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Novel Thiophene-Based Cycloruthenated Compounds: Synthesis, Characterization, and Reactivity

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The reactions between a series of thiophene-based imines with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$, in a basic medium, and in MeCN give a family of ruthenacycles of stoichiometry $[Ru(C\hat{}N)(NCMe)_4]PF_6$ (C^N = orthometalated thiopheneimine). In these species, the C−H activation process is produced in most cases at the thiophene ring. When two C−H bonds are competing (thiophene vs aryl), the cyclometalation can be driven regioselectively to the thiophene unit or to the aryl ring as a function of the location of the iminic C═N bond. Cyclometalation can also be oriented to positions 2 or 3 of the thiophene depending on the situation of the imine in the heterocycle (3 or 2, respectively). In all studied cases, the $\eta^6\text{-}C_6H_6$ ligand was substituted by acetonitrile. The X-ray structures of two representative complexes have been determined. These thiophene-based metallacycles react with iodine under very mild conditions affording, after hydrolysis, substituted 3-iodo-2-formyl(benzo)thiophenes or substituted 2-iodo-3-formyl(benzo)thiophenes, as a function of the organometallic precursor.

Introduction

Cyclometalation, discovered in the early 1960s, has become one of the most popular and useful organometallic reactions,[1] mainly because this strategy represents a mild route for activating C−H bonds selectively, displaying an enormous synthetic potential. Metallacycles have been widely applied in catalysis and metal-mediated organic syntheses,[2] and in the last years, a renewal of interest in these species has appeared, motivated by the multiple applications exhibited by these organometallic entities in several domains of the chemistry. For example, they have been used as sensors,[3] liquid-crystal materials,[4] anticancer agents, or other biorganometallic applications.[5] Although palladium is, without any doubt, the transition metal that has been the most studied to promote the formation of metallacycles,[6] because cyclopalladated compounds are known for numerous families of ligands to date, it is well-known that other metals can be successfully employed for the synthesis of cyclometalated species. In particular, cycloruthenated compounds have emerged in the past

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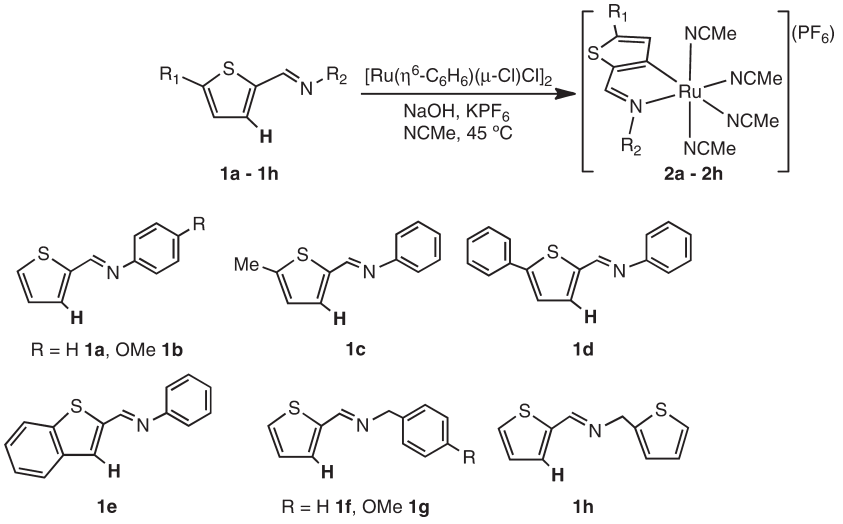
Scheme 1. Synthesis of Ruthenacycles **2a**−**2h**, Showing the Position of the C−H Bond Activated



few years as an extraordinarily versatile family of molecules,[7] displaying interesting applications in several fields. For example, their unique photophysical and electrochemical properties have been exploited in the design of sensitizers for solar cells[8] or electron shuttles in redox-catalyzed processes.[9] In addition, ruthenacycles have been found to display an appealing potential as antitumor agents[10] and are among the most active catalysts reported to date for transfer hydrogenation reactions.[11] It is also remarkable that ruthenium derivatives have been successfully employed to promote organic transformations, presenting in some cases behaviors complementary to those of their much more studied palladium counterparts.[7]

Various examples have appeared recently in the literature dealing with the synthesis of ruthenacycles, implying the participation of a vast range of precursors and ligand settings.[7] However, the number of cycloruthenated complexes from heterocyclic rings is still scarce.[12] Particularly interesting in this aspect is the synthesis of thiophene-containing cyclometalated species, considering that thiophene-based materials are a very important class of organic materials because of their biological, electronic, magnetic, and optical properties.[13] The combination of thiophene moieties with cycloruthenated units could lead to a promising family of complexes with potential in all of the aforementioned areas of chemistry and materials science (solar cells, anticancer activity, electron shuttles, etc.). Moreover, cycloruthenation could offer an attractive alternative strategy for the selective syntheses of modified thiophenes, which continue to attract the attention of synthetic chemists because of their inherent interest (building blocks for synthesis, biological activity, etc.).

For these reasons, we have studied cycloruthenation of thiophene-based imines. We have found that these compounds can be orthometalated selectively under mild conditions. In addition, the cycloruthenated species are adequate starting compounds for the synthesis of iodo-modified thiophenes, an unprecedented reaction in ruthenium complexes, and which provide alternative pathways for the synthesis of these interesting compounds.

Results and Discussion

1. Synthesis of the Cycloruthenated Complexes. The starting imines **1a**−**1o** have been prepared using conventional procedures (see the Experimental Section),[14] which consist of condensation of the appropriate formylthiophene with aniline, benzylamine, or 2-thienylmethylamine. The imines **1a**−**1h** were reacted with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ and KPF_6 (2:1:4 molar ratio) under the same experimental conditions as those reported previously by Pfeffer and co-workers for cycloruthenation of amines (NaOH, 45 °C,

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NCMe).[15] Under these conditions, the orthoruthenated derivatives $[(C^{\wedge}N)Ru(NCMe)_4]PF_6$ (**2a**−**2h**; C^N = cycloruthenated imine; see Scheme 1) were obtained in good yields after flash chromatography over aluminum oxide. Reactions carried out using 2-thienylamine or 2-formylthiophene failed to afford cyclometalated derivatives under the same experimental conditions, indicating that the presence of the imine moiety as a directing group is critical. It was also noted that $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ was a better starting material for obtaining the desired cycloruthenated derivatives than $[(\eta^6\text{-}p\text{-}MeC_6H_4{}^iPr)RuCl(\mu\text{-}Cl)]_2$, an observation commonly interpreted as an indication of the operation of an S_EAr mechanism.[7]

Complexes **2a**−**2h** were fully characterized by NMR spectroscopy, elemental analyses, and mass spectrometry. In addition, complexes **2b** and **2f** were characterized by X-ray diffraction methods (see the crystallographic analyses section). In all studied cases, C−H bond activation takes place regioselectively at the heterocyclic ring, despite the presence of diverse C−H bonds suitable for activation or different directing groups (the imine N atom and the sulfur S atom). Activation of the proton at the 3 position on the thiophene ring is inferred from the ^{1}H NMR spectra of **2a**−**2h**, which showed the disappearance of the characteristic resonance of H_3 of the thiophene moiety. The presence of C_3 σ-bound to the ruthenium center was evidenced by an extremely low-field signal in the ^{13}C NMR spectra (about 200 ppm). Analysis of the spectroscopic data also indicates that the η^6-C_6H_6 ring was replaced by acetonitrile ligands, leading to the formation of octahedral species where the ruthenium coordination sphere is formed by the cyclometalated ligand, bound to the metallic center through the N atom of the imine and one carbon of the thiophene moiety, and four acetonitrile ligands. Displacement of the arene ligands by acetonitrile is a rather common process in the chemistry of the cycloruthenated species[16] and is attributed to the weakening of the metal−arene bond by the strong coordinating character of the cyclometalated ligand.[7,15]

Remarkably, the reaction tolerates the presence of alkyl and aryl groups in the thiophene moiety, as demonstrated by the formation of complexes **2c** and **2d**, containing a methyl group and a phenyl group, respectively (Scheme 1). However, when we attempted orthometalation of imines with electron-withdrawing substituents such as chlorine [SC_4H_2-2-(CH=NPh)-5-Cl] (**1p**) or nitro [SC_4H_2-2-(CH=NPh)-5-NO_2] (**1q**), no transformation was observed, suggesting once more that C−H bond activation occurs through a S_EAr mechanism, in line with previous observations. It is worth noting that this synthetic strategy seems to be valid not only for substituted thiophenes but also for benzothiophenes. For example, the benzothiopheneimine **1e** (Scheme 1) can be successfully orthometalated by reaction with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ under the conditions described above. The compound obtained, **2e**, has incorporated the Ru atom at position 3 of the benzothiophene ring, showing that the presence of the fused aryl ring does not have a significant influence on the reaction result and that the method is applicable to a wide variety of substrates.

