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Communications

Electropolymerized Pd-Containing Thiophene Polymer: A Reusable Supported Catalyst for Cross-Coupling Reactions

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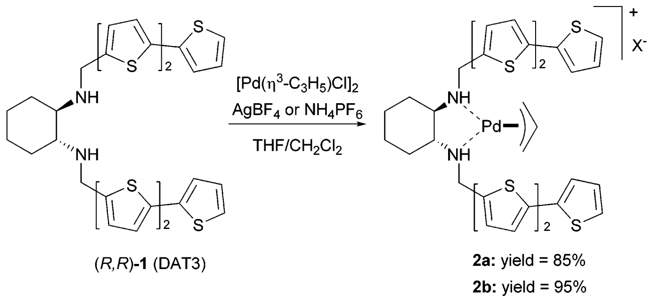
Summary: Electrodeposition of Pd-containing oligothienyl complexes on porous graphite electrodes allows the preparation of a new, reusable heterogeneous organometallic catalyst for intra- as well as intermolecular cross-coupling reactions.

Palladium is one of the most utilized and versatile transition metals in modern synthetic organic chemistry, and a large number of transformations involve this noble metal as a catalyst or organometallic reagent.[1] The scope of Pd-mediated cross-coupling reactions (i.e., Suzuki−Miyaura,[2a] Mizoroki−Heck,[2b] Sonogashira[2c]) continues to broaden,[3] being commonly employed as bench test processes for new homo- and heterogeneous catalysts. As the chemical industry adopts Pd-based processes in manufacturing,[4] demands for ecologically friendly transformations have moved research efforts toward new, easily handled, separable, and recoverable catalytic systems.

To this purpose, anchoring or dispersion of an active catalyst complex onto an inert matrix is a commonly used strategy;[5] however this often requires extensive synthetic steps, and contamination of reaction products by leaching of metal species is a concern.[6]

A relatively unexplored strategy to prepare thin films of organometallic catalysts is the controlled electropolymerization of metal-functionalized oligothiophenes.[7] The direct electrochemical preparation of supported catalysts on electrodes avoids multistep synthetic pathways to introduce anchoring sites as well as spacers in the molecular skeleton. In addition, thin films may be readily deposited on high surface area electrodes such as porous graphite mesh. Thiophene-functionalized bipyridine ligands have been previously suggested as potential precursors of polymeric heterogeneous catalysts,[8a] and Pd catalysts have been attached as pendant groups to polypyrroles;[8b] however the incorporation of a catalytic center directly in the polymer backbone has not been explored.

Scheme 1. Synthesis of [DAT3-Pd(η^3-C_3H_5)][X] (2a: X = BF_4, 2b: X = PF_6).



Our recent findings on the use of chiral diamino-oligothiophenes (DATs), as versatile ligands for catalysts,[9] prompted us to consider the corresponding Pd complexes as suitable candidates for the electrochemical deposition of Pd-containing thiophene polymers on high surface area graphite electrodes.[10]

The electropolymerizable precursor complex [Pd(η^3-C_3H_5)(**1**)][BF_4] (**2a**) was prepared in 85% yield by reacting **1**[9a] (DAT3, 1 equiv) with [Pd(η^3-C_3H_5)Cl]$_2$ (0.5 equiv) in THF/CH_2Cl_2, followed by exchange with $AgBF_4$. Spectroscopic characterization (ESI-MS, IR, UV/vis) and elemental analysis are consistent with the structure shown in Scheme 1.

Although attempts to isolate suitable crystals of **2a** for single-crystal X-ray diffraction were unsuccessful, the molecular

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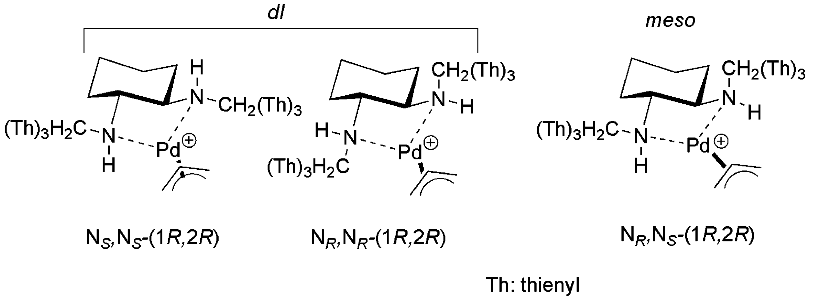

Figure 1. Coordination modes of the Pd(η^3-C_3H_5) unit to substituted *trans*-1,2-diaminocyclohexane.

