DOI: 10.1002/ejoc.200900306

New Electrochemically Generated Polymeric Pd Complexes as Heterogeneous Catalysts for Suzuki Cross-Coupling Reactions

Marco Bandini,*[a] Agostino Pietrangelo,[b] Riccardo Sinisi,[a] Achille Umani-Ronchi,[a] and Michael O. Wolf[b]

Keywords: Cross-coupling / Electropolymerization / Heterogeneous catalysis / Palladium / Sulfur heterocycles

Electrochemically generated films of polymerized (diaminooligothiophene)palladium complexes as heterogeneous catalysts for Suzuki cross-coupling reactions are reported. The electrodeposition of these polymeric species onto porous graphite electrodes allows for easy removal of the organometallic species from the reaction mixture and convenient reuse in subsequent (up to 6) reactions.

Introduction

Green chemical processes will play a critical role in improving the quality of life in an environmentally sustainable fashion.[1] In the fine-chemical and pharmaceutical industries, homogeneous Pd-mediated cross-coupling reactions[2] are widely employed[3] in the production of functionalized oligoarenes, resulting in improved reaction yields, selectivity, turnover numbers (TON), and turnover frequencies (TOF).[4] Immobilization of these catalysts onto solid inert supports is a green alternative to homogeneous systems as it enables the facile removal of the catalytically active species from the reaction solution, thus avoiding time-consuming and expensive workup processes that require additional separation steps and larger volumes of hazardous materials.[5,6]

To date, two main strategies have been used to immobilize catalysts onto inert matrices, namely, (i) binding palladium centres by van der Waals interactions to solid supports such as charcoal,[7] metal oxides,[8] zeolites/molecular sieves,[9] organic polymers[10] or polymer capsules;[11] or (ii) covalently binding palladium complexes to solid supports such as silica[12] or organic polymers.[13] Unfortunately, catalyst poisoning, limited accessibility to sterically encumbered active sites, and poor anchoring linkages are drawbacks that prevent these heterogeneous catalytic systems from being widely used on industrial scales.

[a] Dipartimento di Chimica "G. Ciamician", Alma Mater Studiorum – Università degli Studi di Bologna,
Via Selmi 2, 40126 Bologna, Italy
Fax: +39-051-2099456
E-mail: marco.bandini@unibo.it
[b] Department of Chemistry, University of British Columbia,
Vancouver, BC, V6T 1Z1, Canada
Fax: +1-604-822-2847
E-mail: mwolf@chem.ubc.ca

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900306.

An alternative approach is to covalently anchor the catalytically active species to electrochemically deposited polymer supports.[14] Direct electrodeposition of supported catalysts onto inert electrodes avoids time-consuming multistep syntheses that are required to introduce anchoring sites and spacers to the molecular skeleton, while providing a simple means by which the catalyst can be removed from the reaction system and recycled. Roglans and coworkers have reported the synthesis and characterization of modified electrodes prepared by electrodeposition of Pd^0 complexes containing polypyrrole ligands.[15] These recoverable systems were shown to exhibit moderate to good catalytic activity in Suzuki cross-coupling reactions. More recently, the electropolymerization of (thiophene-salen)chromium derivatives afforded recoverable chiral polymers immobilized onto inert surfaces that exhibit moderate enantioselectivity in hetero-Diels–Alder (HDA) reactions.[16] Thiophene-functionalized bipyridine ligands have been previously reported as potential precursors to polymeric heterogeneous catalysts;[17] however, attempts to electrochemically polymerize and co-polymerize these monomers were unsuccessful.

In a recent communication, we described the synthesis and characterization of a Pd-containing polythiophene (poly-**1**, Figure 1)[18] obtained by electrochemically polymerizing the cationic complex **1** comprised of a chiral diamino ligand (DAT3) with linearly tethered terthienyl groups.[19] These electrochemically modified electrodes proved to be efficient catalysts for several intra- and intermolecular C–C cross-coupling reactions such as the Suzuki–Miyaura,[20a] Mizoroki-Heck,[20b] and Sonogashira[20c] transformations with iodoarenes. Moreover, negligible Pd leaching and no overall loss of polymer from the support was observed after the reactions suggesting that the catalysis was authentically heterogeneous.

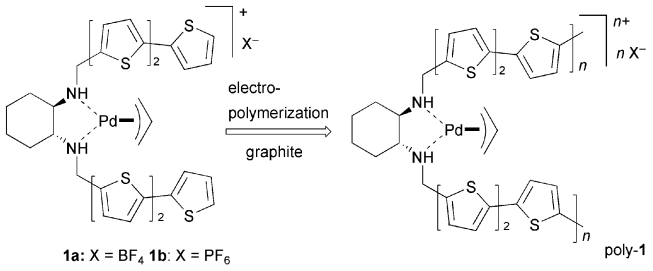
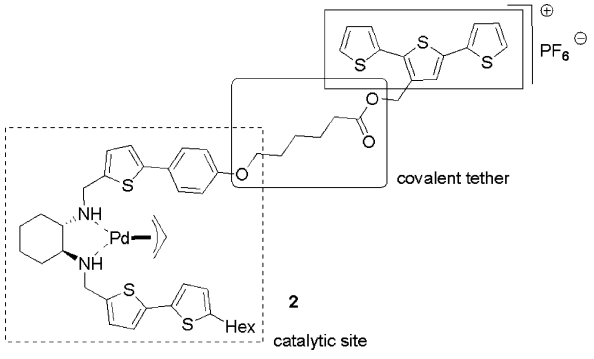


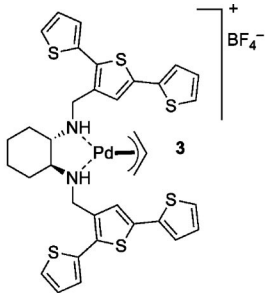
Figure 1. Synthesis of Pd-containing thiophene polymers by electrochemical deposition of monomers **1a**,**b** on graphite.

Here, we expand our investigations to include two novel conjugated polymers that possess the same catalytically active Pd site as poly-**1** but differ in the connectivity to the polythiophene backbone. Due to the location of the diamino ligand site in **1**, the conjugation pathway in poly-**1** is short (a maximum of six rings if α–α coupling occurs exclusively).

The new monomers investigated here have been designed to afford polymers with larger conjugation lengths due to the availability of both α-positions on the thiophene oligomeric moieties. Our objective here was to develop and investigate the electrochemical polymerizability and catalytic performance of these new catalyst architectures. In the novel C_1-symmetric monomer **2**, a terthienyl group is tethered to the catalytically active (DAT2)Pd(allyl) complex through an extended organic linker. Relative to **1a** and **1b**, this Pd complex is anchored some distance from the oligothiophene moiety rendering the catalytically active species isolated from and sterically less confined by the polymer chain. To prevent electrochemical coupling of the bithienyl moiety and to improve the monomer solubility, a hexyl substituent on the α′ position was used as an end-capping group.