C−H bond activation at the thiophene unit in **2a**−**2e** occurs as expected because cyclometalation of the aryl ring is, in principle, disfavored by the fact that it would lead to the formation of highly strained four-membered metallacycles. More interestingly, when these reaction conditions were applied to the thiophene-based benzylamines **1f** and **1g**, where both the heterocycle and the arene units are capable of forming five-membered metallacycles, only the thiophene moiety undergoes cyclometalation through C−H activation, yielding complexes **2f** and **2g**. Therefore, the size of the resulting metallacycle is not a discriminating factor for the orientation of cycloruthenation, and other parameters have to be considered. The preferred orthometalation of the electron-rich thiophene ring, compared with the aryl ring, is in good agreement with a S_EAr mechanism operating for C−H bond activation, in line with previous observations and with the higher reactivity toward electrophiles of the heterocycle versus the arene.[17] In addition, we have to consider that in complexes **2a**−**g** the iminic C=N bond belongs to the ruthenacycle; that is, it is endocyclic. These types of endo structures are typically more stable than the corresponding ones with the C=N bond exocyclic (for instance, those derived from ruthenation at the aryl ring) because of the endo effect.[18] This thermodynamic effect is related to the additional stabilization gained by conjugation of the π-electron density of the C=N double bond, that of the heterocycle, and the appropriate orbitals of the metal. In our experience in dealing with palladium complexes and different types of ligands, the endo effect could be a very strong directing factor and its importance should not be neglected.[18k−n,19] Aiming to determine the importance of the endo effect in the outcome of these reactions, we have carried out cycloruthenation of the bis(imine)thiophene **1h**, which contains two nonequivalent thiophene rings, and this allowed us to minimize the influence of the nature of the aromatic ring. When imine **1h** was reacted with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ under the same experimental conditions

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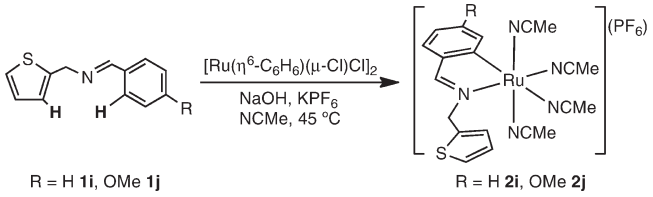
Scheme 2. Synthesis of Thiophene-Based Ruthenacycles **2i** and **2j**



as those described for **1a**−**1g**, complex **2h** was isolated as the only organometallic product, and it was characterized as the endo isomer (Scheme 1). The endo arrangement was determined by selective NOESY-1D experiments, where it was found that irradiation of the signal at 5.12 ppm, attributed to the CH_2 moiety, causes enhancement of the signals at 8.42 and 7.08 ppm, assigned respectively to the imine proton and the thienyl H atom located in the β position of the nonmetalated heterocyclic ring. This fact implies that the thiophene connected to the CH_2 unit keeps the three protons and, therefore, indicates that metalation has taken place in the other thiophene moiety. Irradiation of the imine proton only gave enhancement of the CH_2 unit, as expected for an endo complex. These observations permit one to conclude that when similar electronic conditions are present, the C−H activation process seems to favor formation of the isomer with an endo configuration because it is thermodynamically more stable.[19] It should be noted here that analysis of the reaction crudes has not allowed detection of the presence of exo isomers, although their existence could not be fully discarded.

Once the importance of C=N bond location in systems with similar electron densities was probed (two thiophene rings in **2h**), the next step was investigation of the selectivity of the process when the imine does not belong to the thiophene moiety. The reaction of the Schiff bases **1i** and **1j** with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ under the same conditions as those described above yielded complexes **2i** and **2j** (see Scheme 2), where the benzyl rings were cyclometalated selectively.

The regiochemistry of **2i** and **2j** was initially inferred from the spectroscopic NMR data, where the lack of one of the aryl protons is observed and the thiophene integrity is retained, and, once more, the spectroscopic data indicated that the benzene unit is replaced by acetonitrile ligands. These structural characteristics were confirmed, in the case of **2j**, by an X-ray diffraction study. The poor quality of the data provides a structure not amenable for a discussion of the distances and angles. However, it clearly confirms the connectivity deduced from the NMR data. A drawing of the cation present in **2j** is showed in Figure 1.

Formation of the endo complexes **2i** and **2j** is completely regioselective despite the fact that the thiophene ring seems to be more prone to undergo cyclometalation, assuming a S_EAr mechanism for C−H bond activation. Therefore, formation of **2i** and **2j** indicates that the thermodynamic endo effect is a critical factor in controlling the regiochemistry of these reactions. As a far as we know, the importance of this effect in the formation of ruthenacycles has never been noted previously.

The synthetic strategy described above can be easily expanded for the synthesis of complexes in which C−H activation has occurred at the 2 position of the thiophene,

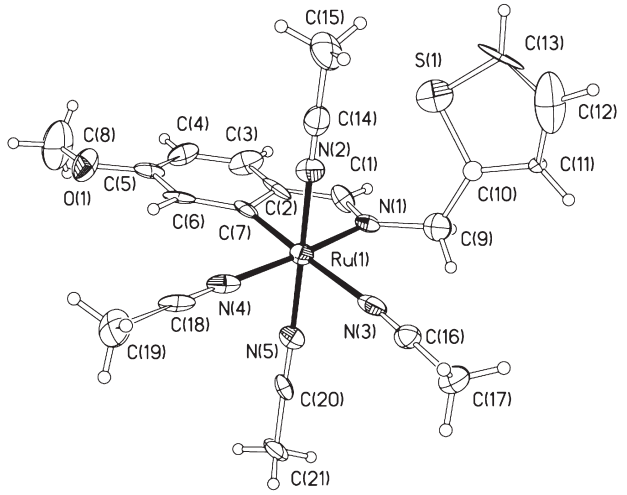


Figure 1. Side view of complex **2j** showing the labeling scheme.

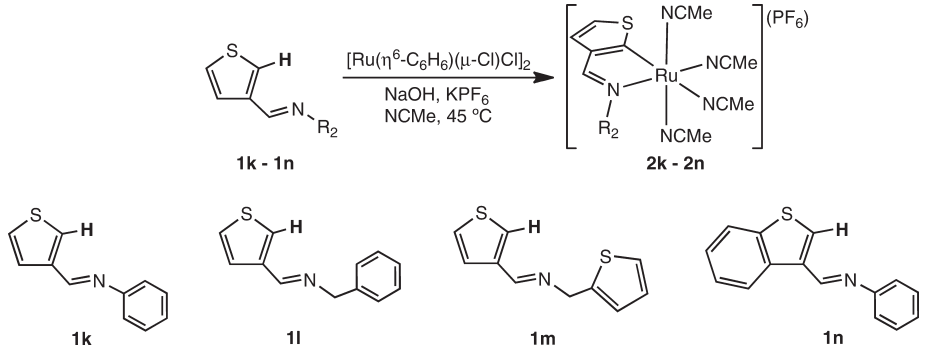
as shown in the Scheme 3. The use of the imines **1k**−**1n** (see Scheme 3) presents the same problem of competitive orthometalation between the thiophene and aryl rings. The presence of the iminic C=N double bond at the 3 position of the thiophene moiety ensures, in principle, formation of the endocyclic isomer by C−H bond activation at the heterocyclic ring. However, even for the endocyclic compound, two different positions, 2 and 4, could be activated, affording two different isomers. The reaction of the imines **1k**−**1n** with $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$, always using the same experimental conditions, affords the corresponding orthoruthenated derivatives **2k**−**2n**, as shown in Scheme 3. Replacement of the benzene ring by acetonitriles also takes place in these reactions. All complexes were fully characterized by analytical and spectroscopic methods, following the same key features as those described for **2a**−**2j**.

