**, table of EDX data, IR and XPS spectra (PDF). An X-ray crystallographic file (CIF) for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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