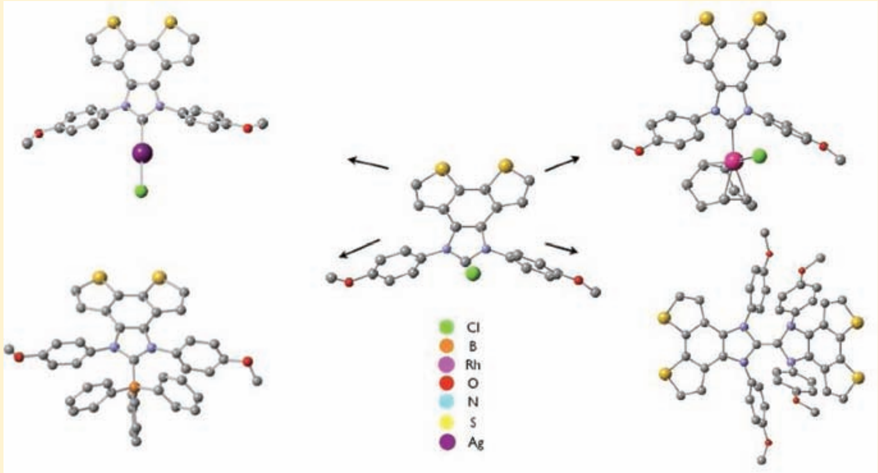
Inorganic Chemistry
Article
pubs.acs.org/IC

An N-Heterocyclic Carbene Containing a Bithiophene Backbone: Synthesis and Coordination Chemistry

Jacquelyn T. Price, Nathan D. Jones, and Paul J. Ragogna*

Department of Chemistry, Western University, 1151 Richmond Street, London, Ontario N6A 5B7, Canada

S *Supporting Information*



ABSTRACT: A new N-heterocyclic carbene (NHC) containing a fused bithiophene backbone has been synthesized along with its silver(I) and BPh_3 complexes. The donor strength of this unique NHC has been determined from the IR stretching frequencies of the isolated NHC-$Rh(CO)_2Cl$ complex. The photophysical properties of all of the novel compounds have been investigated and are presented.

■ INTRODUCTION

Since their discovery in the 1960s, conjugated polymers have drawn significant interest in the field of materials science.[1] Their ability to combine both the electronic and photophysical properties of inorganic semiconductors along with the flexibility and processability of organic plastics have resulted in their wide use in many applications.[1−3] Conjugated organic polymer-based materials have found broad applicability in light-emitting diodes (LED) or light-emitting electrochemical cells (LEC), plastics, lasers, solar cells, field effect transistors, and sensors.[4,5] More specifically, thiophene-based polymers are one of the most studied classes of conjugated polymers because of their synthetic versatility and their ability to be polymerized both chemically and electrochemically.[5−7] It has been demonstrated that the incorporation of transition metals or main-group elements into these thiophene-based systems can significantly heighten their conductivity and optical properties, thus providing a potential handle by which one can tune the polymers for specific applications.[8] Despite functional modifications of thiophene being well established in the literature, designing a thiophene-containing scaffold to support either metals or main-group elements has proven to be challenging because of the rigid coordination sites, difficult carbon−carbon coupling chemistry, and lengthy workup procedures.[9,10]

Inspiration for this work came from the widely used bis(arylimino)acenaphthene (Figure 1, **i**), which has been shown to readily coordinate s-, p-, and d-block elements.[11] We sought to synthesize a similar type of framework containing two fused thiophene rings in the backbone, supporting two flanking α-diamines (**2**). This system would allow for chemical versatility at the donor nitrogen sites while maintaining conjugation between the thiophene fragments in the backbone, which have the potential to undergo polymerization in a subsequent step.

N-heterocyclic carbenes (NHC) have been extensively studied over the last two decades because of their ability to act as strong two-electron donors for transition metals as well stabilizing highly reactive main-group species.[12−20] The use of an NHC would be an ideal fragment within a poly(thiophene) system because of its ability to act as a strong Lewis base.[21] This would enable the facile incorporation of both Lewis acidic transition metals and main-group elements into a polymeric system and enhance or modify the electronic and photophysical properties of the end compound.[22,23] Incorporating an NHC into a conjugated polymer would allow for chemical versatility that is desirable but so often very difficult to achieve in such