In all cases studied, metalation gives the expected endo derivatives and, moreover, it has occurred selectively at the 2 position of the thiophene, as expected for the higher reactivity of this position in electrophilic substitution processes.[20] Traces of other isomers were not observed in the reaction crudes. The reaction is, therefore, totally regioselective with respect to the ring to be metalated and to the position of metalation on the thiophene. As previously explained, the endo effect is responsible of the selective metalation of **1k**−**1m** (the endo character of complex **2m** was determined by selective NOESY-1D experiments) because the same pattern of reactivity as that observed in **2a**−**2h** is found here. However, even if metalation at the 2 position is the most favored process,[20] selectivity of the reaction is noteworthy in the case of **1n** because metalation at the 5 position of benzothiophene, with concomitant formation of a six-membered ruthenacycle, could be competitive with the formation of **2n**.

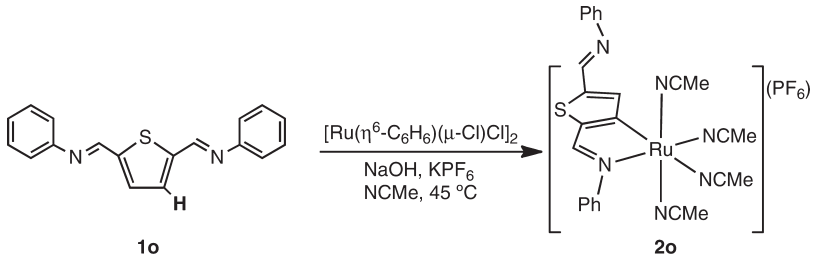
To test the possibility of achieving a double cycloruthenation over the same thiophene ring, the 2,5-bis(imine)-thiophene **1o** was treated with the ruthenium source $[(\eta^6\text{-}C_6H_6)RuCl(\mu\text{-}Cl)]_2$ and KPF_6 (1:1:4 molar ratio), in a basic medium and with acetonitrile as the solvent, affording

(20) Katritzky, A. R.; Taylor, R. *Electrophilic Substitution of Heterocycles, Quantitative Aspects*, Advances in Heterocyclic Chemistry Series; Academic Press: San Diego, CA, 1990; Vol. *47*.

Scheme 3. Synthesis of Ruthenacycles **2k**−**2n**, Showing the Position of the C−H Bond Activated



Scheme 4. Orthometalation of the Bis(imine) **1o**



monocycloruthenated complex **2o** as the only organometallic compound, as shown in Scheme 4. We have attempted different metal/ligand molar ratios and different reaction conditions, but in all cases, **2o** was the only detected species. Probably the presence of the strongly electron-attracting ruthenium metal on the heterocycle deactivates it toward a second orthoruthenation. The presence of three singlets in the ^{1}H NMR spectrum of **2o** (two imine protons and one thiophene proton) accounts for activation of only one of the two heterocyclic protons. Incorporation of only one $Ru(NCMe)_4$ unit to the thiophene moiety is evident from the ^{1}H and ^{13}C NMR spectra but also from the obtained values of elemental analysis and mass spectrometry.

In summary, we have obtained cycloruthenated complexes through C−H bond activation of different thiopheneimine-based ligands. The presence of the imine moiety as a directing group is critical to achieving orthometalation. The reaction is totally regioselective and, in all cases, seems to be driven by the endo effect. The presence of the ruthenium center in different selected points of the thiophene skeleton opens the possibility of further modification of these substrates in a regioselective manner.

2. Iodination Reactions. Halogenation of aromatic compounds is one of the fundamental reactions in organic chemistry.[21] The use of palladacycles as intermediates for the introduction of the halogen functional group has emerged as an attractive strategy[22] because it (a) displays a complete regioselectivity for orthohalogenated compounds, thus providing a complementary method to the most commonly used approaches (e.g., S_EAr or directed lithiation) and (b) eliminates the need to use electron-rich substrates or strong acids/bases. However, as far as we know, no other metal has never been successfully employed to promote the selective orthohalogenation of organic substrates via cyclometalation. We present here the first examples in which a non-palladium-based metallacycle has been demonstrated to react with halogens, providing reliable access to key compounds.

The reaction of **2a** with I_2 in wet acetonitrile affords, after hydrolysis "in situ", the corresponding 2-formyl-3-iodothiophene **3a** (Scheme 5),[23] which can be extracted from the crude mixture with Et_2O.

This halogenation process seems to be general and tolerates different functional groups. The reaction of **2c** and **2d** with elemental iodine, under the same experimental conditions, affords the corresponding 5-methyl-3-iodo-2-formylthiophene (**3c**) and 5-phenyl-3-iodo-2-formylthiophene (**3d**) in very good yields. Characterization of **3c** and **3d** as iodine derivatives is clear from the observation of signals at 96.8 and 105.0 ppm, respectively, in the ^{13}C NMR spectra, typical of the C−I groups.[24] Moreover, treatment of the benzothiophene complex **2e** affords in a clean way 3-iodo-2-formylbenzothiophene (**3e**), showing the versatility of the method. Reactions carried out under analogous conditions with metal-free imines failed to afford the respective halogenated compounds,

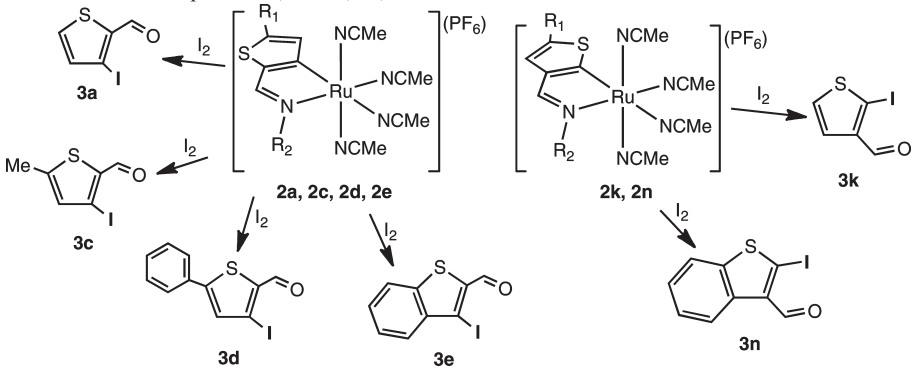
(21) (a) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, 1990. (b) De La Mare, P. B. *Electrophilic Halogenation*; Cambridge University Press: Cambridge, U.K., 1976; Chapter 5.

(22) (a) Kalyani, D.; Dick, R. A.; Anani, Q. W.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 11483. (b) See ref 2g. (c) Giri, R.; Chen, X.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2005**, *44*, 2112.

(23) Synthesis of 3-iodo-2-formylthiophene (**3a**): (a) Antonioletti, R.; D'Auria, M.; D'Onofrio, F.; Piancatelli, G.; Scettri, A. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1755. (b) Guillard, R.; Fournari, P.; Person, M. *Bull. Soc. Chim. Fr.* **1967**, 4121. (c) Sonoda, M.; Kinoshita, S.; Lu, T.; Fukuda, H.; Miki, K.; Umeda, R.; Tobe, Y. *Synth. Commun.* **2009**, *39*, 3315. Synthesis of 2-iodo-3-formylthiophene (**3n**): Wunderlich, S. H.; Knochel, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 7685. Synthesis of 2-iodo-3-formylthiophene (**3k**): Gronomitz, S.; Dahlgren, T. *Chem. Scr.* **1977**, *12*, 57.

(24) Prestch, E.; Bühlman, P.; Affolter, C.; Herrera, A.; Martínez, R. *Structural Determination of Organic Compounds*; Springer-Verlag Ibérica: Barcelona, Spain, 2001.

