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Novel Cyclopalladated Imino-thiophenes: Synthesis and Reactivity Toward Alkynes and Carbon Monoxide

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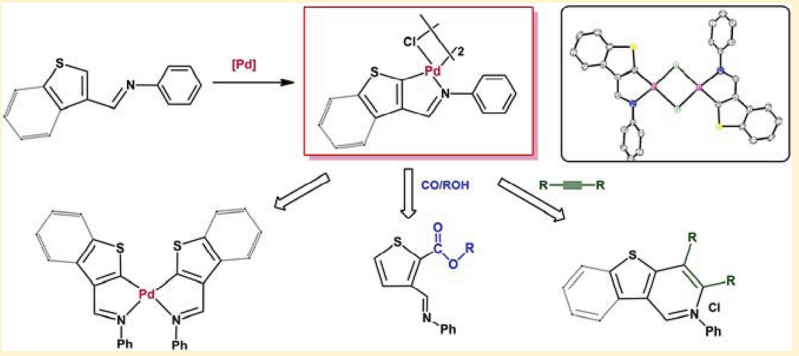
Supporting Information

ABSTRACT:



ortho-palladated complexes based on thiophene and benzothiophene ligands **1a** and **1b** have been synthesized by direct C−H activation under mild conditions. These species were fully characterized, including single-crystal X-ray diffraction analysis. The reactions of these novel complexes with internal alkynes afforded a variety of thieno[3,2-*c*]pyridinium salts substituted at the 6- and 7-positions. The thiophene-based complex **2a** also reacts with carbon monoxide, in the presence of different alcohols, forming the corresponding esters by tandem alkoxycarbonylations. This latter reaction can be exploited for the unexpected, but straightforward, formation of the monomeric bis-cyclometallated complexes **6a** and **6b** from **2a** or **2b**, whose syntheses do not require the employment of transmetallating agents. The structures of these monomeric palladacycles were also fully elucidated by means of X-ray diffraction studies.

INTRODUCTION

Substituted thiophenes and benzothiophenes are relevant molecular targets given their occurrence in a wide variety of natural products and synthetic compounds with biological and pharmaceutical activity.[1] These species also attract the interest of synthetic chemists because they are valuable building blocks for the elaboration of organic materials,[2] for example, novel conducting polymers or devices with nonlinear optical properties. In addition, a considerable variety of molecules containing the thiophene or benzothiophene ring system are exploited by the chemical industry as fragrances or insecticides,[3] among other applications. Therefore, methods for facile and versatile functionalization of this class of heterocycles would be of great interest. Between the transition metal-mediated transformations, cyclopalladation represents one of the most appealing options to achieve this goal, because this synthetic strategy has been proved to be an extremely useful and efficient approach for the functionalization of organic substrates,[4]allowing for the selective incorporation of a large variety of functional groups in a plethora of organic molecules. However, examples of the use of such a process for the functionalization of heterocycles[5] are scarce in comparison with the vast number of examples dealing with the cyclopalladation of arenes. In particular, to the best of our knowledge, the reactivity of thiophene-based palladacycles toward organic molecules has never been described, despite that there seem to be a few examples of the synthesis and isolation of this kind of complexes.[6] Therefore, we have endeavored to explore the synthesis and reactivity of this kind of complex and report some of our results herein. Namely, we describe the synthesis and characterization of novel thiophene- and benzothiophene-based palladacycles, which were generated by direct C−H activation under mild conditions employing imine units as directing groups. Moreover, we developed a new and highly efficient method, based on alkyne insertion, for synthesizing thienopyridinium derivatives, species which have attracted tremendous attention in the last years.[7] Additionally, we have studied the reactivity of these novel palladium complexes toward

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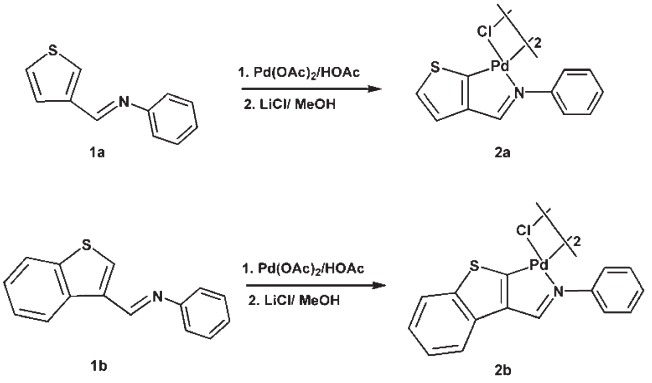
Scheme 1. Synthesis of Thiophene-Based Palladacycles 2a and 2b



carbon monoxide in alcoholic solvents. These reactions allow for the production of valuable ester-substituted thiophene derivatives and offer an unexpected, but straightforward, entry to monomeric bis-cyclometallated complexes, which, in contrast to all the previous reported syntheses, does not require the employment of strong bases or transmetallating agents.[8]

RESULTS AND DISCUSSION

Synthesis and Characterization of ortho-Palladated Complexes 2a−b. The reaction of Schiff bases **1a** and **1b** with 1 equiv of $Pd(OAc)_2$ at room temperature in acetic acid, followed by treatment with lithium chloride in MeOH, afforded the corresponding chloro-bridged complexes **2a** and **2b** in good yields (see Scheme 1). Both ortho-metallated compounds were fully characterized by means of NMR spectroscopy, mass spectrometry, and microanalysis.

The structure of complexes **2a** and **2b** was initially inferred from the NMR data. The ^{1}H NMR spectra in acetone-d_6 solutions of **2a** and **2b** show clearly that one of the thiophene ring protons is lost, and in the $^{13}C\{^1H\}$ NMR, there is a significantly deshielded signal (170.4 ppm for **2a** and 180.3 ppm for **2b**), which is indicative of a carbon σ-bound to the metallic center.[6] Both facts strongly suggest that palladacycle-type structures arising from the activation of a C−H bond of the thiophene ring have been generated. For the compound containing the benzothiophene moiety, the NMR spectroscopic data are only compatible with the formation of the species **2b** depicted in Scheme 1. However, the C−H activation process of the ligand **1a** could proceed, in principle, over the two nonequivalent C−H bonds ortho to the imine (α and β to the sulfur atom), affording two different metallacycles. The NMR data of **2a** shows that it is formed as a single isomer, and the regiochemistry displayed in Scheme 1 for this palladacycle is assigned on the basis of the coupling constant for the remaining two thienyl protons. The observed value for the coupling constant $^3J_{HH}$ (5.2 Hz) indicates that the position 2 (α to the sulfur atom) has been selectively activated, since coupling constants in the range of 4.9−5.8 Hz have been systematically reported for thienyl adjacent protons,[9] and lower values (3.2−3.7 Hz) are expected for the $^4J_{HH}$ coupling of two α-thienyl protons.[9] The structure of **2a** was also studied by X-ray diffraction methods in the solid state, although they provided data of modest quality not amenable for a discussion of the distances and angles. An ORTEP drawing of the structure of **2a** is shown in Figure S1 (see the Supporting Information). The observed regioselectivity is predictable, since it is well known that the reactivity of the α-position, adjacent to the heteroatom, is considerable higher than the reactivity of the β-position.[10]

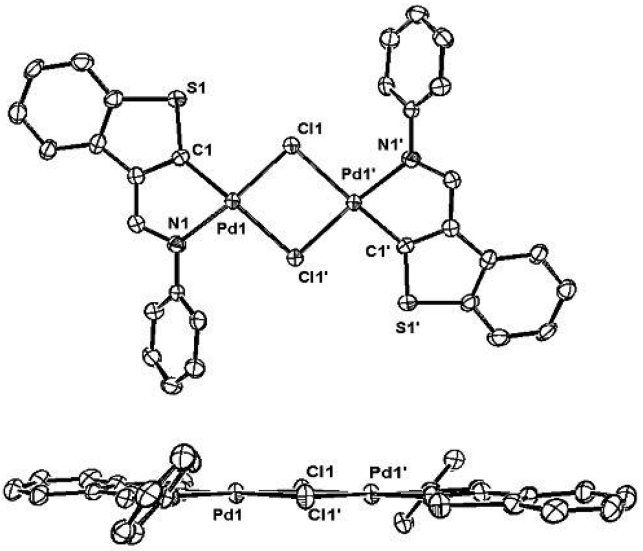


Figure 1. Top and side views of the complex **2b** showing a partial atom-labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms have been removed for clarity. Selected bond distances (Å) and angles (deg) for **2b**: Pd1−C1 1.944(4), Pd1−N1 2.052(4), Pd1−Cl1 2.326(2), Pd1−Cl1′ 2.434(1), C1−Pd1−N1 80.2(2), C1−Pd1−Cl1 94.2(1), N1−Pd1−Cl1′ 97.4(1), Cl1−Pd1−Cl1′ 88.15(4).