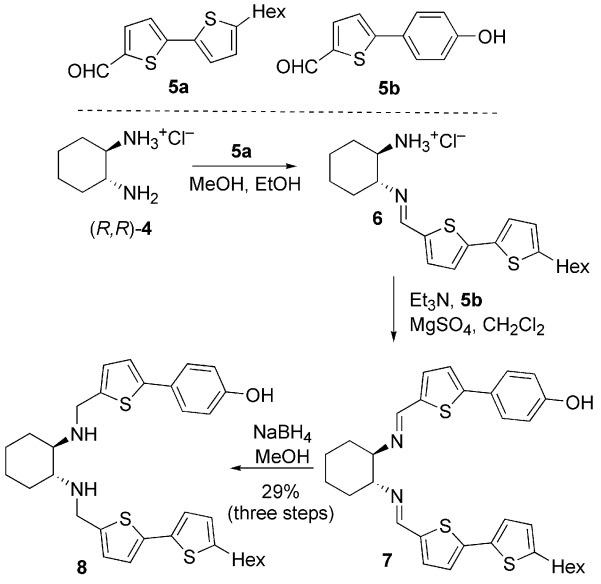
The cationic (DAT3b)Pd(allyl) complex **3** was designed to evaluate the catalytic performance of an electrochemically generated cross-linked π-conjugated metal polymer (poly-**3**) whereby both α positions on each terthienyl moiety are available for polymerization. Cyclic voltammetry studies on **2** and **3** and the catalytic efficiency of the subsequent polymers in promoting Suzuki reactions with bromoarenes are reported.



Results and Discussion

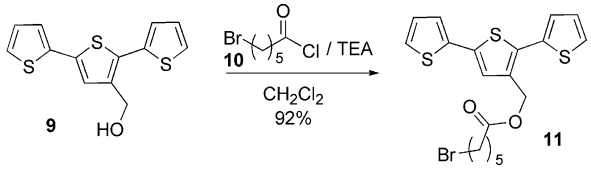
Synthesis of (Diamino-oligothiophene)Pd Complexes

Monomer **2** was prepared according to a convergent synthetic approach. The condensation of 1,2-cyclohexanediamine hydrochloride (*R*,*R*)-**4** with **5a**[21] followed by a second condensation with **5b**[22] in the presence of TEA afforded diimine **7** (Scheme 1). The desired C_1-symmetric (*R*,*R*)-**8** was prepared by the reduction of **7** with $NaBH_4$ in methanol and isolated with an overall yield of 29% after purification by flash chromatography.



Scheme 1. Synthesis of the C_1-symmetric ligand **8**.

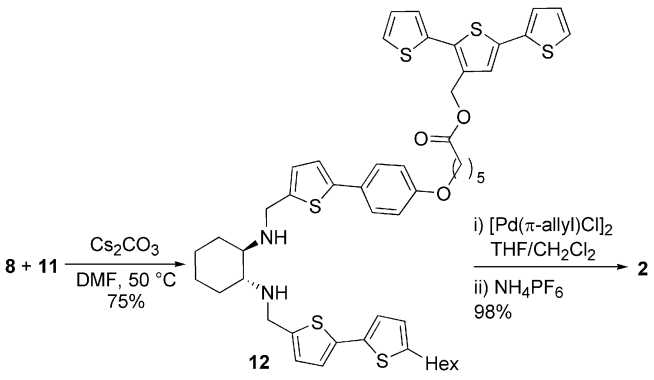
Compound **11** was prepared in 92% yield by the condensation of 6-bromohexanoyl chloride (**10**) with the readily available primary alcohol **9**[23] (Scheme 2).



Scheme 2. Synthesis of ester **11**.

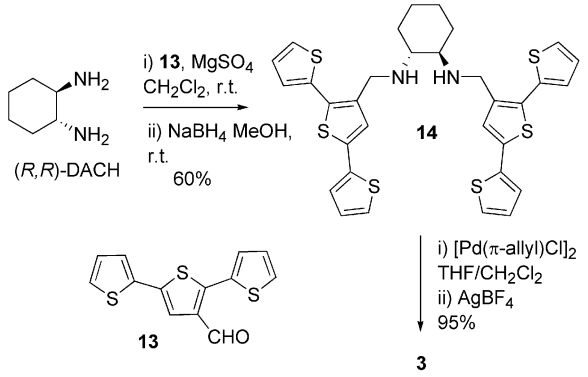
Finally, the reaction of **11** with **8** under basic conditions (Cs_2CO_3, DMF, 50 °C, 16 h) afforded **12** in 75% yield. Subsequent treatment of **12** with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ followed by

anion metathesis with NH_4PF_6 gave the Pd complex **2** as an air-stable pale brown solid in high yield (98%, Scheme 3).



Scheme 3. Synthesis of Pd complex **2**.

Ligand **14** (DAT3b) was prepared by reductive amination between (*R*,*R*)-1,2-cyclohexanediamine (*R*,*R*)-DACH and (2,2′:5′,2′′-terthiophene)-3′-carboxaldehyde (**13**). According to an approach analogous to that used for the preparation of monomer **2**, the corresponding monomer **3** was isolated in 95% yield as an air-stable pale yellow solid (Scheme 4). ^1H NMR spectroscopy ($CDCl_3$, room temp.) was used to investigate the behaviour of **3** in solution. As was the case for complex **1a**, complex **3** exists in solution as a mixture of three isomers in a ratio of ca. 1.15:1.92:1 (as indicated by the three distinct sets of allylic proton signals), suggesting the presence of *dl* and *meso* isomers that arise from the amino stereocenters.[24]



Scheme 4. Synthesis of DAT3b **14** and the corresponding cationic Pd complex **3**.

Electropolymerization of (Diamino-oligothiophene)Pd Complexes

Monomers **2** and **3** were oxidatively polymerized by sweeping the working electrode for a total of 10 cycles between 0 and +1 V vs. SCE (for **2**) and 0 to +1.7 V vs. SCE (for **3**). These experiments were carried out in CH_2Cl_2 solutions containing 1 mM of monomer and 0.1 M $[nBu_4N]PF_6$ in sealed glass three-electrode electrochemical cells.

The cyclic voltammogram (CV) of a typical electrochemical polymerization of **1a** is shown in Figure 2a. The first scan is characterized by the onset of monomer oxidation at 0.92 V reaching a maximum at +1.08 V. This is followed by an associated weak reduction wave at +0.95 V on the return sweep. Repeated cycling gave rise to a second broad redox wave at lower potentials that is attributed to the electrodeposited polymer. The CV trace of **3** (Figure 2c) is nearly identical apart from the distinct shift in monomer oxidation to higher potential, a feature that may be a consequence of the connectivity between the Pd complex and the oligothiophene units (i.e., α-connectivity vs. β-connectivity). The UV/Vis spectrum of poly-**3** grown on an ITO on glass substrate (see Supporting Information) has a broad absorption band with a maximum at ca. 400 nm, 61 nm redshifted from that of monomer **3**.

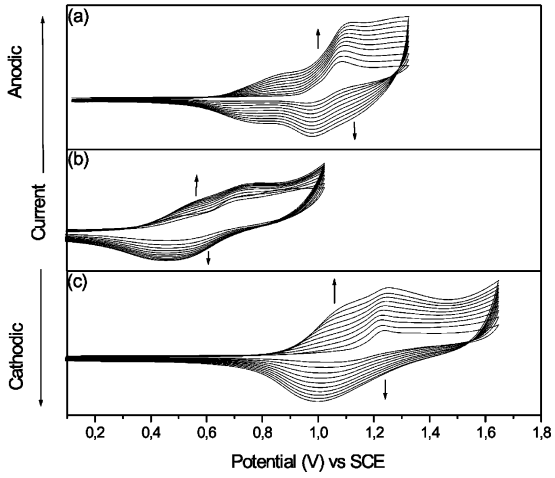


Figure 2. Synthesis of Pd-containing thiophene polymers by electrochemical deposition of (a) **1a**, (b) **2** and (c) **3** on graphite.