Scheme 5. Syntheses of the Iodinated Thiophenes **3a**, **3c**−**3e**, **3k**, and **3n**



demonstrating the fundamental role played by the ruthenium complex. The water in NCMe promotes the final hydrolysis of the putative haloimine intermediate to give the haloaldehyde.

This method can also be applied to the synthesis of other haloformylthiophenes. Therefore, the reaction **2k** or **2n** with I_2 in wet acetonitrile affords the corresponding 2-iodo-3-formylthiophene (**3k**) or 2-iodo-3-formylbenzothiophene (**3n**). These compounds can be isolated in pure form following the same workup as that described previously for **3a** and **3c**−**3e**.

These results offer a promising new synthetic strategy for the formation of 3-iodo-2-formylthiophenes and 2-iodo-3-formylthiophenes, key precursors in the production of multiple thiophene-based materials. This strategy, moreover, is of considerable interest because, contrary to all of the procedures described previously,[23] it offers a synthetic pathway for the selective introduction of a halogen ortho to a preexisting aldehyde in position 2, a regiochemistry that is especially difficult to achieve in this kind of heterocycle because positions 4 and 5 are typically more reactive.

The advantage of this method in terms of accessibility and selectivity is counterbalanced by the drawback of the use of stoichiometric quantities of ruthenium. This makes this method noncompetitive with the traditional organic procedures when simple compounds such as **3a** are considered.[23] However, in the case of the more substituted derivatives, this method can be considered as at least an alternative to the usual preparative procedures, avoiding the use of unstable lithium intermediates, which are difficult to handle and require very low temperatures and where, in some cases, it is difficult to control the position of lithium incorporation. In addition, as far as we know, catalytic halogenation of the heterocycles has not been carried out using palladacycles, in spite of impressive recent developments on arylic substrates.[2g]

3. Crystallographic Analysis of 2b and 2f. The crystal structures of complexes **2b** and **2f** have been determined by X-ray diffraction methods. Representations of the cations present in **2b** and **2f** are shown in Figures 2 and 3, respectively. The two molecules are isostructural and show the Ru atom in an octahedral environment, surrounded by the C and N atoms of the orthometalated thiopheneimine ligand and by the four N atoms of the four acetonitrile ligands.

The distance Ru(1)−C(5) [1.950(9) Å] in **2b** is shorter than those observed for other ruthenacycles [range: 2.076(3)−2.114(4) Å] containing cyclometalated thiophene moieties.[12a,e−g] This shorter distance could be related to the large downfield shift observed in the ^{13}C NMR spectrum for this carbon, suggesting a partial double-bond character. This fact has been observed in other ruthenium complexes.[12b,e] The Ru−N bond lengths imply that the

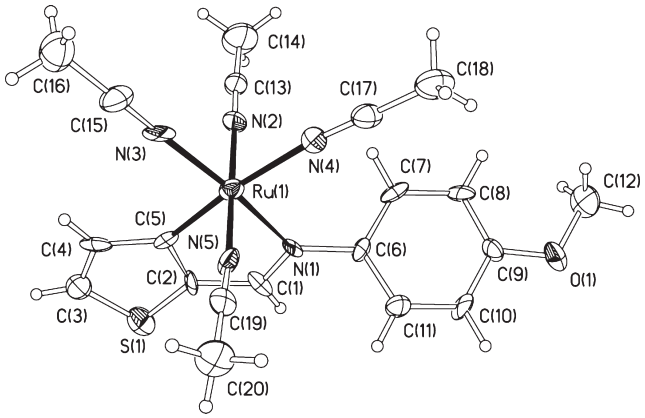


Figure 2. Side view of the cation of **2b**. The PF_6 counteranion has been removed for clarity. Selected distances (Å) and angles (deg): Ru(1)−C(5) 1.950(9), Ru(1)−N(1) 2.081(8), Ru(1)−N(2) 1.975(9), Ru(1)−N(3) 1.992(9), Ru(1)−N(4) 2.076(8), Ru(1)−N(5) 1.995(9); C(5)−Ru(1)−N(1) 79.6(3), N(2)−Ru(1)−N(1) 89.4(3), N(3)−Ru(1)−N(5) 89.9(4), N(5)−Ru(1)−N(1) 92.0(3).

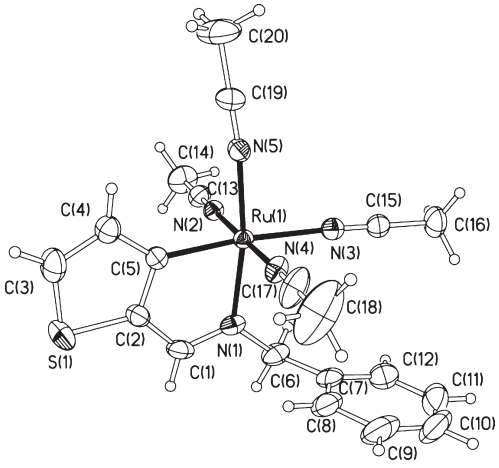


Figure 3. Side view of the cation of complex **2f**. The PF_6 counteranion has been removed for clarity. Selected distances (Å) and angles (deg): Ru(1)−C(5) 2.018(3), Ru(1)−N(1) 2.069(2), Ru(1)−N(2) 2.010(2), Ru(1)−N(3) 2.139(3), Ru(1)−N(4) 2.006(3), Ru(1)−N(5) 2.024(3); C(5)−Ru(1)−N(1) 79.81(11), N(2)−Ru(1)−N(1) 86.71(9), N(5)−Ru(1)−N(1) 170.49(10), N(4)−Ru(1)−N(5) 90.72(10).

chelating imine falls in the usual range of distances found in related structural arrangements.[12] As expected, the Ru−N bond distance for the nitrile located in a trans position with respect to the metalated carbon, Ru(1)−N(3), is slightly longer than the others because of the large trans influence of the σ-bound carbon.

The geometric features of **2f** are similar to the ones observed for **2b**, with a C(5)−Ru(1) bond distance of 2.018(3) Å and a little longer Ru−N distance [Ru(1)−N(3) 2.139(3) Å] for the MeCN situated trans to the metalated carbon. Other structural parameters are as expected and do not merit further comments.

Conclusion

In this Article, we present a versatile strategy for the synthesis of thiophene-based cycloruthenated compounds employing imine units as directing groups. The regiochemistry of these processes is governed by the endo effect, which permits one to direct C−H activation to the heterocycle or to the arene unit. Reactions between these novel organometallic entities and iodine allow for the practical and reproducible syntheses of iodinated formylthiophenes, a strategy based on an unprecedented selective halogenation of ruthenacycles.

Experimental Section

General Methods. Solvents were dried and distilled using standard procedures before use. All reactions were carried out under an argon atmosphere using standard Schlenk techniques. Elemental analyses were carried out with a Perkin-Elmer 2400-B microanalyzer. ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded in CD_3CN or $CDCl_3$ solutions at 25 °C on Bruker AV300, AV400, or Varian Gemini 300 spectrometers (δ in ppm and *J* in Hz) at a ^{1}H NMR operating frequency of 300.13 or 400.13 MHz. ^{1}H and ^{13}C NMR spectra were referenced using the solvent signal as an internal standard, while ^{19}F NMR spectra were referenced to $CFCl_3$ and ^{31}P NMR spectra were externally referenced to H_3PO_4 (85%). The SELNO-1D ^{1}H NMR experiments were performed with optimized mixing times (D8), depending of the irradiated signal. Positive-mode electrospray ionization mass spectrometry (ESI^+ MS) 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.

Imines 1a−1o: General Procedure. The corresponding aldehyde (2.5 mmol) was dissolved in CH_2Cl_2 (15 mL). $MgSO_4$ (0.5 g) was added together with the respective amine (2.5 mmol), and the suspension was stirred overnight at room temperature under an argon atmosphere. Then the mixture was filtered to remove $MgSO_4$ and the solvent removed under reduced pressure. The imines were recovered, and when needed, they were purified according to the reported procedures. The spectral data of the previously reported imines **1a−1c**, **1f−1l**, **1o**, and **1q** were compared with the literature data to confirm their structures.[14] The new imines **1d**, **1e**, **1n**, and **1p** were recystallizated from dichloromethane (DCM)/pentane prior to use, and the imine **1m** was recovered and used without further purification. All of the new imines employed were fully characterized by NMR spectroscopy, mass spectrometry, and elemental analysis.