Received: March 5, 2012
Published: June 6, 2012

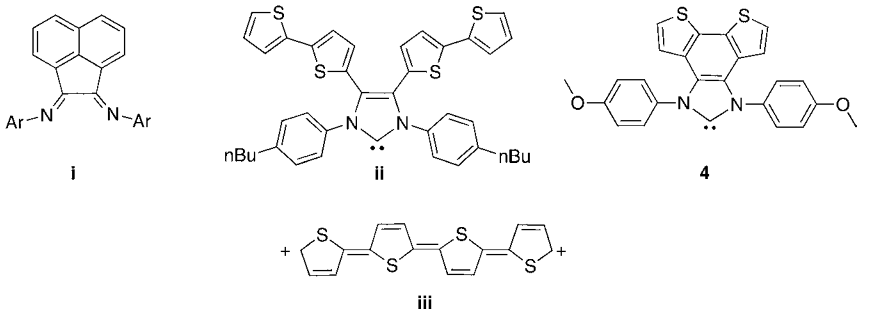
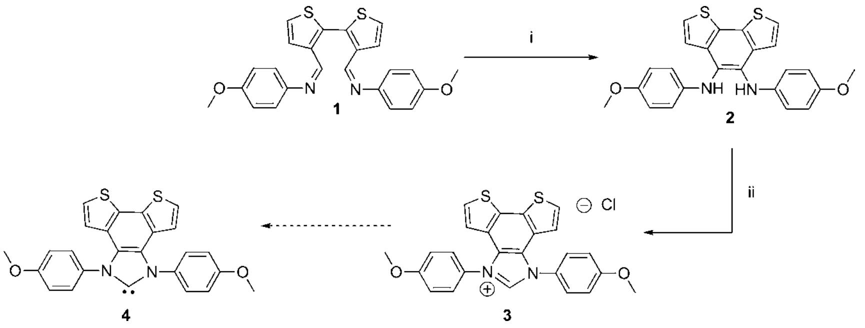


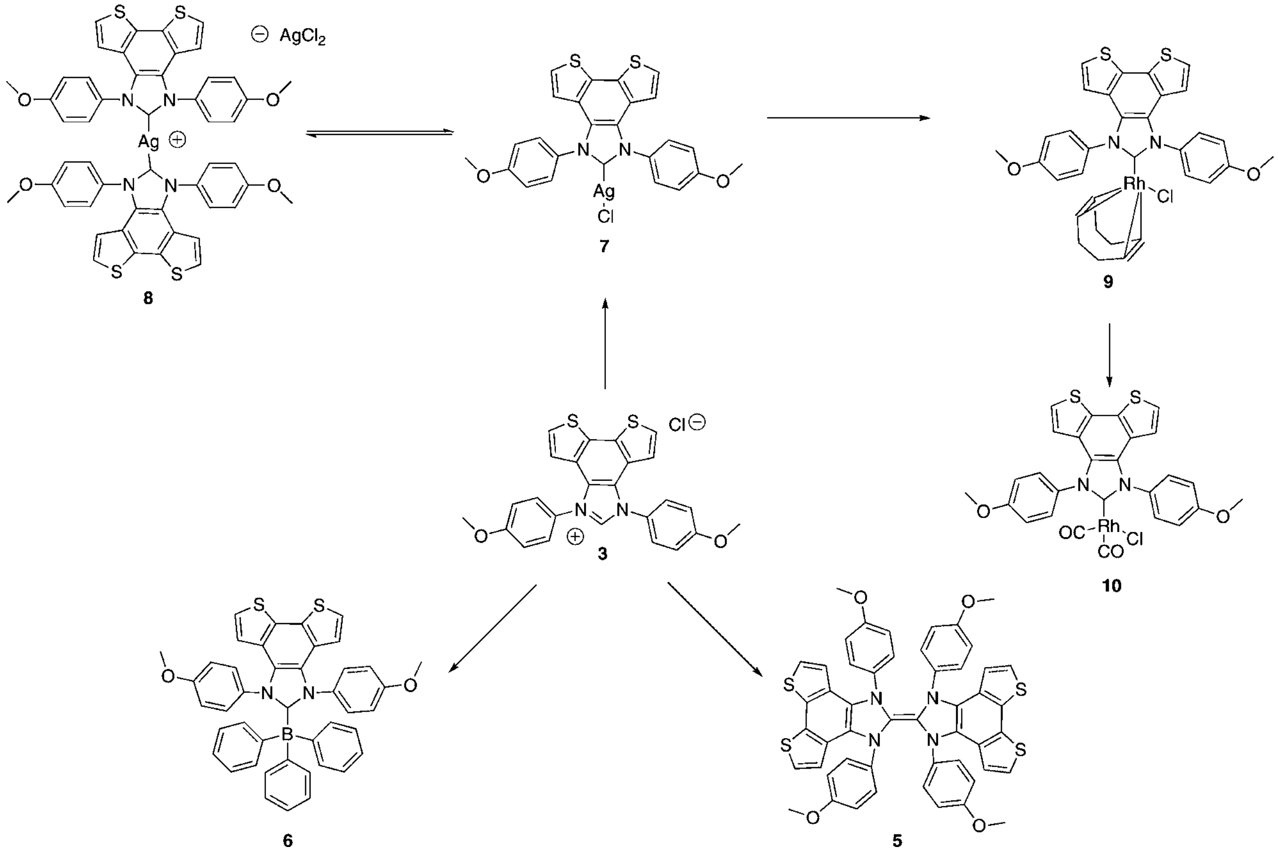
Figure 1. (i) bis(imino)acenaphthene, (ii) NHC orthogonal to the thiophene rings, quinoidal structure of *tert*-thiophene(iii) and our NHC (**4**).