The CV trace of **2** (Figure 2b) exhibits similar features to that of **1a** and **3**; however, redox wave growth appeared to plateau after only a few cycles during which time the solution turned green. Upon further inspection, it became apparent that there was very little film growth on the surface of the Pt disc working electrode. Multiple attempts with different working electrodes (i.e., ITO on glass, Toray carbon paper) and higher monomer concentrations (i.e., 0.2 mM) yielded similar results, suggesting that either (1) oxidative coupling is sluggish on the CV time scale, (2) the polymer is soluble such that deposition does not occur, or (3) the polymer does not adhere to the working electrode. The UV/Vis absorption spectrum of poly-**2** grown on an ITO (see Supporting Information) has bands at 414 and 315 nm, the latter being consistent with those of monomer **2** (λ_{max} = 317 nm) and terthiophene (λ_{max} = 355 nm).[25]

Suzuki Cross-Coupling Catalyzed by Electrodeposited Pd-Containing Polymers

The catalytic performances of monomeric precursors **2** and **3** were investigated (loading 0.16 mol-%)[26] by selecting 4-bromobenzonitrile (**14a**) and $PhB(OH)_2$ (**15a**) as the

model reaction partners. The cross-coupling reactions were carried out in a toluene/MeOH (3:1) mixture, in the presence of K_2CO_3 (2 equiv.), whereas the kinetic profiles were obtained by gas chromatography by periodically withdrawing aliquots from the reaction mixtures for analysis. The corresponding curves are reported in Figure 3.

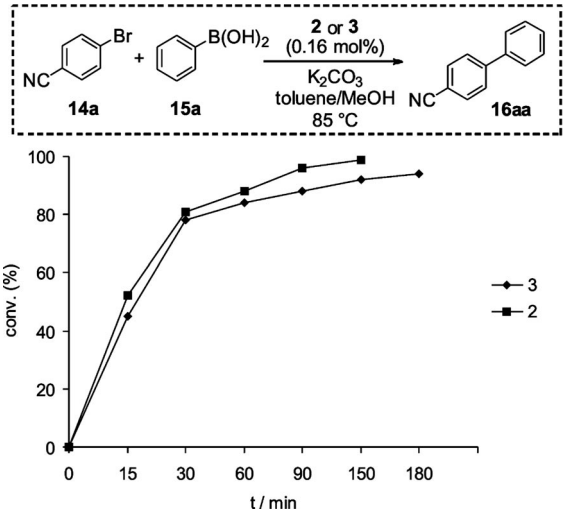


Figure 3. Reaction profiles of the model Suzuki cross-coupling catalyzed by **2** and **3**.

Pd complexes **2** and **3** were found to promote their respective cross-coupling reactions efficiently with comparable initial reaction rates; however, using complex **2** led to nearly complete conversion (> 98%) in a shorter reaction time (2.5 h vs. 7 h). This behaviour is consistent with previous experimental evidence on the stabilization/activation effect of ancillary "non-innocent"[27] thienyl ligands in Pd-catalyzed transformations.[18,28]

In fact, hemilabile interactions of the terthienyl group with the metal center cannot be ruled out during the course of the reaction. For heterogeneous catalytic studies, complexes **2** and **3** were electrochemically polymerized on carbon paper (Toray TGP-H-030) and ITO (indium tin oxide) on glass electrodes. In order to assess the reactivity of poly-**2**-graphite, poly-**3**-ITO and poly-**3**-graphite as heterogeneous catalysts for Suzuki cross-coupling reactions, the experiments were run in the presence of the modified electrode with no stirring to avoid breaking of the inert support (carbon paper).

The reaction profiles for the catalytic coupling reactions of 4-bromobenzonitrile and **15a** by using the heterogeneous catalysts are shown in Figure 4. The heterogeneous catalysts poly-**2** and poly-**3** require longer reaction times (13–24 h) relative to the corresponding homogeneous catalysts for comparable conversion. The longer reaction times for the heterogeneous catalyst may be due to either the heterogeneity of the system or to differences in the amount of catalyst present. As it is very difficult to accurately determine the amount of polymer on the electrode surface, it is not possible to directly compare the reactions with an identical catalyst loading (by weight).

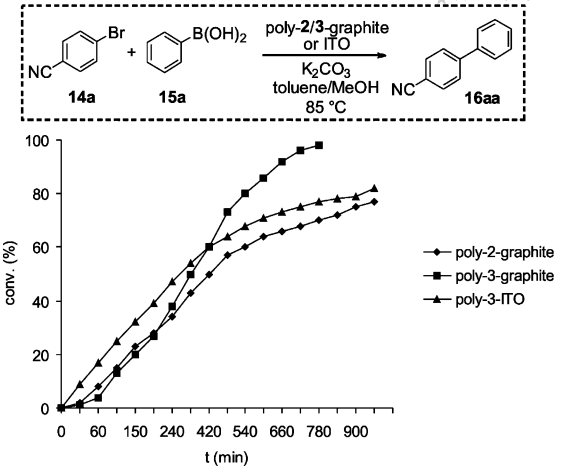


Figure 4. Reaction profiles of the model Suzuki cross-coupling catalyzed by poly-**2**-graphite and poly-**3**-graphite/ITO. Reaction-rate profiles were obtained by GC analysis of aliquots of the solution.

Secondly, the graphite-based catalysts showed an initial induction time (30–45 min) that is absent in the profile of poly-**3**-ITO catalyst. The lag phase observed for the reactions with poly-**2** or poly-**3** on graphite may be related to different rates of adsorption/diffusion of the reagents on the supports. It is possible that during the lag phase recorded for poly-**2**/**3**-graphite, the product is forming but retained on the porous support.

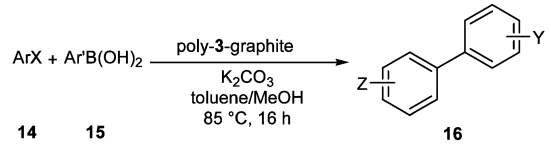
Thirdly, after the induction stage, poly-**3**-graphite promoted the Suzuki cross-coupling to a greater extent with respect to poly-**2**-graphite and poly-**3**-ITO, leading to quantitative coupling after 13 h. This trend is in contrast to the relative performance of the monomeric species **2** and **3** (Figure 3). A possible explanation could be related to the evidence that monomer **3** affords much better films than monomer **2**, hence there may be more catalytically active sites in the poly-**3** film resulting in higher conversion, which is what is observed in Figure 4.