Imine 1d [SC_4H_2-2-(CH=NPh)-5-Ph]. Yield: yellow solid (0.569 g, 86%). Anal. Calcd for $C_{17}H_{13}NS$: C, 77.53; H, 4.98; N, 5.32; S, 12.17. Found: C, 77.73; H, 4.74; N, 5.19; S, 11.97. MS (ESI^+): *m*/*z* 264.0 ($[M + H]^+$). ^{1}H NMR ($CDCl_3$): δ 8.56 (s, 1H, N=C*H*), 7.71 (m, 2H), 7.47−7.36 (m, 7H), 7.29−7.26 (m, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 152.9 (s, CH), 151.4 (s, C), 149.0 (s, C), 141.8 (s, C), 133.8 (s, C), 133.3 (s, CH), 129.3 (s, CH), 129.2 (s, CH), 129.0 (s, CH), 126.1 (s, CH), 126.0 (s, CH), 123.6 (s, CH), 121.1 (s, CH).

Imine 1e [SC_8H_5-2-(CH=NPh)]. Yield: white solid (0.578 g, 97%). Anal. Calcd for $C_{15}H_{11}NS$: C, 75.92; H, 4.67; N, 5.90; S, 13.51. Found: C, 75.63; H, 4.51; N, 5.75; S, 13.27. MS (ESI^+): *m*/*z* 238.0 ($[M + H]^+$). ^{1}H NMR ($CDCl_3$): δ 8.71 (s, 1H, N=C*H*), 7.92−7.84 (m, 2H, C_6H_4), 7.73 (s, 1H, thiophene), 7.46−7.40 (m, 4H, 2 C_6H_4 + 2 Ph), 7.31−7.28 (s, 3H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 158.6 (s, CH), 151.1 (s, C), 143.0 (s, C), 141.1 (s, C), 139.3 (s, C), 129.6 (s, CH), 129.2 (s, CH), 126.5 (s, CH), 126.4 (s, CH), 124.8 (s, CH), 124.7 (s, CH), 122.9 (s, CH), 121.13 (s, CH).

Imine 1m [SC_4H_3-3-(CH=NC_4H_3S)]. Yield: orange oil (0.491 g, 95%). Anal. Calcd for $C_{10}H_9NS_2$: C, 57.94; H, 4.38; N, 6.76; S, 30.93. Found: C, 57.41; H, 4.23; N, 6.25; S, 30.39. MS (ESI^+): *m*/*z* 207.9 ($[M + H]^+$). ^{1}H NMR ($CDCl_3$): δ 8.36 (s, 1H, N=C*H*), 7.64 (m, 2H), 7.33 (m, 1H), 7.27 (s, 1H), 7.04 (m, 2H), 4.96 (s, 2H, CH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 156.6 (s, CH), 142.1 (s, C), 140.3 (s, C), 129.2 (s, CH), 127.0 (s, CH), 126.6 (s, CH), 125.9 (s, CH), 125.1 (s, CH), 124.9 (s, CH), 59.3 (s, CH_2).

Imine 1n [SC_8H_5-3-(CH=NPh)]. Yield: pale-yellow solid (0.571 g, 96%). Anal. Calcd for $C_{15}H_{11}NS$: C, 75.92; H, 4.67; N, 5.90; S, 13.51. Found: C, 75.67; H, 4.70; N, 5.70; S, 13.15. MS (ESI^+): *m*/*z* 237.9 ($[M + H]^+$). ^{1}H NMR ($CDCl_3$): δ 9.00 (dd, 1H, C_6H_4, $^{3}J_{HH}$ = 8.40, $^{4}J_{HH}$ = 1.20), 8.75 (s, 1H, N=C*H*), 7.99 (s, 1H, thiophene), 7.91 (dd, 1H C_6H_4, $^{3}J_{HH}$ = 7.80, $^{4}J_{HH}$ = 0.60), 7.56−7.44 (m, 4H, 2 C_6H_4 + 2 Ph), 7.30−7.28 (s, 3H, Ph). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 154.9 (s, CH), 152.6 (s, C), 140.9 (s, C), 136.6 (s, C), 134.8 (s, CH), 134.3 (s, C), 129.3 (s, CH), 125.9 (s, CH), 125.6 (s, CH), 125.5 (s, CH), 125.4 (s, CH), 122.6 (s, CH), 121.0 (s, CH).

Imine 1p [SC_4H_3-2-(CH=NPh)-5-Cl]. Yield: orange solid (0.511 g, 92%). Anal. Calcd for $C_{11}H_8NSCl$: C, 59.59; H, 3.64; N, 6.32; S, 14.46. Found: C, 59.34; H, 3.39; N, 6.28; S, 13.99. MS (ESI^+): *m*/*z* 221.9 ($[M + H]^+$). ^{1}H NMR ($CDCl_3$): δ 8.34 (s, 1H, N=C*H*), 7.31−7.28 (s, 2H), 7.18−7.11 (m, 4H), 6.88 (d, 1H, thiophene, $^{3}J_{HH}$ = 5.20). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 151.5 (s, CH), 150.3 (s, C), 141.0 (s, C), 135.2 (s, C), 130.8 (s, CH), 128.6 (s, CH), 126.4 (s, CH), 125.7 (s, CH), 120.4 (s, CH).

Ruthenacycles: General Procedure. To a suspension of [(η^6-benzene)RuCl(μ-Cl)]$_2$ (0.100 g, 0.2 mmol), NaOH (0.016 g, 0.4 mmol), and KPF_6 (0.146 g, 0.8 mmol) in MeCN (25 mL) was added the corresponding imine (0.4 mmol), and the mixture was stirred at 45 °C under argon for 48 h. The resulting solution was evaporated in vacuo to dryness. The residue was purified by flash chromatography over Al_2O_3 using MeOH/DCM (1−3%) as the eluent, the orange fraction was collected and concentrated in vacuo to a minimum volume, and a solid precipitated upon the addition of Et_2O (15 mL). The precipitate was washed several times with Et_2O, affording the desired product. The complexes appeared to be very sensitive to oxidation, turning quickly green when exposed to air. Signals due to the NCMe ligands could not be properly assigned on the ^{1}H NMR spectra because of overlap and fast exchange with the deuterated solvent.

Compound 2a. Yield: orange solid (0.125 g, 52%). Anal. Calcd for $C_{19}H_{20}N_5SPF_6Ru\cdot MeCN$: C, 39.56; H, 3.64; N, 13.18; S, 5.03. Found: C, 39.58; H, 3.31; N, 13.52; S, 5.43. MS (ESI^+): *m*/*z* 411.0 ($[M - MeCN]^+$). $^{31}P\{^{1}H\}$ NMR (CD_3CN): δ −144.6 (hpt, $^{1}J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^{1}H NMR (CD_3CN): δ 8.41 (d, 1H, N=C*H*, $^{5}J_{HH}$ = 0.40), 7.82 (d, 1H, thiophene, $^{3}J_{HH}$ = 4.80), 7.62 (dd, 1H, thiophene, $^{3}J_{HH}$ = 4.80, $^{5}J_{HH}$ = 0.40), 7.45−7.41 (m, 2H, Ph), 7.31−7.27 (m, 3H, Ph). $^{13}C\{^{1}H\}$ NMR (CD_3CN): δ 201.2 (s, C, *C*−Ru), 166.9 (s, CH, N=*C*), 152.0 (s, C), 137.5 (s, C), 135.9 (s, CH, thiophene), 132.8 (s, CH, thiophene), 128.7 (s, CH, Ph), 126.0 (s, CH, Ph), 124.1 (s, C, Me*C*N), 123.8 (s, C, Me*C*N), 122.9 (s, CH, Ph), 122.3 (s, C, Me*C*N), 3.3 (s, CH_3, *Me*CN), 3.2 (s, CH_3, *Me*CN), 2.9 (s, CH_3, *Me*CN).