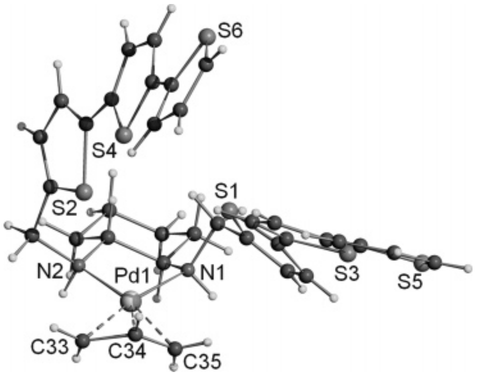

Figure 2. X-ray molecular structure of $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{1})]^+$ as a $[PF_6]^-$ salt (**2b**). The allyl ligand is disordered, and the dominant orientation (55%) is shown. Selected bond lengths (Å): Pd(1)−N(1) 2.110(5), Pd(1)−N(2) 2.101(5), Pd(1)−C(33) 2.137(9), Pd(1)−C(35) 2.199(8), Pd(1)−S(2) 3.306(2).

structure of the analogous $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{1})][PF_6]$ complex **2b** (Figure 2) could be obtained. The structure shows a *N*,*N*-chelating cycle in an envelope conformation with the nitrogen atoms showing opposite configurations [N(1)(*R*) and N(2)(*S*)]. A close intramolecular S(2)···Pd(1) contact [(3.306(2) Å)] is observed similar to that reported in the analogous DAT2−Pd complex [(3.340(1) Å)].[9a]

^{1}H NMR studies of **2a** were carried out to gain insight into the behavior of the cationic Pd complex in solution. The coordination of the Pd(η^3-C_3H_5)unit to the substituted *trans*-1,2-diaminocyclohexane gives a five-membered metallacyclic ring in which the nitrogen atoms are locked in a tetrahedral environment. In **2a** three possible stereoisomers at the nitrogen centers (two *dl* and *meso* isomers) can be formed (Figure 1).[11a,b] Three distinct sets of allylic protons were observed in the ^{1}H NMR spectra in both $CDCl_3$ (−80 → 35 °C) and CD_3CN (−45 → 70 °C) over the entire temperature range studied. It has been shown that in strongly coordinating solvents such as CD_3CN the η^1 and η^3 allyl isomers rapidly equilibrate;[11c,d] thus we attribute the observed sets of allyl protons to the two *dl* isomers and the *meso* species (ratio at room temperature: 1:1.15:1.73). In $CDCl_3$ similar results are observed, suggesting that even in this less coordinating solvent rapid equilibration of the η^1 and η^3 allyl species occurs, possibly due to interaction between the Pd center and the ancillary thienyl groups,[12] as observed in the solid-state structure of **2b**. The UV/vis spectrum of **2a** has λ_{max} = 360 nm, close to the maximum absorption of terthiophene (355 nm).[13]

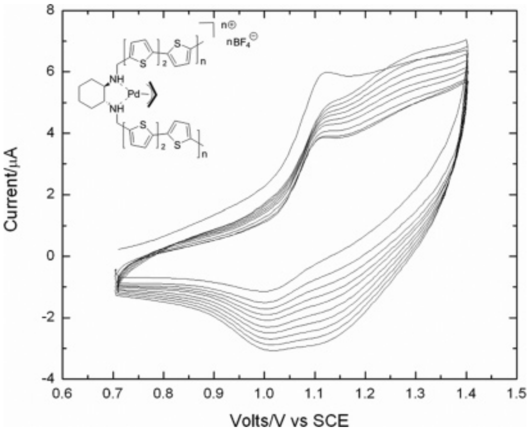

Figure 3. Cyclic voltammogram of **2a** on a Pt electrode.

Complex **2a** was electropolymerized on a Pt electrode (Figure 3). Electropolymerization of related Pd complexes has previously been shown to occur via coupling of the α-positions of the terminal thiophene rings.[14] For catalytic studies, films were electropolymerized on carbon paper (Toray TGP-H-030) by cycling from 0 V to the potential where polymerization starts (10 cycles typically used). The amount of poly-**2a** on the carbon films is difficult to accurately determine, but mass changes of <1 mg for a 1 cm^2 film were recorded. The electropolymerized films were characterized by X-ray photoelectron spectroscopy (XPS) and UV/vis spectroscopy. XPS analysis shows a Pd:S ratio of 1:5.8, similar to the ratio obtained for **2a** cast from solution (Pd:S = 1:5.0). The Pd $3d_{5/2}$ peak appears at 338.5 eV, consistent with the presence of Pd(II) in similar coordination environments.[15] UV/vis spectroscopy shows a slight red-shift in the absorption spectrum (λ_{max} = 384 nm).