The scope of the heterogeneous catalyst poly-**3**-graphite was assessed by screening a range of reagent combinations (Table 1). Tolerance towards many functional groups was observed (i.e. alkyl, aryl, ketones, cyano, and alkoxy groups). Excellent results in terms of conversion were obtained with a variety of functionalized bromo- and iodoarenes. For instance, 1,4-diiodobenzene (**14d**) underwent two carbon–carbon coupling processes in good conversion (Entry 8). Moreover, the sterically congested *o*-tolylboronic acid (**15d**) led to the corresponding adduct **16cd** in reasonable conversion (50%, Entry 7) as a racemic mixture.

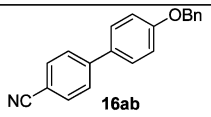
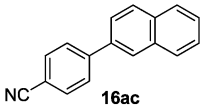
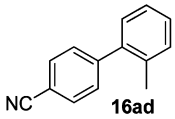
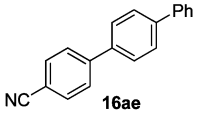
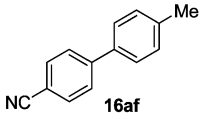
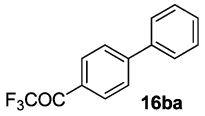
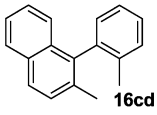
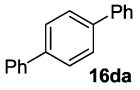
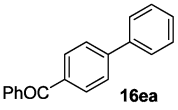
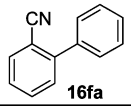
By using the same poly-**3**-graphite electrode in the model **14a**/**15a** cross-coupling reactions, six consecutive Suzuki reactions were carried out with conversions of 90–98% in each case, demonstrating the reusability of the catalytic species (Figure 5).

Several practical advantages of the use of these catalyst-modified surfaces can be highlighted. This type of engineered catalyst system allows for easy removal of the promoter after each run without any appreciable contami-

Table 1. Use of poly-**3**-graphite in the heterogeneous catalysis of the Suzuki reaction.



14b: Ar = *p*-CF_3CO-C_6H_4, X = Br **15b**: Ar' = *p*-BnO-C_6H_4
14c: Ar = α-Br-β-Me-naphth, X = Br **15c**: Ar' = β-naphth
14d: Ar = *p*-I-C_6H_4, X = I **15d**: Ar' = *o*-Me-C_6H_4
14e: Ar = *p*-PhCO-C_6H_4, X = Br **15e**: Ar' = *p*-Ph-C_6H_4
14f: Ar = *o*-NC-C_6H_4, X = Br **15f**: Ar' = *p*-Me-C_6H_4

Entry[a]	ArX	Ar'B(OH)$_2$	Product	Conv. **16** [%]
1	**14a**	**15b**	 **16ab**	92
2	**14a**	**15c**	 **16ac**	98
3	**14a**	**15d**	 **16ad**	98
4	**14a**	**15e**	 **16ae**	98
5	**14a**	**15f**	 **16af**	98
6	**14b**	**15a**	 **16ba**	89
7	**14c**	**15d**	 **16cd**	50
8	**14d**	**15a**	 **16da**	98
9	**14e**	**15a**	 **16ea**	85
10	**14f**	**15a**	 **16fa**	90

[a] All the reactions were carried out in reagent grade solvent at reflux for 16 h, unless otherwise specified. [b] Reaction time 48 h.

nation of the reaction product. Moreover, simple washing of the supported catalyst with MeOH while sonicating for 30 min at room temp., followed by drying under vacuum restores the initial catalytic performance.

In order to ascertain whether the catalysis is authentically heterogeneous, an aliquot (50 μL) from the Suzuki reaction (**14a**/**15a**) run to completion was subjected to the same reaction by the addition of a second batch of reagents. In this case, no appreciable formation of **16aa** was observed after 48 h. This demonstrates that the catalytic activity requires the presence of the polymeric matrix, and no appreciable activity results from leaching from the films. A control experiment with the unmodified electrode (80 °C, 40 h, trace conversion) shows that the support does not participate in the catalysis.

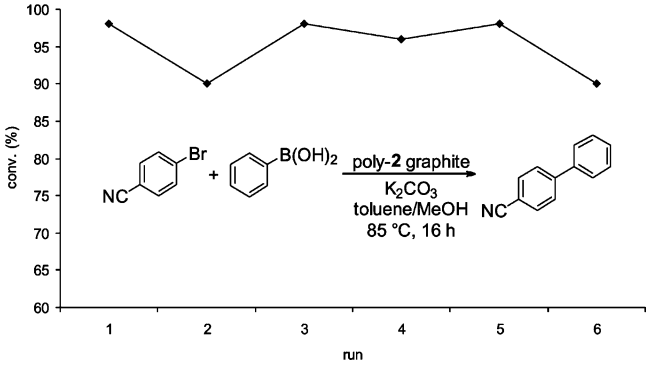


Figure 5. Recovery and reusability of poly-**3**-graphite in model Suzuki reaction (**14**/**15a**).

Conclusions

We have presented a new class of electrochemically modified electrodes with (diamino-oligothienyl)palladium complexes. The poly-**3**-graphite system proved to be efficient in promoting the Suzuki reaction with bromoarenes. Advantages of this approach include the ease of preparation of the catalyst films by using electrochemical deposition and the ease of recycling of the electrodes. This points to new opportunities for carbon–carbon forming processes by using heterogeneous, electrodeposited catalyst films.

Experimental Section

General Methods: All reagents were purchased from Aldrich Inc. and used without further purification. All reactions were carried out under anhydrous conditions unless otherwise specified. GC-MS data was recorded by EI ionization at 70 eV with a Hewlett–Packard 5971 instrument equipped with GC injection. LC electrospray ionization mass spectra were obtained with an Agilent Technologies MSD1100 single-quadrupole mass spectrometer. ^{1}H NMR spectra were recorded with either a Varian 200 (200 MHz) or Varian 300 (300 MHz) spectrometer. Chemical shifts are reported in ppm with respect to tetramethylsilane (TMS). Solution electronic absorption spectra were obtained with a Varian Cary 5000 UV/Vis/NIR spectrophotometer in dichloromethane (CH_2Cl_2), whereas solid-state spectra were acquired from polymeric films grown on an indium tin oxide (ITO) layer on glass. Fluorescence data was obtained with a Photon Technology International QuantaMaster fluorimeter. CH_2Cl_2 used for electrochemistry experiments was purified by passing the solvent through an activated alumina tower.

Electrochemistry: Cyclic voltammetry experiments were carried out with an Autolab potentiostat. The working electrode was either a

Pt disk, an indium tin oxide (ITO) thin film on glass, or Toray carbon paper (TGP-H-030). The counter electrode was a Pt mesh and the reference electrode a silver wire. An internal reference, decamethylferrocene, was added to correct the measured potentials with respect to saturated calomel electrode (SCE). [nBu$_4$N]PF$_6$ was used as a supporting electrolyte and was purified by triple recrystallization from ethanol and dried at 90 °C under vacuum for 3 d. All experiments were carried out in 1 mM CH_2Cl_2 solutions of monomer (0.1 M electrolyte) in sealed glass three-electrode electrochemical cells at a scan rate of 100 mV/s. All monomers were oxidatively polymerized by sweeping the working electrode between 0 V and the onset of current for a total of 10 cycles.