The ortho-palladated complex containing the benzothiophene moiety (**2b**) was characterized in the solid state by means of X-ray diffraction studies. The crystal structure of the binuclear Pd complex **2b** is shown in Figure 1. As usually observed for dimeric chloro-bridged palladacycles,[4] each Pd center is coordinated to the chloride bridge units, and to the respective N and C atoms of the ortho-metallated ligand. The structure is almost planar (Figure 1), the two metallic centers having a slightly distorted square-planar geometry and a mutual transoid arrangement of the two cyclopalladated moieties.

Reaction with Alkynes. Synthesis of Thienopyridinium Derivatives. Among the heterocyclic systems containing thienyl fragments, thienopyridines occupy unquestionably a special place.[7] The considerable attention that they have received recently, mainly motivated by their exceptionally broad spectrum of biological activities,[7a,b] is clearly reflected in the huge number of publications that have appeared recently, including patents.[7a] Nevertheless, most of the reported synthetic approaches for the production of these derivatives require complicated multistep organic syntheses,[7,11] which usually implicate low yields and often suffer from low functional group tolerance. Therefore, the search for alternative routes with improved yields and higher versatility is a field of intense research nowadays. Considering that many different types of palladacycles undergo alkyne insertion,[13] we envisioned that derivatives containing the thieno[3,2-*c*]pyridine core, which remains as one of the isomeric structures more challenging to synthesize,[7,11,12] could be straightforwardly produced by alkyne insertion into complexes **2a** and **2b**, followed by an intramolecular C−N bond coupling.

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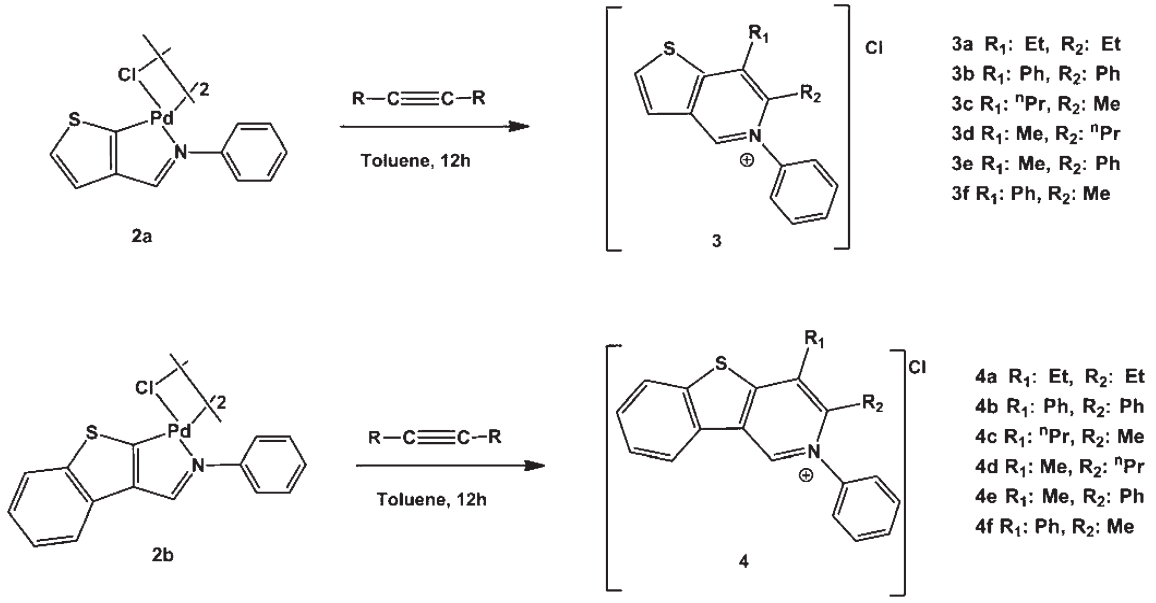
Scheme 2. Synthesis of Thienopyridinium Derivatives by Alkyne Insertion



We initially directed our efforts toward the insertion of 3-hexyne. The alkyne was reacted with the cyclometallated complex **2a** in different solvents, temperatures, and conditions. We found that keeping the reaction overnight at 80 °C in toluene with an excess of the acetylene afforded, after removal of the palladium black generated and purification over neutral alumina, the respective *N*-phenylated thienopyridinium **3a** as a chloride salt (see Scheme 2) in good yield (71%). The derivative **3a** was characterized by NMR spectroscopy, mass spectrometry, and microanalysis. The most significant signal in the ^{1}H NMR is a singlet at 10.03 ppm, assigned to the initially iminic proton and now belonging to the pyridinium ring. In both ^{1}H NMR and ^{13}C NMR spectra are observed the presence of two nonequivalent ethyl groups, indicating that a single alkyne insertion has taken place, irrespective of the amount of alkyne employed. With a small increase of the reaction temperature (112 °C), the thiophene-based palladacycle **2a** also reacts straightforwardly with diphenylacetylene, affording, after the workup, the derivative **3b** in good yield. The complex **2a** was also reacted with unsymmetrical acetylenes, namely, the reaction with 2-hexyne in the same conditions described for the synthesis of **3a** was found to produce a mixture of the corresponding isomers **3c**/**3d** in a 50:50 ratio; these species were isolated and characterized without separation. In the same way, the reaction with 1-phenylpropyne produced a mixture of the two expected regioisomers (**3e**/**3f**) in a molar ratio of 60:40 (the identity of the major/minor compound was not elucidated). In light of these results, we can conclude that the insertion process does not display any steric or electronic discrimination between the different alkyl chains tested (propyl vs methyl) and shows reduced discrimination between phenyl and methyl groups. The reaction with 1-hexyne or phenylacetylene did not produce the desired product, as usually encountered when dealing with terminal alkynes.[13] Attempts to perform the synthesis of the respective thienopyridinium derivatives employing alkynes substituted with ester groups, for instance, DMAD (DMAD = dimethyl acetylenedicarboxylate) or ethyl 3-phenyl propynoate, were also unsuccessful. In this latter case, formation of palladium black does not take place, and complicated mixtures of compounds were formed, probably due to multiple alkyne insertions.

The cyclopalladated complex **2b** also reacts cleanly with the same alkynes described for **2a** under identical reaction conditions, affording in good yields (range of 64−73%) annelated tricyclic systems based on thieno[3,2-*c*]pyridinium salts. Accordingly with the results observed for **2a**, the reaction with 2-hexyne and 1-phenylpropyne yields mixtures of isomers (molar ratios: **4c**/**4d**, 50/50; **4e**/**4f**, 65/35). The formation of the species **4a**−**4f** in such a simple way is remarkable, due to the fact that the synthesis and properties of polycyclic annelated thienopyridines have been particularly extensively studied in the last years, and there is an urgent demand for the development of synthetic strategies amenable for generalization.[7b] It is also noteworthy that, in the syntheses of **3a**−**3f** and **4a**−**4f**, only a single alkyne insertion was observed instead of several successive insertions, as it is typically found with palladacycles and usually causes the formation of undesired carbocyclic systems instead of the targeted heterocyclic products.[13] Likewise observed for complex **2a**, terminal and ester-substituted alkynes do not react satisfactorily. The finding that alkynes containing electron-withdrawing groups do not form the targeted heterocycle could be an indication that the mechanism for the heterocycle liberation probably involves a C−N coupling by attack of the vinylic carbon to the iminic nitrogen.

An interesting aspect of these reactions is that they could be the base for the development of efficient methods for synthesizing different thieno[3,2-*c*]pyridines from readily available starting materials, which might permit the introduction of a broad range of groups on the pyridine ring.