Scheme 1. Synthesis of the Imidazolium Salt 3[a]



[a]Legend: (i) DMF, NaCN, room temperature, 48 h; (ii) 4 M HCl, $HC(OEt)_3$, 145 °C, 2 min.

Scheme 2. Synthetic Scheme of the Bithiophene-Substituted NHCs



materials. While there are many examples of polymeric NHCs,[16,24−29] there is only one recent example combining an NHC within a polythiophene, in which the NHC is orthogonal to the polymer backbone (Figure 1, **ii**). Further functionalization of the system can be achieved via coordination of the carbene to a metal center.[30,31] This is a substantial development in metal-functionalized NHC polymers; however, one downfall is that the thiophene rings are not conjugated. Conjugated thiophene polymers are desirable because they possess a characteristic reduced band gap, and one of the most successful methods of achieving this has been the application of a fused thiophene ring system, giving a quinoidal structure (**iii**), resulting in significant reduction in the band gap.[1]

In this context, we report the synthesis of the first bithiophene-annulated backbone-substituted imidazol-2-ylidene ligand. The N-heterocyclic carbene **4** can act as a Lewis base and form adducts with the Lewis acidic BPh_3 and metal complexes with both silver and rhodium. The donor ability of **4** was also determined by measuring IR stretching frequencies of the carbonyl ligands in $(NHC)Rh(CO)_2Cl$ (**10**). The photophysical properties of all compounds have been investigated, where the absorbance and emission is dominated by the fused bithiophene backbone and not by substitution at the carbenic carbon.

RESULTS AND DISCUSSION

Synthesis. The precursor **2** to the imidazolium salt **3** was synthesized via a benzoin condensation of the diimine **1** using NaCN in dimethylformamide (DMF), yielding the diamine. Compound **2** was placed in a pressure tube, with 2 stoichiometric equiv of 4 M HCl in dioxane and triethyl orthoformate at 145 °C for 2 min (Scheme 1). The yellow precipitate was isolated by filtration and washed with Et_2O. Upon examination of the redissolved powder by ^1H NMR spectroscopy, the imidazolium proton was observed downfield at δ_H 10.44 as well as the disappearance of the NH proton at δ_H 5.63. Single crystals suitable for X-ray diffraction studies were grown from vapor diffusion of Et_2O into a concentrated CH_2Cl_2 solution of the bulk powder at room temperature, confirming the synthesis of **3** (Figure 3).

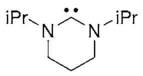
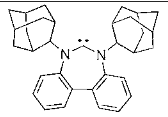
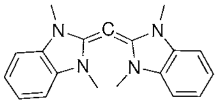
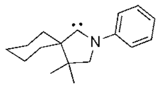
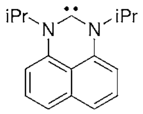
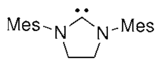
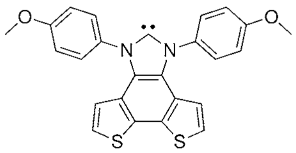
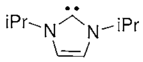
Compound **5** was synthesized from a 1:1 stoichiometric reaction between LiHMDS (lithium bis(trimethylsilylamide)) and **3** in toluene. This resulted in a color change from an orange to a yellow solution with the formation of a white precipitate. The white precipitate was removed by centrifugation, the yellow solution was decanted, and upon concentration of the supernatant, a yellow solid formed. Examination of the redissolved solid by ^1H NMR spectroscopy revealed the imidazolium proton at δ_H 10.44 had disappeared and the aryl peaks shifted significantly upfield ($\Delta\delta_H = 0.6$). The successful deprotonation of the imidazaolium salt was sensitive to the base employed; when either the sodium or potassium salt of HMDS was used, multiple products were observed by ^1H NMR spectroscopy. In solution, an equilibrium between the free carbene and the dimer was observed. This was confirmed through $^{13}C\{^1H\}$ NMR spectroscopy and the addition of a Lewis acid. When the dimer was heated to 80 °C in a solution of C_6D_6, the carbenic carbene was observed at δ_C 214.6. In addition, when BPh_3 was added to a solution containing the isolated dimer, the carbene→borane adduct was formed immediately, as confirmed by $^{11}B\{^1H\}$ NMR spectroscopy with a single peak at δ_B −8.2. X-ray-quality single crystals of compound **5** were grown from vapor diffusion of a pentane/benzene solution giving the carbene dimer (**5**; Scheme 2, Figure 3) in 48% yield.