Synthesis of 8: In a 50 mL two-necked flask, the ammonium salt **4** (1 mmol, 150 mg) and 5′-*n*-hexyl-2,2′-bithienyl-5-carbaldehyde (1 mmol, 278 mg) were dissolved in EtOH/MeOH (1:1) (20 mL). The reaction mixture was stirred at room temperature for 24 h and the solvent removed under reduced pressure to leave the crude imine salt **6** as a brown solid. The solid was washed with Et_2O (3 × 10 mL), and collected by filtration. The crude product (chemical purity > 95% by HPLC and NMR) was used in the next step without further purification. ^{1}H NMR (200 MHz, DMSO): δ = 0.85 (br., 3 H, CH_3), 1.27 (br., 8 H, CH_2), 1.61–1.85 (m, 6 H, CH_2), 2.07 (br., 2 H, CH_2), 2.78 (br., 2 H, CH_2), 3.03 (br., 1 H, CH), 3.23 (br., 1 H, CH), 3.37 (br., 3 H, NH_3), 6.84 (br. s, 1 H, Ar-H), 7.23 (s, 2 H, Ar-H), 7.43 (br. s, 1 H, Ar-H), 8.47 (br., 4 H, Ar-H) ppm. ^{13}C NMR (50 MHz, DMSO): δ = 14.7 (CH_3), 22.8 (CH_2), 23.6 (CH_2), 24.3 (CH_2), 28.8 (CH_2), 29.6 (CH_2), 30.1 (CH_2), 31.7 (CH_2), 31.8 (CH_2), 33.5 (CH_2), 52.1 (CHN), 70.4 ($CHNH_3^+$), 124.0 (C-Ar), 125.7 (C-Ar), 126.6 (C-Ar), 133.8 (C-Ar), 134.4 (C-Ar), 140.8 (C-Ar), 140.9 (C-Ar), 146.8 (C-Ar), 156 (C=N) ppm. IR (neat): $\tilde{\nu}$ = 3423, 2088, 1643, 1444, 1091 cm^{-1}. ESI-MS: m/z = 373 [M – HCl]. Compound **6** (1 mmol, 410 mg) was dissolved in anhydrous CH_2Cl_2 (15 mL) followed by the addition of TEA (2 mmol, 278 μL), aldehyde **5b** (1 mmol, 204 mg) and $MgSO_4$ (3 mmol, 360 mg). The mixture was stirred at room temperature for 24 h. After removal of the CH_2Cl_2 under reduced pressure, the crude product was triturated with Et_2O and the liquid removed under reduced pressure. The crude product **7** was isolated as a yellow solid and used in the next step without further purification. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (br., 3 H, CH_3), 1.26–1.45 (m, 5 H, CH_2), 1.66 (br., 2 H, CH_2), 1.86 (br., 2 H, CH_2), 2.78 (t, J = 7.2 Hz, 2 H, CH_2), 3.10–3.15 (m, 2 H, CH-N), 6.67 (br., 2 H, Ar-H), 6.83–7.02 (m, 8 H, Ar-H), 8.18 (s, 1 H, N=CH), 8.24 (s, 1 H, N=CH) ppm; OH signal not observed. ESI-MS: m/z = 561 [M + H]. Compound **7** (1 mmol, 596 mg) was dissolved in MeOH (15 mL) followed by the dropwise addition of $NaBH_4$ (7 mmol, 266 mg) at 0 °C. The ice bath was then removed and the mixture stirred at room temperature overnight. Water (8 mL) was added to quench the reaction and the product extracted with CH_2Cl_2 (3 × 10 mL). Removal of any volatile compounds by evaporation afforded a crude product that was purified by flash chromatography with CH_2Cl_2/MeOH (99:1) as the eluent. Product **8** was isolated as a pale yellow solid (158 mg, 29% overall yield for three steps from **4**). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (br., 4 H, CH_3, CH), 1.31 (br., 8 H, CH_2), 1.65 (br., 2 H, CH_2), 1.80 (br., 2 H, CH_2), 2.19–2.38 (m, 2 H, CH_2), 2.49 (br., 2 H, CH_2), 2.75 (br., 3 H, CH_2, CH), 3.84 (d, J = 14.4 Hz, 2 H, 2 CHNH), 4.08 (d, J = 14.4 Hz, 2 H, 2 CHNH), 6.61–6.90 (m, 6 H, Ar-H), 7.27 (br., 4 H, Ar-H) ppm; OH and NH signals not observed. IR (neat): $\tilde{\nu}$ = 3410, 2926, 2853, 1693, 1667, 1608, 1453, 1270, 1202, 1173, 1132, 794 cm^{-1}. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.5 (CH_2), 24.7 (2 C, CH_2), 28.7 (2 C, CH_2), 30.1 (2 C, CH_2), 30.9 (CH_2), 31.5(CH_2), 45.1 (2 C, CHN), 59.9 (2 C, CH_2N), 116.0 (C-Ar), 116.4(C-Ar), 120.8 (C-Ar), 122.3(C-Ar), 123.0 (C-Ar), 124.6 (C-Ar), 125.4 (C-Ar), 125.9 (C-Ar), 126.9 (C-Ar), 134.8 (C-Ar), 134.9 (C-Ar), 136.9 (C-Ar), 137.1 (C-Ar), 141.4 (C-Ar), 141.5 (C-Ar), 142.4 (C-Ar), 144.1 (C-Ar), 144.9 (C-Ar) ppm. $C_{32}H_{40}N_2OS_3$ (564.23): calcd. C 68.04, H 7.14, N 4.96; found C 67.99, H 7.10, N 4.85.

Synthesis of 11: To a solution of **9**[23] (2.08 mmol, 578 mg) and TEA (4.16 mmol, 578 μL) in CH_2Cl_2, 6-bromohexanoyl chloride (2.28 mmol, 340 μL) was added dropwise at 0 °C. The mixture was stirred for 24 h. The solvent was removed under reduced pressure and the crude mixture purified by flash chromatography with cyclohexane/AcOEt (9:1) as the eluent. The product was isolated as a yellow oil (865 mg, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43–1.57 (m, 2 H, CH_2), 1.65–1.75 (m, 2 H, CH_2), 1.83–1.93 (m, 2 H, CH_2), 2.41 (t, J = 7.5 Hz, 2 H, CH_2CO), 3.40 (t, J = 6.9 Hz, 2 H, CH_2Br), 5.16 (s, 2 H, CH_2OCO), 7.03 (dd, J = 3.6, 5.1 Hz, 1 H, Ar-H), 7.10 (dd, J = 3.6, 5.1 Hz, 1 H, Ar-H), 7.19–7.21 (m, 3 H, Ar-H), 7.25 (dd, J = 1.2, 5.1 Hz, 1 H, Ar-H), 7.37 (dd, J = 1.2, 5.1 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9 (CH_2), 27.5 (CH_2), 32.2 (CH_2), 33.4 (CH_2), 33.9 (CH_2Br), 59.8 (CH_2O), 123.9 (C-Ar), 124.8 (C-Ar), 126.3 (C-Ar), 126.4 (C-Ar), 126.7 (C-Ar), 127.8 (C-Ar), 127.8 (C-Ar), 132.8 (C-Ar), 134.1 (C-Ar), 134.2 (C-Ar), 135.8 (C-Ar), 136.4 (C-Ar), 173.0 (CO) ppm. IR (neat): $\tilde{\nu}$ = 3104, 2938, 2863, 1731, 1461, 1415, 1371, 1349, 1246, 1159, 1078, 1047, 957, 882, 696, 637 cm^{-1}. ESI-MS: m/z = 478 [M + Na]. $C_{19}H_{19}BrO_2S_3$ (453.97): calcd. C 50.10, H 4.20; found C 50.01, H 4.15.