Alkoxycarbonylations. Synthesis of Ester-Substituted Thiophenes and Monomeric bis-Cyclopalladated Complexes. Treatment of palladacycles with carbon monoxide is a very suitable synthetic method for the production of a myriad of carbo- and heterocyclic organic compounds.[4x,13a] Prompted by the results obtained with alkynes, we decided to attempt the stoichometric insertion of carbon monoxide into the Pd−C bond of palladacycles **2a** and **2b**, aiming to synthesize heterocyclic

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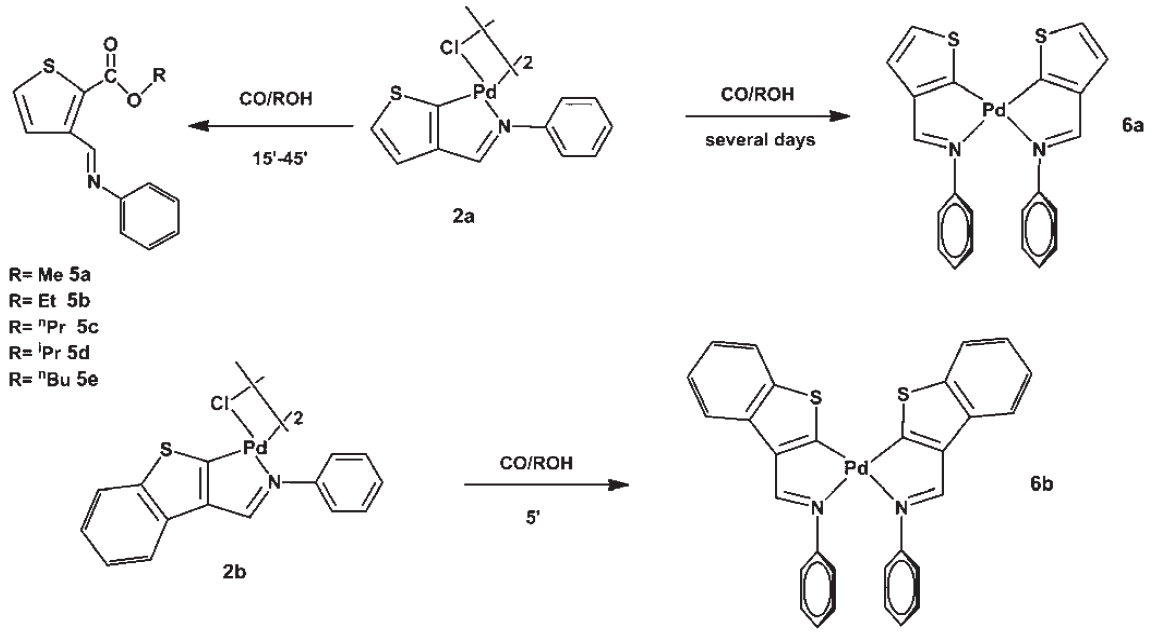
Scheme 3. Synthesis of Ester-Substituted Thiophenes Generated by Alkoxycarbonylation and Formation of the Monomeric bis-Cyclopalladated Complexes 6a and 6b



derivatives. Under all the conditions tested, the attempted carbonylation process does not take place, and usually a reduction process prevails. However, when the reaction is carried out in MeOH as the solvent, the corresponding alkoxylated product **5a** is formed (see Scheme 3), as a result of a tandem process in which the alcohol probably intercepts the acyl-palladium intermediate. The ester-substituted thiophene **5a** is isolated by a chromatographic column over silica gel with a yield of 63%, and its nature is inferred from the IR, ^{1}H and ^{13}C NMR, mass spectrum, and elemental analyses. For example, the ^{1}H NMR of **5a** in $CDCl_3$ exhibits two doublets for the thiophene protons (7.89 and 7.52 ppm) and two singlets for the imine and methoxy groups (9.33 and 3.95 ppm, respectively), in addition to the phenyl resonances. On the basis of the ^{13}C NMR data, the formation of the ester-functionalized thiophene is evident, because the signals corresponding to the ester carbonyl group (162.6 ppm) and the methoxy unit (52.7 ppm) are easily identified. The IR analysis also indicates the presence of an ester moiety, because a characteristic band is observed at 1709 cm^{-1}. Because the facile and efficient preparation of functionalized thiophenes is of considerable interest for synthetic chemists, we decide to carry out the carbonylation reaction in other alcoholic solvents, intending to generate ester-substituted thiophenes with different alkyl chains. Employing the adequate solvent and reaction time (15−45 min), we succeeded in the synthesis of the species **5b**−**5e**, which have incorporated ethyl, *n*-propyl, isopropyl, and *n*-butyl side chains in the organic skeleton (see Scheme 3). All the species were straightforwardly synthesized in optimal yields and were characterized by conventional methods. The incorporation of the respective alkoxy groups is at first inferred from the ^{1}H NMR spectra, where the characteristic multiplets of each alkyl chain are observed, and confirmed by the analysis of the IR, ^{13}C NMR and mass spectra, and elemental analyses.

The reaction times described for the preparation of compounds **5a**−**5e** are essential to achieve good yields, because, when longer reactions times were studied, we observed the moderately slow, but continual, disappearance of the derivatives **5a**−**5e**, and their transformation into the interesting monomeric bis-cyclopalladated complex **6a** (see scheme 3). The alkyl chain nature of the derivatives **5a**−**5e** seems to be somehow related to the rate of the formation of complex **6a**. For instance, the derivative containing a methoxy group is totally consumed after 2 days, isolating the bis-cyclometallated complex **6a** with a yield of 61%, whereas compound **5d**, which has an isopropoxy substituent, only shows a 30% conversion after the same time.

The elucidation of the structure of the derivative **6a** was carried out by X-ray diffraction analysis, and confirmed by NMR spectroscopy, mass spectrometry, and elemental analysis. The solid-state structure of **6a** is shown in Figure 2a. The structure reveals the formation of a monomeric complex, which contains two independent cyclometallated thiophene-based imines **1a** bound to the same palladium atom. The Pd atom lies in a slightly distorted square-planar geometry, surrounded by two iminic N atoms and two ortho-palladated C atoms in a mutual cis arrangement. The formation of this cis conformation can be attributed to the combination of the strong trans influence of the carbanionic ligands and to the antisymbiotic effect,[14] which forces the molecule to adopt this particular arrangement.[15] The mutual cis disposition of the two C atoms of bis(ortho-palladated) derivatives is a well-established fact, which has been observed in most of the bis-cyclopalladated complexes characterized up to now.[16] As a consequence of this geometrical situation, the phenyl rings are positioned in close proximity and with a parallel disposition, displaying a considerable aryl−aryl π-stacking interaction in the solid state. This situation seems to being retained in solution, as judged by the significant mutual shielding displayed for the phenyl protons in the ^{1}H NMR spectrum, which resonate at 6.78−6.90 ppm.

When analogous alkoxycarbonylation reactions were attempted for the cyclopalladated complex **2b** with the same alcoholic

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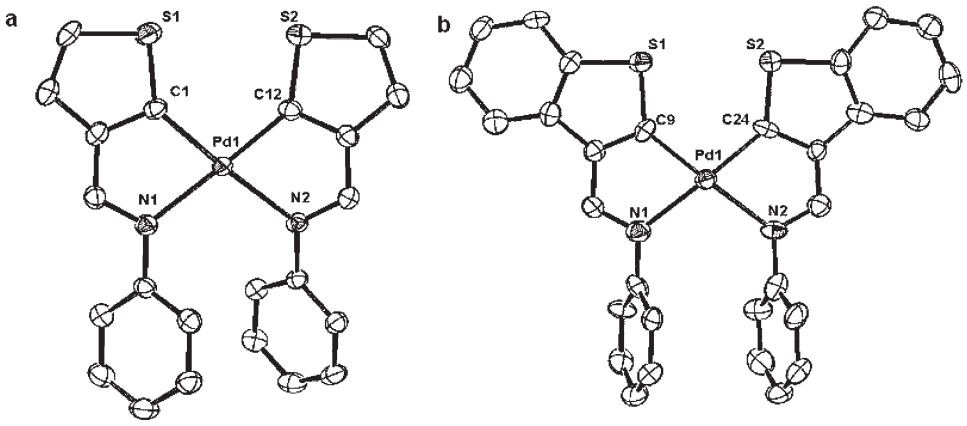

Figure 2. Top views of the complexes **6a** and **6b** showing a partial atom-labeling scheme: (a) complex **6a** and (b) complex **6b**. Displacement ellipsoids are scaled to the 50% probability level. Hydrogen atoms have been removed for clarity. Selected bond distances (Å) and angles (deg) for **6a**: Pd1−C1 1.974(2), Pd1−C12 1.969(2), Pd1−N1 2.150(2), Pd1−N2 2.143(2), C1−Pd1−N1 79.48 (8), C1−Pd1−C12 97.11(9), C12−Pd1−N2 79.51(8), N2−Pd1−N1 103.78(7). Selected bond distances (Å) and angles (deg) for **6b**: Pd1−C9 1.965(7), Pd1−C24 1.975(7), Pd1−N1 2.144(7), Pd1−N2 2.137(5), C9−Pd1−N1 78.3(3), C9−Pd1−C24 99.2(3), C24−Pd1−N2 79.1(3), N2−Pd1−N1 103.4(2).

solvents tested for **2a**, the corresponding ester-functionalized benzothiophenes were not detected, observing in all the cases the formation of the monomeric complex **6b**, even when reaction times as short as 5 min were employed. The structure of **6b** was studied by means of X-ray diffraction. The results, shown in Figure 2b, indicate that **6b** is a monomeric bis-cyclometallated complex analogous to the derivative **6a**. Accordingly, the palladium center is located in a square-planar environment and bound to the N iminic and C thienyl atoms of the ortho-metallated benzothiophene ligands. The complex **6b** also displays a cis arrangement of the σ-coordinated C atoms, forcing the phenyl rings to be in close parallel disposition.