Compound 2b. Yield: orange solid (0.127 g, 51%). Anal. Calcd for $C_{20}H_{22}N_5OSPF_6Ru$: C, 38.34; H, 3.54; N, 11.18; S, 5.12. Found: C, 37.98; H, 3.19; N, 11.52; S, 4.73. MS (ESI^+): *m*/*z* 441.0 ($[M - MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.37 (s, 1H, N=C*H*), 7.80 (d, 1H thiophene, $^3J_{HH}$ = 4.80), 7.61 (d, 1H, thiophene, $^3J_{HH}$ = 4.80), 7.25−7.23 (m, 2H, C_6H_4OMe), 6.98−6.95 (m, 2H, C_6H_4OMe), 3.84 (s, 3H, O*Me*). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 200.1 (s, C, *C*−Ru), 166.1 (s, CH, N=*C*), 158.0 (s, C), 145.8 (s, C), 137.4 (s, C), 135.9 (s, CH, thiophene), 132.3 (s, CH, thiophene), 129.8 (s, C, Me*C*N), 128.0 (s, C, Me*C*N), 123.8 (s, CH, C_6H_4OMe), 122.3 (s, C, Me*C*N), 113.7 (s, CH, C_6H_4OMe), 55.2 (s, CH_3, O*Me*), 3.3 (s, CH_3, *Me*CN), 3.2 (s, CH_3, *Me*CN), 2.9 (s, CH_3, *Me*CN). Single crystals suitable for X-ray diffraction analysis were obtained by the slow diffusion of Et_2O into a solution of **2b** in MeCN.

Compound 2c. Yield: red solid (0.139 g, 57%). Anal. Calcd for $C_{20}H_{22}N_5SPF_6Ru$: C, 39.35; H, 3.63; N, 11.47; S, 5.25. Found: C, 39.42; H, 3.67; N, 11.87; S, 5.19. MS (ESI^+): *m*/*z* 425.0 ($[M - MeCN]^+$. $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.24 (s, 1H, N=C*H*), 7.43−7.38 (m, 2H, Ph), 7.32 (s, 1H, thiophene), 7.30−7.25 (m, 3H, Ph). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 204.9 (s, C, *C*−Ru), 165.9 (s, CH, N=*C*), 152.5 (s, C), 149.3 (s, C), 136.4 (s, C), 135.6 (s, CH, thiophene), 128.7 (s, CH, Ph), 125.8 (s, CH, Ph), 123.9 (s, C, Me*C*N), 123.0 (s, C, Me*C*N), 122.4 (s, CH, Ph), 120.1 (s, C, Me*C*N), 15.0 (s, CH_3, *Me*−thiophene), 3.3 (s, CH_3, *Me*CN), 3.2 (s, CH_3, *Me*CN), 2.9 (s, CH_3, *Me*CN).

Compound 2d. Yield: dark-red solid (0.141 g, 52%). Anal. Calcd for $C_{25}H_{24}N_5SPF_6Ru \cdot 0.5MeCN$: C, 45.06; H, 3.71; N, 11.11; S, 4.63. Found: C, 45.68; H, 3.25; N, 10.82; S, 5.02. MS (ESI^+): *m*/*z* 487.0 ($[M - MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.40 (s, 1H, N=C*H*), 7.98 (s, 1H, thiophene), 7.87−7.84 (m, 2H, Ph), 7.50−7.48 (m, 4H, Ph), 7.46−7.31 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 203.8 (s, C, *C*−Ru), 166.4 (s, CH, N=*C*), 152.4 (s, C), 151.7 (s, C), 138.2 (s, C), 134.6 (s, C), 132.9 (s, CH, thiophene), 129.1 (s, CH, Ph), 128.7 (s, CH, Ph), 128.2 (s, CH, Ph), 126.2 (s, CH, Ph), 126.0 (s, CH, Ph), 124.3 (s, C, Me*C*N), 123.8 (s, C, Me*C*N), 122.9 (s, CH, Ph), 122.5 (s, C, Me*C*N), 3.5 (s, CH_3, *Me*CN), 3.2 (s, CH_3, *Me*CN), 2.9 (s, CH_3, *Me*CN).

Compound 2e. Yield: yellow solid (0.127 g, 49%). Anal. Calcd for $C_{23}H_{22}N_5SPF_6Ru \cdot CH_2Cl_2$: C, 39.41; H, 3.31; N, 9.57; S, 4.38. Found: C, 39.75; H, 3.59; N, 9.81; S, 4.24. MS (ESI^+): *m*/*z* 460.8 ($[M - MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.58 (s, 1H, N=C*H*), 8.53−8.50 (m, 1H, C_6H_4), 8.03−8.00 (m, 1H, C_6H_4), 7.53−7.48 (m, 4H, 3 Ph + 1 C_6H_4), 7.42−7.36 (m, 3H, 2 Ph + 1 C_6H_4). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 199.6 (s, C, *C*−Ru), 168.3 (s, CH, N=*C*), 152.3 (s, C), 149.7 (s, C), 145.4 (s, C), 135.5 (s, C), 128.8 (s, CH), 128.7(s, CH), 126.4 (s, CH), 126.3 (s, CH), 124.0 (s, CH), 123.9 (s, C, Me*C*N), 123.8 (s, C, Me*C*N), 123.0 (s, CH), 123.1 (s, CH), 122.6 (s, C, Me*C*N), 3.3 (s, CH_3, *Me*CN), 3.2 (s, CH_3, *Me*CN), 2.9 (s, CH_3, *Me*CN).

Compound 2f. Yield: yellow solid (0.141 g, 58%). Anal. Calcd for $C_{20}H_{22}N_5SPF_6Ru$: C, 39.35; H, 3.63; N, 11.47; S, 5.25. Found: C, 38.73; H, 3.91; N, 12.09; S, 5.57. MS (ESI^+): *m*/*z* 425.0 ($[M - MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.43 (s, 1H, N=C*H*), 7.69 (d, 1H, thiophene, $^3J_{HH}$ = 4.80), 7.51 (d, 1H, thiophene, $^3J_{HH}$ = 4.80), 7.38−7.31 (m, 5H, Ph), 4.99 (s, 2H, CH_2−Ph). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 198.3 (s, C, *C*−Ru), 168.1 (s, CH, N=*C*), 139.5 (s, C), 136.6 (s, CH, thiophene), 136.4 (s, C), 131.81 (s, CH, thiophene), 129.3 (s, CH, Ph), 129.0 (s, CH, Ph), 128.1 (s, CH, Ph), 124.7 (s, C, Me*C*N), 124.2 (s, C, Me*C*N), 122.5 (s, C, Me*C*N), 65.5 (s, CH_2, *C*H_2−Ph), 4.2 (s, CH_3, *Me*CN), 4.1 (s, CH_3, *Me*CN), 3.7 (s, CH_3, *Me*CN). Single crystals suitable for X-ray diffraction analysis were obtained by diffusion of Et_2O into a solution of **2f** in MeCN.

Compound 2g. Yield: yellow solid (0.137 g, 53%). Anal. Calcd for $C_{21}H_{24}N_5OSPF_6Ru \cdot 1.5CH_2Cl_2$: C, 35.19; H, 3.54; N, 9.12; S, 4.17. Found: C, 35.55; H, 3.44; N, 9.13; S, 3.62. MS (ESI^+): *m*/*z* 413.9 ($[M - 2MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.39 (s, 1H, N=C*H*), 7.68 (d, 1H, thiophene, $^3J_{HH}$ = 4.50), 7.50 (d, 1H, thiophene, $^3J_{HH}$ = 4.50), 7.26−7.23 (m, 2H, C_6H_4OMe), 6.94−6.91 (m, 2H, C_6H_4OMe), 4.92 (s, 2H, CH_2−Ph), 3.77 (s, 3H, O*Me*). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 197.0 (s, C, *C*−Ru), 166.7 (s, CH, N=*C*), 158.9 (s, C), 135.7 (s, CH, thiophene), 135.2 (s, C), 130.7 (s, CH, thiophene), 130.4 (s, C), 129.8 (s, CH, C_6H_4OMe), 123.7 (s, C, Me*C*N), 123.2 (s, C, Me*C*N), 121.5 (s, C, Me*C*N), 113.5 (s, CH, C_6H_4OMe), 63.9 (s, CH_2, *C*H_2−Ph), 54.9 (s, CH_3, O*Me*), 3.3 (s, CH_3, *Me*CN), 3.2 (s, CH_3, *Me*CN), 2.9 (s, CH_3, *Me*CN).