Synthesis of 12: To a solution of **11** (0.2 mmol, 93 mg) in dry THF/DMF (7.0:0.7 mL) stirred under nitrogen, cesium carbonate (0.41 mmol, 134 mg) and **8** (0.20 mmol, 116 mg) were added. The mixture was heated to reflux for 24 h. The reaction mixture was cooled to room temperature and then quenched with water (3 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). Evaporation of the volatiles afforded a crude product that was purified by flash chromatography with CH_2Cl_2/MeOH (98:2 → 95:5). The product was isolated as a yellow oil (158 mg, 75% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 (t, J = 5.8 Hz, 3 H CH_3), 1.32 (br., 8 H, CH_2), 1.52–1.84 (m, 10 H, CH_2), 2.18 (br., 4 H), 2.32–2.36 (m, 2 H, CHNH), 2.44 (t, J = 7.4 Hz, 2 H, CH_2CO), 2.76 (t, J = 7.6 Hz, 2 H, NH), 3.87 (dd, J = 5.6, 14.2 Hz, 2 H, 2 CHNH), 3.94 (t, J = 6.2 Hz, 2 H, CH_2O), 4.09 (dd, J = 5.6, 14.2 Hz, 2 H, 2 CHNH), 5.17 (s, 2 H, CH_2OCO), 6.61 (dd, J = 3.6 Hz, 1 H, Ar-H), 6.82 (dd, J = 3.6, 12.4 Hz, 4 H, Ar-H), 6.90 (t, J = 3.4 Hz, 2 H, Ar-H), 7.00–7.03 (m, 2 H, Ar-H), 7.09 (dd, J = 3.6, 3.8 Hz, 1 H, Ar-H), 7.17–7.23 (m, 4 H, Ar-H), 7.35 (d, J = 4.8 Hz, 1 H, Ar-H), 7.46 (d, J = 8.8 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (CH_3), 22.5 (CH_2), 24.7 (CH_2), 24.8 (CH_2), 25.6 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 29.7 (CH_2), 30.1 (CH_2), 31.1 (CH_2), 31.2 (CH_2), 31.5 (CH_2), 34.1 (CH_2), 45.4 (CH_2), 59.9 CHN, 2 C, (), 60.1 (CH_2N), 60.2 (CH_2N), 67.6 (CH_2O), 77.2 (CH_2O), 114.7 (2 C, C-Ar), 121.3 (C-Ar), 122.3 (C-Ar), 122.9 (C-Ar), 124.0 (C-Ar), 124.6 (C-Ar), 124.8 (C-Ar), 125.2 (C-Ar), 125.7 (C-Ar), 126.3 (C-Ar), 126.5 (C-Ar), 126.7 (C-Ar), 126.8 (2 C, C-Ar), 127.3 (C-Ar), 127.8 (C-Ar), 127.9 (C-Ar), 132.9 (C-Ar), 134.1 (C-Ar), 134.3 (C-Ar), 135.0 (C-Ar), 135.9 (C-Ar), 136.5 (C-Ar), 136.9 (C-Ar), 142.6 (C-Ar), 142.9 (C-Ar), 143.3 (C-Ar), 144.9 (C-Ar), 158.4 (C-Ar), 173.3 (CO) ppm. IR (neat): $\tilde{\nu}$ = 3423, 2924, 2853, 1727, 1640, 1547, 1512, 1461, 1377, 1261, 1117, 1073, 794, 697 cm^{-1}. ESI-MS: m/z = 940 [M + 1]. $C_{50}H_{56}N_2O_3S_6$ (924.26): calcd. C 64.90, H 6.10, N 3.03; found C 64.85, H 6.01, N 2.95.

Synthesis of [12-(Pdallyl)PF$_6$] Complex (2): In a Schlenk flask, flame-dried and flushed with nitrogen, **12** (0.03 mmol, 28 mg) was

dissolved in THF/CH_2Cl_2 (1:1) (3.6 mL). $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.015 mmol, 5.5 mg) was added and the mixture stirred at room temperature for 4 h. NH_4PF_6 (0.03 mmol, 4.9 mg) was added and the mixture stirred in the dark overnight. The mixture was then filtered and the solvent removed under reduced pressure. The product was dried under vacuum. The residue was washed with Et_2O (5 mL) and the desired Pd complex recovered as an air-stable dark yellow solid by filtration (40 mg, yield 98%). ^1H NMR (300 MHz, $CDCl_3$, fluxional, mixture of three isomers): diagnostic signals: (a) δ = 5.78–5.58 (m, 1 H, allyl-CH), 3.74 (br., 2 H, allyl-CH), 3.40–3.35 (m, 1 H, allyl-CH), 3.04 (d, J = 12.0 Hz, 1 H, allyl-CH) ppm; (b) 5.48–5.38 (m, 1 H, allyl-CH), 4.12 (br., 2 H, allyl-CH), 3.04 (d, J = 12.0 Hz, 1 H, allyl-CH) ppm; (c) 5.17 (br., 1 H, allyl-CH), 2.91 (d, J = 13.2 Hz, 1 H, allyl-CH), 2.79 (br., 2 H, allyl-CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): diagnostic signals: δ = 14.0 (CH_3), 15.2 (CH_2), 22.5 (CH_2), 23.7 (CH_2), 24.6 (CH_2), 25.6 (CH_2), 26.8 (CH_2), 28.8 (CH_2), 29.6 (CH_2), 30.1 (CH_2), 31.5 (CH_2), 34.1 (CH_2), 38.7 (CH_2), 59.9 (2 C, CHN), 65.8 (2 C, CH_2N), 67.7 (CH_2O), 77.1 (CH_2O), 114.9 (C-Ar), 124.0 (C-Ar), 124.8 (C-Ar), 126.3 (C-Ar), 126.5 (C-Ar), 126.7 (C-Ar), 127.8 (C-Ar), 132.9 (C-Ar), 135.9 (C-Ar), 136.5 (C-Ar), 173.3 (CO). UV/Vis (CH_2Cl_2): λ_{max} (ε) = 317 nm (35000 $L\,mol^{-1}\,cm^{-1}$). IR (neat): $\tilde{\nu}$ = 2932, 2857, 1729, 1608, 1511, 1432, 1251, 1179, 1166, 1024, 829, 699, 559 cm^{-1}. $C_{54}H_{63}F_6N_2O_3PPdS_6$ (1230.18): calcd. C 52.65, H 5.15, N 2.27; found C 52.30, H 5.25, N 2.21.