Our proposed rationale for the formation of complexes **6a** and **6b**, admittedly a purely speculative one, is that they are formed via decarboxylative processes by reaction of the respective ester-substituted thiophenes with palladium (0) species formed in the reaction mixture. It is well known that decarboxylation of esters can be mediated or catalyzed by palladium (0) derivatives,[17] and the formation of metallic palladium in the reaction medium is evident in all the reactions carried out. In the case of **6b**, apparently this decarboxylation reaction is so fast that the ester-functionalized benzothiophene intermediates cannot be detected. Aiming to gain some insight into the process of formation of the bis(ortho-palladated) derivatives, we have performed some experiments. It is clear that, at the beginning of the reaction, when the concentration of **5** is still low, the main species in the reaction mixture is the dinuclear complex **2a**. Therefore, and due to the fact that Pd(II) is also able to promote the decarboxylation process,[18] we have reacted **5a** with **2a** in the absence of CO. However, the mixture remains unaltered and **6a** was not observed even at the level of traces. On the other hand, the formation of **6a** from **2a** in MeOH seems to be drastically decelerated when Hg(0) is present in the solution. Because it is well established that elemental mercury is an excellent scavenger for Pd(0) heterogeneous species,[19] this observation supports the idea that decarboxylative processes initiated by palladium (0) species are the source of the monomeric bis-cyclometallated complexes.[20]

We believe that the simple and straightforward synthesis of the bis-cyclometallated complexes **6a** an **6b** is particularly interesting. Complexes containing two cyclometallated ligands over the same metal are attracting substantial attention, mainly because they have been intensively exploited as models for C−X (X = C, N, O, halogen) bond-forming reactions via oxidative coupling mediated by palladacycles, providing notable mechanistic insights,[21] but also because they can display interesting photochemical and photophysical properties.[22] However, the synthesis of this kind of doubly metallated complexes is not simple, because, although the first metallacycle might be formed quite easily, the second one always involves a transmetallation process.[8,16] This second metallation step usually implies the use of highly reactive organolithium and magnesium derivatives, which display important drawbacks, such as their low tolerance of functional groups or the existence of side reactions. Other transmetallating agents have been tested (mainly B, Sn, Si, Hg, and Au reagents).[8] Unfortunately, they are not as efficient as the organolithium and magnesium species, and the most versatile ones (Sn- or Hg-based materials) are toxic species. In principle, the CO-mediated reaction described in this Article offers an unexplored synthetic route for the production of this kind of complex, which displays obvious advantages over the previous reported strategies.

CONCLUSION

In summary, this Article reports the synthesis by direct C−H activation under mild conditions of ortho-palladated complexes based on imino-thiophene and imino-benzothiophene ligands. The reactivity studies carried out with these complexes revealed that cyclopalladation has an enormous potential as a versatile and efficient tool for the synthesis of new and interesting thiophene-based structures. The reaction of internal alkynes with the cyclometallated complexes provides an unexplored and efficient tool for the metal-mediated synthesis of thieno[3,2-*c*]pyridinium salts, a particularly important family of heterocyclic molecules. Further studies of the scope of the reaction, and efforts to perform this transformation in a catalytic way, are currently in progress. Ester-substituted thiophenes are also accessible by simple one-pot alkoxycarbonylations carried out by reaction of the ortho-palladated complexes with CO in alcoholic solvents. In addition, the latter reaction offers an unexpected, but simple and

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appealing, route for the production of a very special class of organometallic complexes, namely, monomeric bis-cyclometallated systems.

EXPERIMENTAL SECTION

General Methods. Solvents were dried and distilled using standard procedures before use. All reactions were carried out under an Ar atmosphere (except in the carbonylations) using standard Schlenck techniques. Flash column liquid chromatography was performed on silica gel Kieselgel 60 (63−200 μm, 70−230 mesh) or on aluminum oxide 90 neutral (50−200 μm). Elemental analyses were carried out on a PerkinElmer 2400-B microanalyser. ^{1}H and ^{13}C NMR spectra were recorded in acetone-d_6 or $CDCl_3$ solutions at 25 °C on a Bruker AV300 or AV400 or Varian Gemini 300 spectrometers (δ in ppm, J in Hz) at a ^{1}H operating frequency of 300.13 or 400.13 MHz. ^{1}H and ^{13}C spectra were referenced using the solvent signal as an internal standard. The infrared spectra (4000−380 cm^{-1}) were recorded on a PerkinElmer Spectrum One spectrophotomer. ESI (ESI+) mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served as both the nebulizer gas and the dry gas. The imines **1a**[23] and **1b**[24] were synthesized according to published methods. In the ^{1}H NMR spectra of compounds **5** measured in $CDCl_3$, there is an overlapping of the $CHCl_3$ and phenyl signals; therefore, the ^{1}H NMR data of **5a**−**5f** are also given in acetone-d_6. In the latter solvent, the AB system of the thiophene protons collapses to a singlet.

Complex 2a. Palladium acetate was added (540 mg, 2.40 mmol) to a solution of **1a** (450 mg, 2.40 mmol) in glacial acetic acid (15 mL). The resulting solution was stirred overnight at room temperature, and the solvent was removed under vacuum. The slurry obtained was dissolved in methanol (25 mL) and an excess of lithium chloride (206 mg, 4.80 mmol) was added. The resulting solution was allowed to stir at room temperature during 30 min and filtered through Celite to remove black palladium. The solvent was evaporated under reduce pressure, and the residue was redissolved in DCM (DCM = dichloromethane) and filtered across a short plug of silica gel to remove the inorganic salts. The resulting yellow solution was evaporated under vacuum to a small volume and precipitated by addition of Et_2O. The solid was washed with Et_2O (10 mL) and dried to afford **2a** as a yellow solid. Crystals for X-ray diffraction were grown by slow diffusion of Et_2O into a saturated solution of **2a** in acetone. Yield: (541 mg, 69%). MS (ESI+): 620.8 [M − Cl]$^+$. ^{1}H NMR (acetone-d_6): δ = 7.99 (s, 1H, *H*C═N), 7.42−7.39 (m, 2H, Ph), 7.31−7.27 (m, 2H, Ph), 7.22−7.17 (m, 2H, 1H Ph + 1H thiophene), 7.03 (d, $^3J_{HH}$ = 5.2, 1H, thiophene). ^{13}C{^{1}H} NMR (acetone-d_6): δ = 170.4 (C), 168.9 (CH), 150.1 (C), 145.8 (C), 128.4 (CH), 126.5 (CH), 124.4 (CH), 124.3 (CH), 124.2 (CH). Anal. Calcd for [$C_{22}H_{16}Cl_2N_2Pd_2S_2$]: C, 40.26; H, 2.46; N, 4.27; S, 9.77. Found: C, 40.50; H, 2.79; N, 4.01; S, 9.43.