Compound 2h. Yield: yellow solid (0.103 g, 42%). Anal. Calcd for $C_{18}H_{20}N_5S_2PF_6Ru \cdot 0.5MeCN$: C, 35.82; H, 3.40; N, 12.09; S, 10.06. Found: C, 35.57; H, 3.36; N, 11.76; S, 10.79. MS (ESI^+): *m*/*z* 430.9 ($[M - MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.42 (s, 1H, N=C*H*), 7.70 (d, 1H, thiophene-cyclometalated, $^3J_{HH}$ = 4.70), 7.49 (d, 1H, thiophene-cyclometalated, $^3J_{HH}$ = 4.70), 7.31 (dd, 1H, H_5 thiophene, $^4J_{HH}$ = 1.20, $^3J_{HH}$ = 5.10), 7.08 (m, 1H, H_3 thiophene), 7.00 (dd, 1H, H_4 thiophene, $^3J_{HH}$ = 5.10 and 3.60), 5.12 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 197.9 (s, C, *C*−Ru), 167.0 (s, CH, N=*C*), 141.5 (s, C), 135.8 (s, CH), 135.5 (s, C), 131.3 (s, CH), 127.2 (s, CH), 127.0 (s, CH), 125.4 (s, CH), 124.7 (s, C, Me*C*N), 123.7 (s, C, Me*C*N), 121.9 (s, C, Me*C*N), 58.2 (s, CH_2, *C*H_2 thiophene), 3.5 (s, CH_3, *Me*CN), 3.4 (s, CH_3, *Me*CN), 2.9 (s, CH_3, *Me*CN).

Compound 2i. Yield: orange solid (0.112 g, 45%). Anal. Calcd for $C_{20}H_{22}N_5SPF_6Ru$: C, 39.35; H, 3.63; N, 11.47; S, 5.25. Found: C, 39.21; H, 3.15; N, 11.78; S, 5.71. MS (ESI^+): *m*/*z* 426.0 ($[M - MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.41 (s, 1H, N=C*H*), 7.84−7.81 (m, 1H, thiophene), 7.46 (dd, 1H, C_6H_4, $^4J_{HH}$ = 1.20, $^3J_{HH}$ = 7.50), 7.29 (dd, 1H, C_6H_4, $^4J_{HH}$ = 1.20, $^3J_{HH}$ = 5.10), 7.05 (m, 1H, thiophene), 6.81 (m, 2H, 1H C_6H_4 + 1H thiophene), 6.75 (m, 1H, C_6H_4), 5.10 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 189.7 (s, C, *C*−Ru), 175.4 (s, CH, N=*C*), 148.2 (s, C), 139.8 (s, C), 137.3 (s, CH), 127.9 (s, CH), 127.4 (s, CH), 126.8 (s, CH), 126.4 (s, CH), 125.0 (s, CH), 123.3 (s, C, Me*C*N), 123.2 (s, C, Me*C*N), 120.2 (s, C, Me*C*N), 119.8 (s, CH), 58.2 (s, CH_2, *C*H_2 thiophene), 2.8 (s, CH_3, *Me*CN), 2.7 (s, CH_3, *Me*CN), 2.2 (s, CH_3, *Me*CN).

Compound 2j. Yield: orange solid (0.119 g, 46%). Anal. Calcd for $C_{21}H_{24}N_5OSPF_6Ru$: C, 39.38; H, 3.78; N, 10.93; S, 5.01. Found: C, 39.99; H, 3.82; N, 11.28; S, 5.43. MS (ESI^+): *m*/*z* 455.0 ($[M - MeCN]^+$. $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.30 (s, 1H, N=C*H*), 7.40 (d, 1H, C_6H_3, $^3J_{HH}$ = 8.10), 7.33 (d, 1H, C_6H_3, $^4J_{HH}$ = 2.40), 7.27 (m, 1H, thiophene), 7.03 (m, 1H, thiophene), 6.96 (m, 1H, thiophene), 6.41 (dd, 1H, C_6H_3, $^4J_{HH}$ = 2.40, $^3J_{HH}$ = 8.10), 5.04 (s, 2H, CH_2), 3.78 (s, 3H, O*Me*). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 193.1 (s, C, *C*−Ru), 174.5 (s, CH, N=*C*), 159.3 (s, C), 141.8 (s, C), 140.9 (s, C), 129.8 (s, CH), 127.1 (s, CH), 126.9 (s, CH), 125.4 (s, CH), 123.9 (s, C, Me*C*N), 123.0 (s, C, Me*C*N), 122.4 (s, CH), 121.2 (s, C, Me*C*N), 106.4 (s, CH), 58.4 (s, CH_2, *C*H_2 thiophene), 54.5 (s, CH_3, O*Me*), 3.4 (s, CH_3, *Me*CN), 3.3 (s, CH_3, *Me*CN), 2.9 (s, CH_3, *Me*CN). Single crystals suitable for X-ray diffraction analysis were obtained by the slow diffusion of Et_2O into a solution of **2j** in MeCN.

Compound 2k. Yield: orange solid (0.132 g, 55%). Anal. Calcd for $C_{19}H_{20}N_5SPF_6Ru \cdot CH_2Cl_2$: C, 35.25; H, 3.25; N,

10.28; S, 4.70. Found: C, 34.68; H, 3.17; N, 10.40; S, 4.43. MS (ESI^+): *m*/*z* 452.0 ($[M]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.19 (s, 1H, N=C*H*), 7.46−7.23 (m, 7H). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 207.7 (s, C, *C*−Ru), 169.1 (s, CH, N=*C*), 153.2 (s, C), 148.3 (s, C), 129.7 (s, CH), 129.2 (s, CH), 126.8 (s, CH), 125.1 (s, C, Me*C*N), 124.8 (s, C, Me*C*N), 124.7 (s, CH), 123.7 (s, CH), 123.6 (s, C, Me*C*N), 3.3 (s, CH_3, *Me*CN), 3.1 (s, CH_3, *Me*CN), 3.0 (s, CH_3, *Me*CN).

Compound 2l. Yield: orange solid (0.147 g, 60%). Anal. Calcd for $C_{20}H_{22}N_5SPF_6Ru$: C, 39.35; H, 3.63; N, 11.47; S, 5.25. Found: C, 39.03; H, 3.62; N, 11.79; S, 5.06. MS (ESI^+): *m*/*z* 425.0 ($[M - MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.32 (s, 1H, N=C*H*), 7.40−7.38 (m, 3H, 1H thiophene + 2H Ph), 7.35−7.28 (m, 3H, Ph), 7.11 (d, 1H, thiophene, $^3J_{HH}$ = 5.10), 4.96 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 201.1 (s, C, *C*−Ru), 168.9 (s, CH, N=*C*), 146.2 (s, C), 138.6 (s, C), 128.3 (s, CH, Ph), 128.1 (s, CH, Ph), 127.2 (s, CH, Ph), 125.0 (s, CH, thiophene), 124.8 (s, CH, thiophene), 123.8 (s, C, Me*C*N), 123.2 (s, C, Me*C*N), 121.9 (s, C, Me*C*N), 64.5 (s, CH_2, *C*H_2−Ph), 3.3 (s, CH_3, *Me*CN), 3.0 (s, CH_3, *Me*CN), 2.8 (s, CH_3, *Me*CN).