Synthesis of *N*,*N*′-Bis[(2,2′:5′,2′′-terthiophen-3′-yl)methyl]cyclohexane-1,2-diamine (14): In a 25 mL two-necked flask, 2,2′:5′,2′′-terthiophene-3′-carbaldehyde (**13**) (0.47 mmol, 130 mg) and (1*R*,2*R*)-diaminocyclohexane (DACH, 0.23 mmol, 27 mg) were dissolved in dry CH_2Cl_2 (8 mL) under N_2. Magnesium sulfate ($MgSO_4$, 1.18 mmol, 142 mg) was added and the mixture stirred at room temperature for 48 h. The crude reaction mixture was filtered and the solvent evaporated under reduced pressure to afford 116 mg of the intermediate imine (DIT3b) as a yellow oil (purity > 90% by ^1H NMR). The crude product was used without further purification. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.38–1.65 (m, 2 H, CH_2), 1.67–1.75 (m, 2 H, CH_2), 1.88 (br., 4 H, CH_2), 3.27–3.41 (m, 2 H, CH=N), 6.90 (q, J = 3.0 Hz, 4 H, Ar-H), 7.02 (dd, J = 3.6, 3.8 Hz, 2 H, Ar-H), 7.17–7.27 (m, 6 H, Ar-H), 7.58 (s, 2 H, Ar-H), 8.30 (s, 2 H, CH=N) ppm. IR (neat): $\tilde{\nu}$ = 3404, 3104, 3073, 2927, 2855, 1711, 1671, 1629, 1446, 1434, 1383, 1281, 1245, 1183, 1170, 1080, 1045, 987, 833, 731, 695 cm^{-1}. To a solution of crude DIT3b (0.18 mmol, 116 mg) in MeOH (10 mL), sodium borohydride ($NaBH_4$, 1.26 mmol, 48 mg) was added at 0 °C. The ice bath was then removed and the reaction mixture stirred at room temperature overnight. Water was added to quench the reaction and the methanol removed under reduced pressure. The aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL), dried with sodium sulfate (Na_2SO_4) and concentrated under vacuum. The crude product was purified by chromatography on silica using a CH_2Cl_2/MeOH (95:5) as the eluent. Product **14** was isolated as a yellow solid (119 mg, 63% yield based on DACH). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.30–1.37 (m, 2 H, CH_2), 1.83–1.93 (m, 5 H, CH_2, CH), 2.26–2.42 (m, 3 H, CH_2, CH), 3.98 (dd, J = 13.2, 3.8 Hz, 4 H, CH_2NH), 7.07–7.13 (m, 4 H, Ar-H), 7.21–7.28 (m, 7 H, Ar-H), 7.34–7.39 (m, 3 H, Ar-H) ppm; NH signal not observed. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9 (2 C, CH_2), 31.4 (2 C, CH_2), 44.5 (2 C, CHN), 60.9 (2 C, CH_2N), 123.6 (2 C, C-Ar), 124.4 (2 C, C-Ar), 125.7 (2 C, C-Ar), 126.2 (2 C, C-Ar), 126.4 (2 C, C-Ar), 127.5 (2 C, C-Ar), 127.7 (2 C, C-Ar), 131.2 (2 C, C-Ar), 135.0 (2 C, C-Ar), 135.4 (2 C, C-Ar), 137.0 (2 C, C-Ar), 138.2 (2 C, C-Ar) ppm. IR (neat): $\tilde{\nu}$ = 3424, 2927, 2853, 1726, 1641, 1502, 1448, 1261, 1176, 1117, 1044, 907, 819, 729, 692 cm^{-1}. ESI-MS: m/z = 635 [M + 1]. $C_{32}H_{30}N_2S_6$ (634.07): calcd. C 60.53, H 4.76, N 4.41; found C 60.45, H 4.68, N 4.35.

Synthesis of [14-(Pdallyl)BF_4] (3): In a flame-dried Schlenk tube flushed with N_2, **14** (0.08 mmol, 50 mg) was dissolved in THF/CH_2Cl_2 (6:1) (7 mL). $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.04 mmol, 14 mg) was added and the mixture stirred at room temperature for 4 h. Silver tetrafluoroborate ($AgBF_4$, 0.08 mmol, 15.6 mg) was added to the reaction mixture and stirred in the absence of light overnight. The mixture was filtered and the solvent removed under reduced pressure. The resulting product was dried under vacuum. The residue was washed with Et_2O (5 mL) and the desired Pd complex isolated as a yellow solid by filtration (61 mg, yield 95%). ^1H NMR (300 MHz, $CDCl_3$, fluxional, mixture of three isomers): diagnostic signals: (a) δ = 5.60–5.70 (m, 1 H, allyl-CH), 4.24 (d, J = 6.3 Hz, 2 H, allyl-CH), 3.21 (d, J = 11.7 Hz, 2 H, allyl-CH) ppm; (b) 5.12–5.35 (m, 1 H, allyl-CH), 3.67 (d, J = 9.0 1 H, allyl-CH), 3.52 (br., 1 H, allyl-CH); c) 4.80–4.95 (m, 1 H, allyl-CH), 3.30 (d, J = 6.9 Hz, 1 H, allyl-CH), 3.02 (d, J = 13.6 Hz, 1 H, allyl-CH), 2.86 (d, J = 6.9 Hz, 1 H, allyl-CH), 2.60 (d, J = 13.6 Hz, 1 H, allyl-CH) ppm. ESI-MS: m/z = 783 $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{14})]^+$. $C_{35}H_{35}BF_4N_2PdS_6$ (868.02): calcd. C 48.36, H 4.06, N 3.22; found C 48.28, H 4.00, N 3.45.

Supporting Information (see footnote on the first page of this article): Typical experimental procedure for the Suzuki reaction, analytical characterization of biaryls **16** [Table 1 (SI)] and photophysical characterization of **2**/poly-**2** and **3**/poly-**3** [Figures 1 and 2 (SI)].

Acknowledgments

This work was supported by M. I. U. R. (Rome), the University of Bologna and the Natural Sciences and Engineering Research Council of Canada. We thank also Pasquale Olivelli (University of Bologna) for part of the Experimental Section. Thanks also to Fondazione del Monte di Bologna e Ravenna for financial support.

[1] a) *Report of the United Nations Conference on Environment and Development*, Rio de Janeiro, **1992**, http://www.un.org/esa/sustdev; b) P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, University Press, Oxford, **1998**, p. 30; c) P. T. Anastas; L. G. Heine, T. C. Williamson, *Green Chemical Syntheses and Processes*, American Chemical Society, Washington, **2000**; d) N. Winterton, *Green Chem.* **2001**, *3*, G73; e) A. D. Curzons, D. J. C. Constable, D. N. Mortimer, V. L. Cunningham, *Green Chem.* **2001**, *3*, 1–6.

[2] a) M. T. Reetza, J. G. de Vriesb, *Chem. Commun.* **2004**, 1559–1563; b) J.-P. Corbet, G. Mignani, *Chem. Rev.* **2006**, *106*, 2651–2710.

[3] a) J. Tsuji, in *Palladium Reagents and Catalysts*, *New Perspectives for the 21th Century*, Wiley, Chichester, England, **2004**; b) *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, New York, **2004**.

[4] M. Beller, *Transition Metals for Organic Synthesis, Building Blocks and Fine Chemicals*, 2nd ed., Wiley-VCH, Weinheim, **2004**.

[5] a) B. M. Bhanage, M. Arai, *Catal. Rev. Sci. Eng.* **2001**, *43*, 315–344; b) C. E. Garret, K. Prasad, *Adv. Synth. Catal.* **2004**, *346*, 899–900.