Complex 2b. The synthesis was carried out in an analogous way as that described before for **2a**, employing palladium acetate (470 mg, 2.10 mmol), imine **1b** (500 mg, 2.10 mmol), and lithium chloride (180 mg, 4.20 mmol). Crystals suitable for X-ray diffraction were grown by slow evaporation of a saturated solution of **2b** in acetone. Yield: (594 mg, 75%). MS (ESI+): 723.3 [M − Cl]$^+$. ^{1}H NMR (acetone-d_6): δ = 8.38 (s, 1H, *H*C═N), 7.93 (m, 1H, C_6H_4), 7.80 (m, 1H, C_6H_4), 7.49−7.46 (m, 2H, Ph), 7.35−7.30 (m, 2H, Ph), 7.27−7.23 (m, 2H, 1H Ph + 1H C_6H_4), 7.20−7.14 (m, 1H, C_6H_4). ^{13}C{^{1}H} NMR (acetone-d_6): δ = 180.3 (C), 166.9 (CH), 150.5 (C), 141.4 (C), 140.0 (C), 137.1 (C), 128.2 (CH), 126.6 (CH), 124.8 (CH), 124.7 (CH), 122.6 (CH), 122.2 (CH), 120.2 (CH). Anal. Calcd for [$C_{30}H_{20}Cl_2N_2Pd_2S_2$]: C, 47.64; H, 2.67; N, 3.70; S, 8.48. Found: C, 47.82; H, 2.79; N, 3.43; S, 8.11.

Compound 3a. A solution of the ortho-palladated complex **2a** (150 mg, 0.229 mmol) and 3-hexyne (0.260 mL, 2.29 mmol) in toluene (15 mL) was heated during 12 h at 80 °C. After cooling the solution, the solvent was removed under vacuum. The solid obtained was dissolved in DCM (25 mL), filtered with Celite to remove black palladium, and the solution was evaporated to a small volume (ca. 2 mL). Et_2O (20 mL) was then added, and the resulting precipitate was washed several times with the same solvent. The product was purified by flash chromatography over neutral alumina using DCM/MeOH (98/2) as the eluent and isolated, after removal of the solvent, as a dark red solid. Yield: (98 mg, 71%). MS (ESI+): 268.0 [M − Cl]$^+$. ^{1}H NMR ($CDCl_3$): δ = 10.03 (s, 1H, pyridinium), 8.40 (d, $^3J_{HH}$ = 5.4, 1H, thiophene), 7.91 (d, $^3J_{HH}$ = 5.4, 1H, thiophene), 7.66 (m, 5H, Ph), 3.12 (q, $^3J_{HH}$ = 7.6, 2H, CH_2), 2.91 (q, $^3J_{HH}$ = 7.6, 2H, CH_2), 1.47 (t, $^3J_{HH}$ = 7.6, 3H, CH_3), 1.12 (t, $^3J_{HH}$ = 7.6, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 156.4 (C), 146.3 (C), 143.1 (CH), 141.3 (C), 135.4 (C), 135.2 (C), 132.8 (CH), 131.4 (CH), 130.4 (CH), 127.2 (CH), 126.5 (CH), 25.8 (CH_2), 23.3, (CH_2), 14.07 (CH_3), 13.4 (CH_3). Anal. Calcd for [$C_{17}H_{18}ClNS$]·2 CH_2Cl_2: C, 48.17; H, 4.68; N, 2.96; S, 6.77. Found: C, 47.92; H, 4.46; N, 3.11; S, 6.79.

Compound 3b. A solution of the ortho-palladated complex **2a** (150 mg, 0.229 mmol) and diphenyl acetylene (409 mg, 2.29 mmol) was refluxed in toluene (15 mL) for 12 h (112 °C). After cooling the solution, the solvent was removed under vacuum, and the residue generated was dissolved in DCM (25 mL). The solution was filtered with Celite to remove black palladium, and evaporated to a small volume (ca. 2 mL). Addition of Et_2O (20 mL) caused the precipitation of a yellow solid, which was washed several times with Et_2O. The product was purified by flash chromatography over neutral alumina using DCM/MeOH (98/2) as the eluent and isolated as a yellow solid. Yield: (130 mg, 71%). MS (ESI+): 364.1 [M − Cl]$^+$. ^{1}H NMR ($CDCl_3$): δ = 10.51 (s, 1H, pyridinium), 8.55 (d, $^3J_{HH}$ = 5.4, 1H, thiophene), 7.95 (d, $^3J_{HH}$ = 5.4, 1H, thiophene), 7.61 (m, 2H, Ph), 7.36−7.29 (m, 8 H, Ph), 7.10−7.06 (m, 5H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 158.0 (C), 144.3 (CH), 144.1 (C), 142.9 (C), 136.6 (C), 136.0 (C), 135.2 (CH), 134.8 (C), 131.9 (CH), 131.2 (C), 130.8 (CH), 130.2 (CH), 130.1 (CH), 130.0 (CH), 129.7 (CH), 129.6 (CH), 128.7 (CH), 127.8 (CH), 127.5 (CH). Anal. Calcd for [$C_{25}H_{18}ClNS$]: C, 75.08; H, 4.54; N, 3.50; S, 8.02. Found: C, 74.78; H, 4.61; N, 3.24; S, 7.76.

Compounds 3c/3d. 2-Hexyne (0.257 mL, 2.29 mmol) was added to a solution of the ortho-palladated complex **2a** (150 mg, 0.229 mmol) in toluene (15 mL), and the mixture was heated during 12 h at 80 °C. The solvent was removed under vacuum, and the residue obtained was dissolved in DCM (25 mL) and filtered with Celite. The resulting solution was evaporated to a small volume (ca. 2 mL), and the addition of Et_2O (20 mL) caused the precipitation of a dark red solid, which was washed several times with Et_2O. Finally, purification over neutral alumina using DCM/MeOH (98/2) as the eluent afforded the regioisomers **3c**/**3d** in a ratio of 50:50 (determined by ^{1}H NMR integration, assignation of the signals to the different isomers **3c**/**3d** was not possible). Yield: (94 mg, 68%). MS (ESI+): 268.0 [M − Cl]$^+$. ^{1}H NMR ($CDCl_3$): δ = 10.11 (s, 1H, pyridinium), 10.09 (s, 1H, pyridinium′), 8.44 (d, $^3J_{HH}$ = 5.7, 1H, thiophene), 8.40 (d, $^3J_{HH}$ = 5.7, 1H, thiophene′), 7.93−7.92 (m, 2H, thiophene + thiophene′), 7.65 (m, 10H, Ph + Ph′), 3.09 (q, $^3J_{HH}$ = 8.1, 2H, CH_2−CH_2−CH_3), 2.83 (q, $^3J_{HH}$ = 8.1, 2H, CH_2′−CH_2−CH_3), 2.80 (s, 3H, Me), 2.53 (s, 3H, Me), 1.84 (m, 2H, CH_2−CH_2−CH_3), 1.51 (m, 2H, CH_2−CH_2′−CH_3), 1.13 (t, $^3J_{HH}$ = 8.1, 3H, CH_2−CH_2−CH_3), 0.82 (t, $^3J_{HH}$ = 8.1, 3H, CH_2−CH_2−CH_3′). ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 157.2 (C), 156.7 (C), 145.9 (C), 142.2 (CH), 142.0 (CH), 141.9 (C), 141.8 (C), 141.5 (C), 135.0 (C), 134.8 (C), 134.7 (C), 133.4 (CH), 133.1 (CH), 131.5 (CH), 131.4 (CH), 130.8 (CH), 130.5 (CH), 130.2 (C), 126.7 (CH), 126.6 (CH), 126.4 (CH), 126.2 (CH), 35.2 (CH_2), 32.3 (CH_2), 22.6, (CH_2), 21.9 (CH_2), 18.2 (CH_3), 17.9 (CH_3), 14.6 (s, CH_3), 14.3

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(s, CH_3). Anal. Calcd for $[C_{17}H_{18}ClNS]\cdot CH_2Cl_2$: C, 55.61; H, 5.19; N, 3.60; S, 8.25. Found: C, 55.27; H, 5.56; N, 3.43; S, 7.94.