A poly-**2a** film was used as the catalyst in the Suzuki cross-coupling reaction between 2-fluoro-1-iodobenzene **3** and phenylboronic acid **4** under basic conditions (K_2CO_3). After 40 h at 80 °C, 91% conversion of the desired cross-coupled biaryl **5** was achieved (Scheme 2a). XPS analysis of the modified electrode after the catalysis showed a Pd:S ratio of 1:6.3 and minimal change in the Pd $3d_{5/2}$ binding energy. This is consistent with negligible loss of Pd from the polymer backbone. The signal intensities for the Pd and S peaks are comparable before and after catalysis, indicating that overall loss of metallopolymer from the support is small.

In order to ascertain whether the catalysis is authentically heterogeneous, aliquots of liquid were removed from a Suzuki

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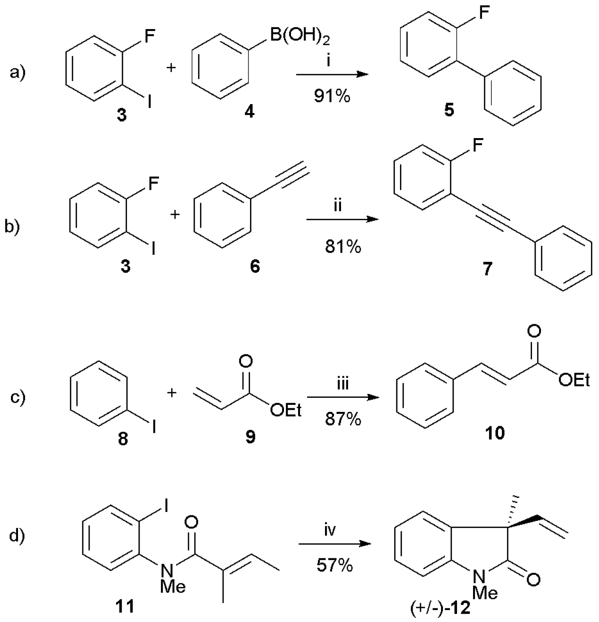
Scheme 2[a]



[a] Reagents and conditions: (i) poly-**2a**, K_2CO_3, toluene, MeOH, 80 °C, 24 h; (ii) poly-**2a**, TEA (3 equiv), 70 °C; (iii) poly-**2a**, TEA, toluene, CH_3CN, reflux, 24 h; (iv) poly-**2a**, DIPEA, DMA, 80 °C, 48 h.

reaction run to completion from which the catalyst film had been removed, and a fresh **3**/**4**/K_2CO_3 mixture was added. In this case, the formation of only trace **5** was observed (7% conversion, 48 h reflux). This demonstrates that negligible activity results from leaching of catalyst from the films and that the catalysis is heterogeneous. Moreover, control experiments with **2b** in solution (loading 1 mol %, 80 °C, 40 h, conversion 98%) and with the unmodified electrode (80 °C, 40 h, trace conversion) showed that the support neither significantly affects the activity of the electrodeposited polymer nor participates in the catalysis.

The reusability of the catalyst was tested by removing the electrode from solution, washing with MeOH, followed by drying under vacuum. This simple procedure allowed five consecutive Suzuki reactions (**3** + **4** → **5**) to be carried out in high conversions (89−98%, Table S1). The Sonogashira cross-coupling of **3** with phenylacetylene **6** under copper ligand-free, phosphine ligand-free, and solvent-free conditions in the presence of poly-**2a** was successful (81%, 24 h, Scheme 2b). Good reaction conversion was also obtained in the Heck coupling of iodobenzene **8** and ethyl acrylate **9** (Scheme 2c). The use of excess Et_3N as a scavenger resulted in 87% conversion after 24 h. Moreover, the intramolecular Heck reaction involving (*E*)-α,β-unsaturated 2-haloanilides **11**[16] also proceeded in the presence of a poly-**2a** film, with racemic oxindole **12** obtained chemoselectively in 57% isolated yield after 48 h at 80 °C (Scheme 2d).[17]

In conclusion, we report here a novel approach to heterogeneous organometallic catalysts via electrodeposition of oligothienyl complexes on porous graphite electrodes. The thin films are efficient in catalyzing several cross-coupling reactions and in the case of the Suzuki reaction allow for the easy recovery and reuse of the supported Pd polymer over several runs without appreciable loss in activity. Studies directed toward the use of this chiral polymeric oligothienyl-Pd complex in chemical and electrochemical asymmetric catalysis are currently underway.

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Supporting Information Available: Synthesis and characterization of the catalyst, CIF file of **2b**, and cross-coupling procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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