Compound 2m. Yield: yellow solid (0.118 g, 48%). Anal. Calcd for $C_{18}H_{20}N_5S_2PF_6Ru \cdot 0.5MeCN$: C, 35.82; H, 3.40; N, 12.09; S, 10.06. Found: C, 36.13; H, 3.78; N, 11.82; S, 9.75. MS (ESI^+): *m*/*z* 430.9 ($[M - MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.34 (s, 1H, N=C*H*), 7.40 (d, 1H, H_4 thiophene-cyclometalated, $^3J_{HH}$ = 3.80), 7.35 (dd, 1H, H_5 thiophene, $^3J_{HH}$ = 3.90, $^4J_{HH}$ = 0.90), 7.12 (d, 1H, H_5 thiophene-cyclometalated, $^3J_{HH}$ = 3.80), 7.10 (dd, 1H, H_3 thiophene, $^3J_{HH}$ = 2.70, $^4J_{HH}$ = 0.90), 7.05 (dd, 1H, H_4 thiophene, $^3J_{HH}$ = 3.90, $^3J_{HH}$ = 2.70), 5.12 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 201.7 (s, C, *C*−Ru), 168.0 (s, CH, N=*C*), 146.2 (s, C), 141.6 (s, C), 126.9 (s, CH), 126.8 (s, CH), 125.3 (s, CH), 125.1 (s, CH), 124.9 (s, CH), 124.4 (s, C, Me*C*N), 123.8 (s, C, Me*C*N), 123.4 (s, C, Me*C*N), 58.2 (s, CH_2, *C*H_2 thiophene), 3.3 (s, CH_3, *Me*CN), 3.2 (s, CH_3, *Me*CN), 2.8 (s, CH_3, *Me*CN).

Compound 2n. Yield: yellow solid (0.128 g, 50%). Anal. Calcd for $C_{23}H_{22}N_5SPF_6Ru$: C, 42.73; H, 3.43; N, 10.83; S, 4.96. Found: C, 42.95; H, 3.88; N, 10.41; S, 4.74. MS (ESI^+): *m*/*z* 461.0 ($[M - MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.61 (s, 1H, N=C*H*), 7.88−7.81 (m, 2H, C_6H_4), 7.48−7.43 (m, 2H, Ph), 7.35−7.26 (m, 4H, 3H Ph + 1H C_6H_4), 7.13 (m, 1H, C_6H_4). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 218.7 (s, C, *C*−Ru), 167.3 (s, CH, N=*C*), 153.3 (s, C), 144.8 (s, C), 143.0 (s, C), 139.6 (s, C), 129.7 (s, CH, Ph), 126.9 (s, CH, Ph), 125.2 (s, C, Me*C*N), 125.1 (s, CH, C_6H_4), 124.7 (s, C, Me*C*N), 124.1 (s, CH, Ph), 123.9 (s, C, Me*C*N), 122.3 (s, CH, C_6H_4), 121.8 (s, CH, C_6H_4), 118.7 (s, CH, C_6H_4), 3.4 (s, CH_3, *Me*CN), 3.2 (s, CH_3, *Me*CN), 2.9 (s, CH_3, *Me*CN).

Compound 2o. Yield: dark-red solid (0.137 g, 49%). Anal. Calcd for $C_{26}H_{25}N_6SPF_6Ru \cdot MeCN$: C, 45.41; H, 3.81; N, 13.24; S, 4.33. Found: C, 45.13; H, 3.46; N, 13.69; S, 4.69. MS (ESI^+): *m*/*z* 514.0 ($[M - MeCN]^+$). $^{31}P\{^1H\}$ NMR (CD_3CN): δ −144.6 (spt, $^1J_{PF}$ = 706.5). ^{19}F NMR (CD_3CN): δ −72.9 (d). ^1H NMR (CD_3CN): δ 8.89 (s, 1H, N=C*H*), 8.50 (s, 1H, RuN=C*H*), 8.12 (s, 1H, thiophene), 7.51−7.44 (m, 4H, Ph), 7.39−7.29 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 200.1 (s, C, *C*−Ru), 167.4 (s, CH, RuN=*C*), 154.2 (s, CH, N=*C*), 152.2 (s, C), 151.5 (s, C), 149.2 (s, C), 142.9 (s, C), 142.5 (s, CH, thiophene), 129.3 (s, CH, Ph), 128.8 (s, CH, Ph), 126.5 (s, CH, Ph), 126.2 (s, CH, Ph), 124.8 (s, C, Me*C*N), 124.5 (s, C, Me*C*N), 122.8 (s, CH, Ph), 122.6 (s, C, Me*C*N), 121.1 (s, CH, Ph), 3.6 (s, CH_3, *Me*CN), 3.2 (s, CH_3, *Me*CN), 2.9 (s, CH_3, *Me*CN).

Iodinations: General Procedure. Iodine (152 mg, 0.6 mmol) was added to a solution of the respective complex (0.2 mmol) in undried MeCN (15 mL). The mixture was stirred at room temperature under argon for 48 h, and the solvent was removed. The dark residue was extracted with Et_2O (3 × 15 mL), and the solution was washed with saturated aqueous $Na_2S_2O_3$ (2 × 10 mL). The organic phases were collected and dried over $MgSO_4$. After filtration, the solvent was evaporated in vacuo and the iodinated thiophene was recovered. The derivatives **3a**, **3k**, and **3n** were identified by comparison with the reported ^1H NMR spectra.[23]

Aldehyde 3c [SC_4H-2-(CHO)-3-I-5-Me]. Yield: yellow solid (0.035 g, 69%). Anal. Calcd for C_6H_5IOS: C, 28.59; H, 2.00; S, 12.72. Found: C, 28.13; H, 1.66; S, 12.39. MS (ESI^+): *m*/*z* 252. ^1H NMR ($CDCl_3$): δ 9.69 (s, 1H, C*H*O), 6.97 (q, 1H, thiophene, $^4J_{HH}$ = 0.90), 2.56 (d, 3H, *Me*, $^4J_{HH}$ = 0.90). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 185.1 (s, CH, *C*HO), 152.1 (s, C), 137.1 (s, C), 135.8 (s, CH, thiophene), 96.8 (s, C, *C*−I), 15.63 (s, C, Me).

Aldehyde 3d [SC_4H-2-(CHO)-3-I-5-Ph]. Yield: yellow solid (0.039 g, 62%). Anal. Calcd for $C_{11}H_7IOS$: C, 42.06; H, 2.25; S, 10.21. Found: C, 41.73; H, 2.01; S, 9.79. MS (ESI^+): *m*/*z* 314. ^1H NMR ($CDCl_3$): δ 9.76 (s, 1H, C*H*O), 7.68−7.64 (m, 2H, Ph), 7.49 (s, 1H, thiophene), 7.47−7.45 (m, 3H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 185.4 (s, CH, *C*HO), 154.5 (s, C), 144.9 (s, C), 137.8 (s, C), 137.8 (s, CH, thiophene), 132.8 (s, CH, Ph), 129.4 (s, CH, Ph), 126.4 (s, CH, Ph), 105.0 (s, C, *C*−I).

Aldehyde 3e [SC_8H_4-2-(CHO)-3-I]. Yield: yellow solid (0.037 g, 64%). Anal. Calcd for C_9H_5IOS: C, 37.52; H, 1.75; S, 11.13. Found: C, 37.09; H, 1.41; S, 10.76. MS (ESI^+): *m*/*z* 288. ^1H NMR ($CDCl_3$): δ 10.15 (s, 1H, C*H*O), 8.14−7.99 (m, 1H, C_6H_4), 7.87−7.76 (m, 1H, C_6H_4), 7.55−7.51 (m, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 187.3 (s, CH, *C*HO), 145.4. (s, C), 140.9 (s, C), 139.7 (s, C), 129.2 (s, CH, C_6H_4), 127.3 (s, CH, C_6H_4), 126.1 (s, CH, C_6H_4), 123.3 (s, CH, C_6H_4), 102.1 (s, C, *C*−I).

X-ray Crystallography. X-ray data collections were performed on an Oxford Diffraction Xcalibur2 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A single crystal was mounted at the end of a quartz fiber in a random orientation, covered with perfluorinated oil, and placed under a cold stream of dinitrogen gas. In all cases, a hemisphere of data was collected based on ω- or ϕ-scan runs. The diffraction frames were integrated using the program or *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-H atoms were refined with anisotropic displacement parameters. The H 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]

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Supporting Information Available: CIF of complexes **2b** and **2f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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