Compounds 3e/3f. A mixture of the ortho-palladated complex **2a** (150 mg, 0.229 mmol) and 1-phenylpropyne (0.287 mL, 2.29 mmol) is refluxed in toluene (15 mL) during 12 h. The solvent was removed under vacuum; the residue obtained was dissolved in DCM (25 mL) and filtered with Celite. Addition of Et_2O (20 mL) caused the precipitation of a dark red solid, which was washed several times with Et_2O. The product was purified by flash chromatography over neutral alumina using DCM/MeOH (98/2) as the eluent and isolated as a mixture of the regioisomers **3e**/**3f** in a ratio of 60:40 (determined by ^{1}H NMR integration without elucidating the identity of the major/minor compound, and assignation of the signals to the different isomers **3e**/**3f** was not possible). Yield: (108 mg, 70%). MS (ESI+): 302.0 $[M - Cl]^+$. ^{1}H NMR ($CDCl_3$): δ = 10.30 (s, 1H, pyridinium), 10.07 (s, 1H, pyridinium′), 8.55 (d, $^3J_{HH}$ = 5.4, 1H, thiophene), 8.36 (d, $^3J_{HH}$ = 5.4, 1H, thiophene′), 8.03 (d, $^3J_{HH}$ = 5.4, 1H, thiophene), 7.09−7.85 (m, 2H, 1H thiophene′ + 1H Ph), 7.68−7.60, 7.54−7.51, 7.36−7.20 (m, 19 H, Ph + Ph′), 2.57 (s, 3H, Me), 2.41 (s, 3H, Me′). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 157.2 (C), 156.4 (C), 143.7 (C), 142.3 (CH), 142.2 (CH), 142.0 (C), 141.6 (C), 135.4 (C), 134.8 (s, C), 134.3 (s, C), 133.9 (CH), 133.6 (CH), 130.9 (CH), 130.6 (C), 130.5 (s, C), 130.4 (CH), 130.3 (CH), 130.0 (CH), 129.9 (CH), 129.8 (CH), 129.5 (CH), 129.3 (CH), 128.7 (CH), 128.6 (CH), 127.4 (CH), 126.2 (CH), 126.1 (CH), 125.8 (CH), 19.4 (CH_3), 18.8 (CH_3). Anal. Calcd for $[C_{20}H_{16}ClNS]\cdot 1/2CH_2Cl_2$: C, 64.74; H, 4.51; N, 3.68; S, 8.43. Found: C, 64.77; H, 4.91; N, 3.62; S, 8.17.

Compound 4a. A mixture of the ortho-palladated complex **2b** (150 mg, 0.200 mmol) and 3-hexyne (0.227 mL, 2.00 mmol) was heated in toluene (15 mL) at 80 °C during 12 h. The resulting solution was evaporated under vacuum, and the residue obtained was dissolved in DCM (25 mL). The black palladium formed was removed by filtration with Celite, and the solution was concentrated to a small volume (ca. 2 mL). Et_2O (20 mL) was then added, and the obtained precipitate was washed with the same solvent several times. The product was purified by flash chromatography over neutral alumina using DCM/MeOH (98/2) as the eluent and isolated, after removal of the solvent, as a yellow solid. Yield: (102 mg, 72%). MS (ESI+): 318.1 $[M - Cl]^+$. ^{1}H NMR ($CDCl_3$): δ = 10.67 (s, 1H, pyridinium), 9.01 (m, 1H, C_6H_4), 7.91 (m, 1H, C_6H_4), 7.78−7.63 (m, 7H, 2H C_6H_4 + 5H Ph), 3.15 (q, $^3J_{HH}$ = 7.6, 2H, CH_2), 2.97 (q, $^3J_{HH}$ = 7.6, 2H, CH_2), 1.50 (t, $^3J_{HH}$ = 7.6, 3H, CH_3), 1.16 (t, $^3J_{HH}$ = 7.6, 3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 157.4 (C), 149.3 (C), 140.7 (C), 140.2 (CH), 138.7 (C), 134.8 (C), 132.5 (C), 131.7 (C), 131.8 (CH), 130.1 (CH), 130.0 (CH), 127.2 (CH), 126.4 (CH), 125.9 (CH), 122.3 (CH), 25.6, (CH_2), 23.3 (CH_2), 13.7 (CH_3), 12.8 (CH_3). Anal. Calcd for $[C_{21}H_{20}ClNS]\cdot CH_2Cl_2$: C, 60.21; H, 5.05; N, 3.19; S, 7.31. Found: C, 60.12; H, 4.88; N, 3.51; S, 7.61.

Compound 4b. Diphenylacetylene (357 mg, 2.00 mmol) was added into a solution of complex **2b** (150 mg, 0.200 mmol) in toluene (15 mL), and the mixture was refluxed overnight (12 h). The solvent was removed under vacuum, and the resulting solid was dissolved in DCM (25 mL). The black palladium formed was removed by filtration with Celite, and the solution was concentrated to a small volume (ca. 2 mL). Addition of Et_2O (20 mL) caused the precipitation of a yellow solid, which was washed with additional Et_2O (2 × 10 mL). The product was isolated by flash chromatography over neutral alumina using DCM/MeOH (98/2) as the eluent. Yield: (131 mg, 73%). MS (ESI+): 414.1 $[M - Cl]^+$. ^{1}H NMR ($CDCl_3$): δ = 10.90 (s, 1H, pyridinium), 9.14 (m, 1H, C_6H_4), 7.94 (m, 1H, C_6H_4), 7.74−7.66 (m, 4H, 2H C_6H_4 + 2H Ph), 7.45−7.38 (m, 8H, Ph), 7.19−7.08 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 159.0 (C), 146.6 (C), 141.8 (C), 140.3 (CH), 140.2 (C), 135.2 (C), 133.9 (C), 132.6 (C), 132.4 (C), 130.9 (CH), 130.4 (C), 130.1 (CH), 130.2 (CH), 129.3 (CH), 129.2 (CH), 129.1 (CH), 128.9 (CH), 128.8 (CH), 127.8 (CH), 127.0 (2 CH), 125.6 (CH), 122.6 (CH). Anal. Calcd for $[C_{29}H_{20}ClNS]$: C, 77.40; H, 4.48; N, 3.11; S, 7.13. Found: C, 77.27; H, 4.79; N, 2.87; S, 6.75.

Compounds 4c/4d. 2-Hexyne (0.224 mL, 2.00 mmol) was added to a solution of the ortho-palladated complex **2b** (150 mg, 0.200 mmol) in toluene (15 mL), and the mixture was heated during 12 h at 80 °C. The solvent was removed under vacuum. The residue was dissolved in DCM (25 mL) and filtered over Celite. The solution was evaporated to a small volume (ca. 2 mL), then addition of Et_2O (20 mL) caused the precipitation of a yellow solid, which was washed several times with Et_2O. Purification over neutral alumina using DCM/MeOH (98/2) as the eluent afforded the regioisomers **4c**/**4d** in a ratio of 50:50 (determined by ^{1}H NMR integration; assignation of the signals to the different isomers **4c**/**4d** was not possible). Yield: (97 mg, 69%). MS (ESI +): 318.1 $[M - Cl]^+$. ^{1}H NMR ($CDCl_3$): δ = 10.54 (s, 1H, pyridinium), 10.49 (s, 1H, pyridinium′), 8.93−8.91 (m 2H, 1H C_6H_4 + 1H C_6H_4′), 7.89−7.87 (m, 2H, 1H C_6H_4 + 1H C_6H_4′), 7.70−7.60 (m, 14H, 4H C_6H_4/C_6H_4′ + 10 Ph/Ph′), 3.09 (q, $^3J_{HH}$ = 8.1, 2H, $CH_2-CH_2-CH_3$), 2.91 (q, $^3J_{HH}$ = 8.4, 2H, CH_2′$-CH_2-CH_3$), 2.87 (s, 3H, Me), 2.60 (s, 3H, Me′), 1.83 (m, 2H, $CH_2-CH_2-CH_3$), 1.55 (m, 2H, CH_2-CH_2′$-CH_3$), 1,14 (t, $^3J_{HH}$ = 7.2, 3H, $CH_2-CH_2-CH_3$), 0.84 (t, $^3J_{HH}$ = 7.2, 3H, $CH_2-CH_2-CH_3$′). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 158.2 (C), 157.7 (C), 149.2 (C), 145.3 (C), 141.5 (C), 141.1 (C), 139.6 (CH), 139.4 (CH), 139.0 (C), 134.4 (C), 132.8 (C), 132.7 (C), 131.8 (C), 131.4 (C), 131.3 (CH), 131.2 (CH), 130.5 (CH), 130.2 (CH), 130.1 (CH), 130.0 (CH), 129.8 (C), 129.7 (C), 127.3 (CH), 127.2 (CH), 126.6 (CH), 126.4 (CH), 125.7 (CH), 125.6 (CH), 122.5 (2 CH), 35.3 (CH_2), 32.7 (CH_2), 22.5, (CH_2), 21.7 (CH_2), 18.4 (CH_3), 18.3 (CH_3), 14.6 (CH_3), 14.4 (CH_3). Anal. Calcd for $[C_{21}H_{20}ClNS]\cdot 1/2CH_2Cl_2$: C, 65.15; H, 5.34; N, 3.53; S, 8.09. Found: C, 65.07; H, 5.41; N, 3.62; S, 8.32.