[6] a) H.-U. Blaser, A. Indolese, S. Schnyder, H. Steiner, M. Studer, *J. Mol. Catal. A* **2001**, *173*, 3–18; b) R. A. Sheldon, H. van Bekkum, in *Fine Chemicals through Heterogeneous Catalysis*, Wiley-VCH, Weinheim, Germany, **2001**; c) A. Zapf, M. Beller, *Top. Catal.* **2002**, *19*, 101–108; d) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133–173.

[7] M. Seki, *Synthesis* **2006**, 2975–2992.

[8] K. Köhler, M. Wagner, L. Djakovitch, *Catal. Today* **2001**, *66*, 105–114, and references cited therein.
[9] a) L. Djakovitch, K. Koehler, *J. Am. Chem. Soc.* **2001**, *123*, 5990–5999; b) A. Biffis, M. Zecca, M. Basato, *Eur. J. Inorg. Chem.* **2001**, 1131–1133.
[10] a) A. Biffis, M. Zecca, M. Basato, *J. Mol. Catal. A* **2001**, *173*, 249–274; b) B. P. Chauhan, J. S. Rathore, M. Chauhan, A. Krawicz, *J. Am. Chem. Soc.* **2003**, *125*, 2876–2877.
[11] a) S. Kobayashi, R. Akiyama, *Chem. Commun.* **2003**, 449–460; b) C. Ramarao, S. V. Ley, S. C. Smith, I. M. Shirley, N. DeAlmeida, *Chem. Commun.* **2002**, 1132–1133; c) S. V. Ley, C. Ramarao, R. S. Gordon, A. B. Holmes, A. J. Morrison, I. F. McConvey, I. M. Shirley, S. C. Smith, M. D. Smith, *Chem. Commun.* **2002**, 1134–1135; d) H. Hagio, M. Sugiura, S. Kobayashi, *Org. Lett.* **2006**, *8*, 375–378, and references cited therein; e) D. S. Bohle, L. E. McQuade, I. Perepichka, L. Zhang, *J. Org. Chem.* **2007**, *72*, 3625–3631; f) J. Toubiana, M. Chidambaram, A. Santo, Y. Sasson, *Adv. Synth. Catal.* **2008**, *350*, 1230–1234.
[12] For representative examples, see: a) J. H. Clark, D. J. Macquarrie, E. B. Mubofu, *Green Chem.* **2000**, *2*, 53–55; b) E. B. Mubofu, J. H. Clark, D. J. Macquarrie, *Green Chem.* **2001**, *3*, 23–25; c) S. Paul, J. H. Clark, *Green Chem.* **2003**, *5*, 635–638; d) M. Bandini, R. Luque, V. Budarin, D. J. Macquarrie, *Tetrahedron* **2005**, *61*, 9860–9868; e) N. Erathodiyil, S. Ooi, A. M. Scayad, Y. Han, S. S. Lee, J. Y. Ying, *Chem. Eur. J.* **2008**, *14*, 3118–3125.
[13] a) R. Akiyama, S. Kobayashi, *Angew. Chem.* **2002**, *114*, 2714–2716; *Angew. Chem. Int. Ed.* **2002**, *41*, 2602–2604; b) R. Akiyama, S. Kobayashi, *J. Am. Chem. Soc.* **2003**, *125*, 3412–3413; c) R. Nishio, M. Sugiura, S. Kobayashi, *Chem. Asian J.* **2007**, *2*, 983–995.
[14] a) M. O. Wolf, *Adv. Mater.* **2001**, *13*, 545–553; b) B. J. Holliday, T. M. Swager, *Chem. Commun.* **2005**, 23–36.
[15] A. Llobet, E. Masllorens, M. Rodríguez, A. Roglans, J. Benet-Buchholz, *Eur. J. Inorg. Chem.* **2004**, 1601–1604.
[16] A. Zulauf, M. Mellah, R. Guillot, E. Schulz, *Eur. J. Org. Chem.* **2008**, 2118–2129.
[17] J. Papillon, E. Schulz, S. Gélinas, J. Lessard, M. Lemaire, *Synth. Met.* **1998**, *96*, 155–160.
[18] V. G. Albano, M. Bandini, C. Moorlag, F. Piccinelli, A. Pietrangelo, S. Tommasi, A. Umani-Ronchi, M. O. Wolf, *Organometallics* **2007**, *26*, 4373–4375.
[19] For some examples of (oligothienyl)metal complexes in catalysis, see: a) V. G. Albano, M. Bandini, M. Melucci, M. Monari, F. Piccinelli, S. Tommasi, A. Umani-Ronchi, *Adv. Synth. Catal.* **2005**, *347*, 1507–1512; b) V. G. Albano, M. Bandini, G. Barbarella, M. Melucci, M. Monari, F. Piccinelli, S. Tommasi, A. Umani-Ronchi, *Chem. Eur. J.* **2006**, *12*, 667–675; c) F. Colombo, R. Annunziata, M. Benaglia, *Tetrahedron Lett.* **2007**, *48*, 2687–2690; d) M. Bandini, F. Piccinelli, S. Tommasi, A. Umani-Ronchi, C. Ventrici, *Chem. Commun.* **2007**, 616–618.
[20] a) A. Suzuki, *Chem. Commun.* **2005**, 4759–4763; b) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009–3066; c) K. Sonogashira, in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.:F. Diederich, P. J. Stang), Wiley-VCH, New York, **1998**.
[21] a) E. J. Campbell, S. T. Nguyen, *Tetrahedron Lett.* **2001**, *42*, 1221–1225; b) M. Bandini, M. Benaglia, T. Quinto, S. Tommasi, A. Umani-Ronchi, *Adv. Synth. Catal.* **2006**, *348*, 1521–1527.
[22] P. Frère, J.-M. Raimundo, P. Blanchard, J. Delaunay, P. Richomme, J.-L. Sauvajol, J. Orduna, J. Garin, J. Roncali, *J. Org. Chem.* **2003**, *68*, 7254–7265.
[23] G. E. Collis, A. K. Burrell, E. J. Blandford, D. L. Officer, *Tetrahedron* **2007**, *63*, 11141–11152.
[24] E. Rafii, B. Dassonneville, A. Heumann, *Chem. Commun.* **2007**, 583–585.
[25] C. V. Pham, A. Burkhardt, R. Shabana, D. D. Cunningham, H. B. Mark, H. Zimmer, *Phosphorus Sulfur Silicon Relat. Elem.* **1989**, *46*, 153–168.
[26] For a representative example of a ligand-free Pd-catalyzed Suzuki reaction with aryl halides at low catalyst loading, see: A. Alimardanov, L. S. de Vondervoort, A. H. M. de Vries, J. G. de Vries, *Adv. Synth. Catal.* **2004**, *346*, 1812–1817.
[27] For a recent perspective article on the role of non-innocent ligands in Pd-catalyzed cross-coupling reactions, see: I. J. S. Fairlamb, *Org. Biomol. Chem.* **2008**, *6*, 3645–3656, and references cited therein.
[28] M. Bandini, M. Melucci, F. Piccinelli, R. Sinisi, S. Tommasi, A. Umani-Ronchi, *Chem. Commun.* **2007**, 4519–4521.

Received: March 21, 2009
Published Online: June 16, 2009