Given the observed dimerization of the NHC, we sought to trap the free carbene by the addition of a Lewis acid (BPh_3). A THF solution of a 1:1:1 mixture of the imidazolium salt, LiHMDS, and triphenylborane was stirred at room temperature for 45 min, where the solution turned from orange to yellow along with the formation of a white precipitate. The precipitate was separated by centrifuge, and the volatiles were removed under reduced pressure, yielding a yellow powder. Examination of the redissolved yellow solid by ^1H NMR spectroscopy revealed that the imidazolium proton at δ_H 10.44 was again absent. Signals belonging to the thiophene ring were shifted upfield from δ_H 7.48 and 6.79 to δ_H 7.19 and 5.88, respectively. The $^{11}B\{^1H\}$ NMR spectrum showed a peak with an upfield shift from δ_B 86.0 for free BPh_3 to δ_B −8.2 and is similar to other NHCs coordinated to triphenylborane.[32] Single crystals were grown from vapor diffusion of pentane/CH_2Cl_2, and X-ray diffraction studies confirmed the synthesis of the carbene→borane adduct (**6**; Scheme 2, Figure 3).

Access to the silver NHC complex **7** was obtained by metalation of the imidazolium chloride using Ag_2O. Upon collection of the ^1H NMR spectrum, the imidazolium proton at δ_H 10.44 was not observed and the aromatic signals shifted significantly upfield, reminiscent of the carbene→triphenylborane adduct. The signal for the carbenic carbon was absent in the $^{13}C\{^1H\}$ NMR spectrum at room temperature, suggesting a fast exchange in solution between **7** and **8** due to the silver−carbon bond lability.[33] This has previously been observed in other reported silver NHC species.[31,33] When the solution was cooled to −50 °C and the $^{13}C\{^1H\}$ NMR spectrum recollected, two sets of doublets were observed as a result of carbon−silver coupling ($^1J_{^{13}C-^{107}Ag} = 226.3$ Hz and $^1J_{^{13}C-^{109}Ag} = 296.1$ Hz). The NHC bis-carbene complex **8** was also detected by ESI mass spectrometry, providing further evidence that in solution the bis-carbenic species **8** exists. Single crystals of the silver complex containing one NHC ligand were grown in the dark from the vapor diffusion of Et_2O into CH_2Cl_2 (Scheme 2, Figure 3).

Synthesizing the bithiophene NHC rhodium complex **10** provided the opportunity of evaluating the donor properties of our NHC ligand relative to those of others. The (NHC)Rh(COD)Cl precursor **9** was made by the transmetalation of **7** with $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) in refluxing toluene for 12 h.[34] In comparison to the starting material, the aryl protons shifted downfield in the ^1H NMR spectrum (δ_H 8.04 to 8.51) and the vinyl protons belonging to the COD ligand were now distinct as separate multiplets (δ_H 3.04 (cis); δ_H 4.00 (trans)). Upon examination of the $^{13}C\{^1H\}$ NMR spectrum, the COD C_{CH} for the rhodium complex **9**, two doublets at δ_C 67.9 ($^1J_{^{13}C-^{103}Rh} = 14.9$ Hz, trans to the carbene) and δ_C 98.1 ($^1J_{^{13}C-^{103}Rh} = 6.2$ Hz, cis to the carbene), and the $C_{carbene}$ could only be observed at −40 °C appearing as a doublet downfield at δ_C 191.3 ($^1J_{^{13}C-^{103}Rh} = 49.2$ Hz). Single crystals suitable for X-ray diffraction studies were grown from vapor diffusion of Et_2O into a concentrated CH_2Cl_2 solution of **9**. Only low-quality crystals could be obtained, confirming the connectivity; however, the quality of the full structure solution does permit the discussion of the metrical parameters (Figure SI-17, Supporting Information). The synthesis of **10** was accomplished by bubbling CO gas into a CH_2Cl_2 solution of **9** over a period of 2 h. The yellow solution was concentrated under reduced pressure, yielding a yellow powder. The ^1H NMR spectrum of the redissolved yellow powder revealed that the COD peaks were no longer present and the aryl peaks appeared as a broad singlet. Similar to the case for the other metal−NHC complexes, the carbenic carbon as well as the carbonyl carbons were not observed at room temperature. When the sample was cooled to −50 °C, three sets of doublets