Compounds 4e/4f. 1-Phenylpropyne (0.250 mL, 2.00 mmol) was added into a solution of complex **2b** (150 mg, 0.200 mmol) in toluene (15 mL), and the resulting mixture was refluxed for 12 h. The solvent was removed under vacuum; the solid obtained was dissolved in DCM (25 mL) and filtered over Celite. Addition of Et_2O (20 mL) caused the precipitation of a yellow solid, which was washed several times with Et_2O. Purification by means of flash chromatography over neutral alumina using DCM/MeOH (98/2) as the eluent allowed for the isolation of the regioisomers **3e**/**3f** in a ratio of 65:35 (determined by ^{1}H NMR integration without elucidating the identity of the major/minor compound; assignation of the signals to the different isomers **4e**/**4f** was not possible). Yield: (99 mg, 64%). MS (ESI+): 352.1 $[M - Cl]^+$. ^{1}H NMR ($CDCl_3$): δ = 10.74 (s, 1H, pyridinium), 10.49 (s, 1H, pyridinium′), 9.06 (m, 1H, C_6H_4), 8.89 (m, 1H, C_6H_4′), 8.00 (m, 1H, C_6H_4), 7.92 (m, 1H, C_6H_4), 7.80 (m, 1H, C_6H_4′), 7.72−7.56 (m, 13H, 1H C_6H_4 + 2H C_6H_4′ + 10H Ph/Ph′), 7.33−7.28 (m, 10H, Ph/Ph′), 2.54 (s, 3H, Me), 2.46 (s, 3H, Me′). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 158.9 (C), 158.1 (C), 147.3 (C), 146.3 (C), 142.0 (C), 141.6 (C), 140.0 (C), 139.7 (CH), 139.6 (CH), 139.5 (C), 135.0 (C), 134.6 (C), 132.9 (C), 132.6 (C), 132.5 (C), 131.9 (C), 131.2 (CH), 130.9 (2C), 130.5 (CH), 130.4 (CH), 130.3 (CH), 130.2 (CH), 130.1 (CH), 129.8 (CH), 129.5 (CH), 129.1 (CH), 128.9 (CH), 128.0 (CH), 127.5 (CH), 127.3 (CH), 127.2 (CH), 126.6 (CH), 126.2 (CH), 125.7 (CH), 124.2 (CH), 122.8 (CH), 122.6 (CH), 20.1 (CH_3), 19.2 (CH_3). Anal. Calcd for $[C_{24}H_{18}ClNS]$: C, 74.31; H, 4.68; N, 3.61; S, 8.27. Found: C, 74.12; H, 4.87; N, 3.40; S, 8.09.

Compound 5a. The ortho-palladated complex **2a** (150 mg, 0.229 mmol) was dissolved in methanol (20 mL) and stirred under a CO atmosphere (approximately 1 atm) during 10 min. The dark suspension was filtered through a plug of Celite, and the yellow solution was evaporated to dryness. The residue was dissolved in DCM and purified by flash chromatography over silica gel employing DCM as the eluent. The compound **5a** was isolated as a yellow oil. Yield: (70 mg, 63%). MS (ESI+): 245.9 $[M + 1H]^+$. ^{1}H NMR ($CDCl_3$): δ = 9.3 (s, 1H, *HC*═N),

7.88 (d, $^3J_{HH}$ = 5.2, 1H, thiophene), 7.51 (d, $^3J_{HH}$ = 5.2, 1H, thiophene), 7.41 (m, 2H, Ph), 7.28−7.26 (m, 3H, Ph), 3.95 (s, 3H, OCH_3). ^1H NMR (acetone-d_6): δ = 9.33 (s, 1H, *HC*=N), 7.86 (s, 2H, thiophene), 7.46 (m, 2H, Ph), 7.32−7.28 (m, 3H, Ph), 3.95 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 162.6 (C), 155.1 (CH), 152.0 (C), 144.9 (C), 133.2 (C), 130.7 (CH), 129.5 (CH), 128.4 (CH), 126.8 (CH), 121.4 (CH), 52.6 (CH_3). IR: ν = 1709 cm^{-1} (C=O). Anal. Calcd for [$C_{13}H_{11}NO_2S$]: C, 63.65; H, 4.52; N; 5.71, S 13.07. Found: C, 63.87; H, 4.71; N, 5.61; S, 12.89.

Compound 5b. The ortho-palladated complex **2a** (150 mg, 0.229 mmol) was dissolved in ethanol (20 mL) and placed under a CO atmosphere (approximately 1 atm). The reaction was stirred during 15 min, and the dark suspension was filtered through a plug of Celite. The solvent was removed under vacuum, and the yellow residue was purified by silica gel flash chromatography employing DCM as the eluent. The compound **5b** was isolated as a yellow oil. Yield: (74 mg, 62%). MS (ESI+): 260.0 [M + 1H]$^+$. ^1H NMR ($CDCl_3$): δ = 9.32 (s, 1H, *HC*=N), 7.85 (d, $^3J_{HH}$ = 5.2, 1H, thiophene), 7.48 (d, $^3J_{HH}$ = 5.2, 1H, thiophene), 7.40 (m, 2H, Ph), 7.27−7.25 (m, 3H, Ph), 4.40 (q, $^3J_{HH}$ = 6.9, 2H, OCH_2−CH_3), 1.40 (t, $^3J_{HH}$ = 6.9, 3H, OCH_2−CH_3). ^1H NMR (acetone-d_6): δ = 9.32 (s, 1H, *HC*=N), 7.83 (s, 2H, thiophene), 7.42 (m, 2H, Ph), 7.28−7.26 (m, 3H, Ph), 4.39 (q, $^3J_{HH}$ = 7.2, 2H, OCH_2−CH_3), 1.38 (t, $^3J_{HH}$ = 7.2, 3H, OCH_2−CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 162.5 (C), 155.3 (CH), 152.3 (C), 143.1 (C), 134.4 (C), 130.8 (CH), 129.4 (CH), 128.3 (CH), 127.6 (CH), 121.0 (CH), 61.9 (CH_2), 14.1 (CH_3). IR: ν = 1710 cm^{-1} (C=O). Anal. Calcd for [$C_{14}H_{13}NO_2S$]: C, 64.84; H, 5.05; N, 5.40; S, 12.36. Found: C, 64.72; H, 5.21; N, 5.26; S, 12.11.

Compound 5c. Complex **2a** (150 mg, 0.229 mmol) was dissolved in *n*-propanol (20 mL) and stirred under a CO atmosphere (approximately 1 atm) during 30 min. The dark suspension formed was filtered through a plug of Celite, and the yellow solution was evaporated under vacuum. The resulting residue was purified by silica gel flash chromatography employing DCM as the eluent, affording **5c** as a yellow oil. Yield: (88 mg, 70%). MS (ESI+): 274.0 [M + 1H]$^+$. ^1H NMR ($CDCl_3$): δ = 9.32 (s, 1H, *HC*=N), 7.85 (d, $^3J_{HH}$ = 5.3, 1H, thiophene), 7.48 (d, $^3J_{HH}$ = 5.3, 1H, thiophene), 7.40 (m, 2H, Ph), 7.27−7.25 (m, 3H, Ph), 4.30 (q, $^3J_{HH}$ = 6.6, 2H, OCH_2−CH_2−CH_3), 1.81 (m, 2H, OCH_2−CH_2−CH_3), 1.03 (t, $^3J_{HH}$ = 7.5, 3H, OCH_2−CH_2−CH_3). ^1H NMR (acetone-d_6): δ = 9.31 (s, 1H, *HC*=N), 7.83 (s, 2H, thiophene), 7.43 (m, 2H, Ph), 7.28−7.25 (m, 3H, Ph), 4.30 (q, $^3J_{HH}$ = 6.6, 2H, OCH_2−CH_2−CH_3), 1.80 (m, 2H, OCH_2−CH_2−CH_3), 1.01 (t, $^3J_{HH}$ = 7.5, 3H, OCH_2−CH_2−CH_3). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ = 162.4 (C), 155.3 (CH), 152.9 (C), 145.1 (C), 134.5 (C), 132.1 (CH), 130.1 (CH), 128.5 (CH), 127.3 (CH), 121.8 (CH), 67.6 (CH_2), 22.7 (CH_2), 10.7 (CH_3). IR: ν = 1701 cm^{-1} (C=O). Anal. Calcd for [$C_{15}H_{15}NO_2S$]: C, 65.91; H, 5.53; N, 5.12; S, 11.73. Found: C, 65.87; H, 5.51; N, 5.06; S, 11.71.

Compound 5d. A solution of the ortho-palladated complex **2a** (150 mg, 0.229 mmol) in *iso*-propanol (20 mL) was placed under a CO atmosphere (approximately 1 atm), and the mixture was stirred 45 min. The black palladium formed was removed by filtration with Celite, and the yellow solution was evaporated under vacuum. The residue was purified by silica gel flash chromatography with DCM as the eluent. Compound **5d** was isolated as a yellow oily material. Yield: (90 mg, 72%). MS (ESI+): 274.1 [M + 1H]$^+$. ^1H NMR ($CDCl_3$): δ = 9.33 (s, 1H, *HC*=N), 7.85 (d, $^3J_{HH}$ = 5.2, 1H, thiophene), 7.47 (d, $^3J_{HH}$ = 5.2, 1H, thiophene), 7.40 (m, 2H, Ph), 7.27−7.25 (m, 3H, Ph), 5.24 (sep, $^3J_{HH}$ = 6.3, 1H, $CH(CH_3)_2$), 1.39 (d, $^3J_{HH}$ = 6.3, 6H, $CH(CH_3)_2$). ^1H NMR (acetone-d_6): δ = 9.32 (s, 1H, *HC*=N), 7.82 (s, 2H, thiophene), 7.43 (m, 2H, Ph), 7.28−7.25 (m, 3H, Ph), 5.23 (sep, $^3J_{HH}$ = 6.2, 1H, $CH(CH_3)_2$), 1.39 (d, $^3J_{HH}$ = 6.2, 6H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ = 161.2 (C), 154.8 (CH), 152.3 (C), 144.3 (C), 134.2 (C), 132.1 (CH), 131.4 (CH), 129.5 (CH), 127.9 (CH), 121.2 (CH), 69.6 (CH), 21.4 (CH_3). IR: ν = 1701 cm^{-1} (C=O). Anal. Calcd for [$C_{15}H_{15}NO_2S$]: C, 65.91; H, 5.53; N, 5.12; S, 11.73. Found: C, 65.73; H, 5.64; N, 4.94; S, 11.59.

Compound 5e. The ortho-palladated complex **2a** (150 mg, 0.229 mmol) was dissolved in *n*-butanol (20 mL) and stirred under a CO atmosphere (approximately 1 atm) during 45 min. The dark suspension was filtered through a plug of Celite to remove the black palladium, and the yellow solution was evaporated under vacuum. Compound **5e** was isolated as a yellow oil by means of flash chromatography over silica gel with DCM as the eluent. Yield: (93 mg, 71%). MS (ESI+): 288.1 [M + 1]$^+$. ^1H NMR ($CDCl_3$): δ = 9.33 (s, 1H, *HC*=N), 7.86 (d, $^3J_{HH}$ = 5.4, 1H, thiophene), 7.49 (d, $^3J_{HH}$ = 5.4, 1H, thiophene), 7.40 (m, 2H, Ph), 7.29−7.26 (m, 3H, Ph), 4.35 (t, $^3J_{HH}$ = 6.6, 2H, OCH_2−CH_2−CH_2−CH_3), 1.75 (m, 2H, OCH_2−CH_2−CH_2−CH_3), 1.49 (m, 2H, OCH_2−CH_2−CH_2−CH_3), 0.98 (t, $^3J_{HH}$ = 7.5, 3H, OCH_2−CH_2−CH_2−CH_3). ^1H NMR (acetone-d_6): δ = 9.32 (s, 1H, *HC*=N), 7.82 (m, 2H, thiophene), 7.44 (m, 2H, Ph), 7.31−7.26 (m, 3H, Ph), 4.36 (t, $^3J_{HH}$ = 6.4, 2H, OCH_2−CH_2−CH_2−CH_3), 1.76 (m, 2H, OCH_2−CH_2−CH_2−CH_3), 1.47 (m, 2H, OCH_2−CH_2−CH_2−CH_3), 0.97 (t, $^3J_{HH}$ = 7.3, 3H, OCH_2−CH_2−CH_2−CH_3). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ = 161.6 (C), 154.5 (CH), 152.0 (C), 144.2 (C), 133.7 (C), 131.2 (CH), 129.2 (CH), 127.6 (CH), 126.4 (CH), 121.4 (CH), 65.1 (CH_2), 30.5 (CH_2), 19.0 (CH_2), 13.1 (CH_3). IR: ν = 1703 cm^{-1} (C=O). Anal. Calcd for [$C_{16}H_{17}NO_2S$]: C, 66.87; H, 5.96; N, 4.87; S, 11.16. Found: C, 66.61; H, 6.02; N, 4.89; S, 11.19.

Complex 6a. A solution of the ortho-palladated complex **2a** (150 mg, 0.229 mmol) in methanol (20 mL) was stirred under a CO atmosphere (approximately 1 atm) during 2 days. The dark suspension was filtered through a plug of Celite, and the orange-yellowish solution was evaporated to dryness. The residue was dissolved in DCM and purified by chromatography over silica gel. The first yellow band eluted with DCM was collected and evaporated under vacuum, yielding complex **6a** as an orange-yellowish solid. Recrystallization from DCM/pentane afforded crystals suitable for X-ray diffraction analysis. Yield: (67 mg, 61%). MS (ESI+): 478.7 [M]$^+$. ^1H NMR ($CDCl_3$): δ = 8.06 (s, 1H, *HC*=N), 7.30 (m, 2H, thiophene), 6.91−6.77 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 168.4 (C), 167.1 (CH), 149.1 (C), 147.7 (C), 128.3 (CH), 127.5 (CH), 125.8 (CH), 125.3 (CH), 121.4 (CH). Anal. Calcd for [$C_{22}H_{16}N_2PdS_2$]: C, 55.17; H, 3.37; N, 5.85; S, 13.39. Found: C, 55.41; H, 3.24; N, 5.92; S, 13.44.

Complex 6b. Complex **2b** (150 mg, 0.200 mmol) was dissolved in methanol (20 mL), and the solution was stirred under a CO atmosphere (approximately 1 atm) during 15 min. The dark suspension was filtered through a plug of Celite to remove black palladium, and the orange solution was evaporated under vacuum. Complex **6b** was isolated as an orange solid by means of chromatography over silica gel employing DCM as the eluent. Recrystallization from DCM/pentane afforded crystals suitable for X-ray diffraction analysis. Yield: (89 mg, 77%). MS (ESI+): 341.3 [M − 1L, (L = $C_{15}H_{10}NS$)]$^+$. ^1H NMR ($CDCl_3$): δ = 8.36 (s, 1H, *HC*=N), 7.92 (m, 1H, C_6H_4), 7.78 (m, 1H, C_6H_4), 7.34 (m, 1H, C_6H_4), 7.28 (m, 1H, C_6H_4), 6.96−6.86 (m, 5H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 177.5 (C), 165.7 (CH), 149.5 (C), 143.8 (C), 141.9 (C), 137.2 (C), 128.7 (CH), 126.1 (CH), 124.9 (CH), 122.8 (CH), 122.5 (CH), 121.8 (CH), 119.2 (CH). Anal. Calcd for [$C_{30}H_{20}N_2PdS_2$]: C, 62.23; H, 3.48; N, 4.84; S, 11.08. Found: C, 61.94; H, 3.42; N, 4.93; S, 11.21.

X−ray Crystallography. X-ray data collection was performed on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monocromated Mo−Kα radiation (λ = 0.71073 Å). A single crystal was mounted in each case at the end of a quartz fiber in a random orientation, covered with perfluorinated oil and placed under a cold stream of N_2 gas. In all cases, a hemisphere of data was collected based on ω-scan or ϕ-scan runs. The diffraction frames were integrated using the program CrysAlis RED,[25] and the integrated intensities were corrected for absorption with

SADABS.[26] The structures were solved and developed by Patterson and Fourier methods.[27] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each H atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[28]

■ ASSOCIATED CONTENT

Supporting Information. CIF files of complexes **2b**, **6a**, and **6b**, and Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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