Table 1. Average CO Stretching Frequencies (ν_{ave}) of Various (carbene)Rh(CO)$_2$Cl Complexes

Entry	Carbene	ν_{ave}/cm^{-1}	Ref.	Entry	Carbene	ν_{ave}/cm^{-1}	Ref.
1		2012	35	5		2033	36
2		2014	37	6		2036	38
3		2020	39	7		2038	40
4		2033	This work	8		2041	40

appeared downfield, the C$_{\text{CO}}$ at δ_{C} 185.4 ($J_{^{13}\text{C}-^{103}\text{Rh}}$ = 55.3 Hz) and δ_{C} 180.8 ($J_{^{13}\text{C}-^{103}\text{Rh}}$ = 42.9 Hz) and the C$_{\text{carbene}}$ at δ_{C} 182.4 ($J_{^{13}\text{C}-^{103}\text{Rh}}$ = 75.2 Hz). The relative donor ability of the bithiophene NHC **4** was determined by the IR stretching frequencies of the carbonyl ligands, which were compared to those of other (NHC)Rh(CO)$_2$Cl complexes. The IR stretching frequencies of **10** (2074 and 1991 cm^{-1}, ν_{avg} 2033 cm^{-1}) indicate that **4** is a stronger donor than the saturated and unsaturated five-membered NHCs; however, it is not quite as strong as the acyclic and six-membered NHC derivatives (Table 1).

Photophysical Properties. The photophysical properties of the bithiophene carbenes were examined and are summarized in Figure 2 and Table 2. All of the compounds were yellow and absorbed UV light in the 300−400 nm region. The UV spectrum for compound **3** had two $\lambda_{\max}$ values at 310 and 323 nm and a broad peak of lower intensity at 427 nm, and upon formation of the ene-tetramine **5** there is a hypsochromic shift in the spectrum with $\lambda_{\max}$ values of 282, 308, 327, and 342 nm along with a shoulder at 416 nm. These bands are attributed to both $\pi-\pi^*$ transitions from the phenyl and thiophene rings and n−π^* transitions from the thiophenes. Upon coordination to a metal center, a third absorption band appears at lower energy for compound **6** ($\lambda_{\max}$ 307, 320 and 334) and compound **7** ($\lambda_{\max}$ 305, 318, 332). Compounds **9** and **10** also had three large bands similar to those observed in compounds **6** and **7**, in addition to a smaller band at lower energy appearing at 397 nm for compound **9** and 370 nm for compound **10**. These peaks are also attributed to the $\pi-\pi^*$ and

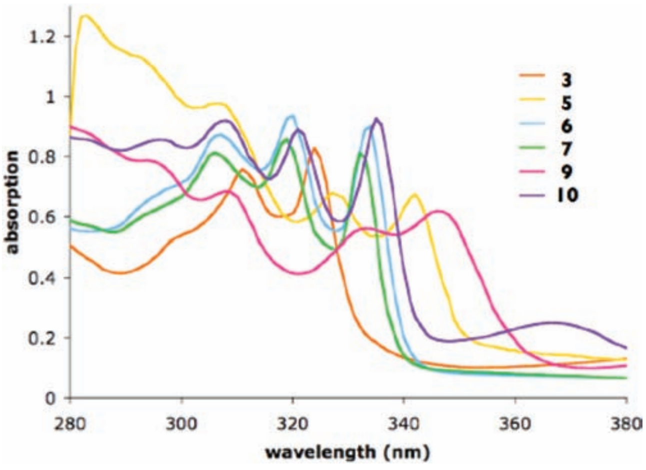


Figure 2. UV−visible spectra of compounds **3**, **6**, **7**, **9**, and **10** in CH$_2$Cl$_2$ and compound **5** in toluene.

Table 2. Photophysical Properties of the Bithiophene NHC[a]

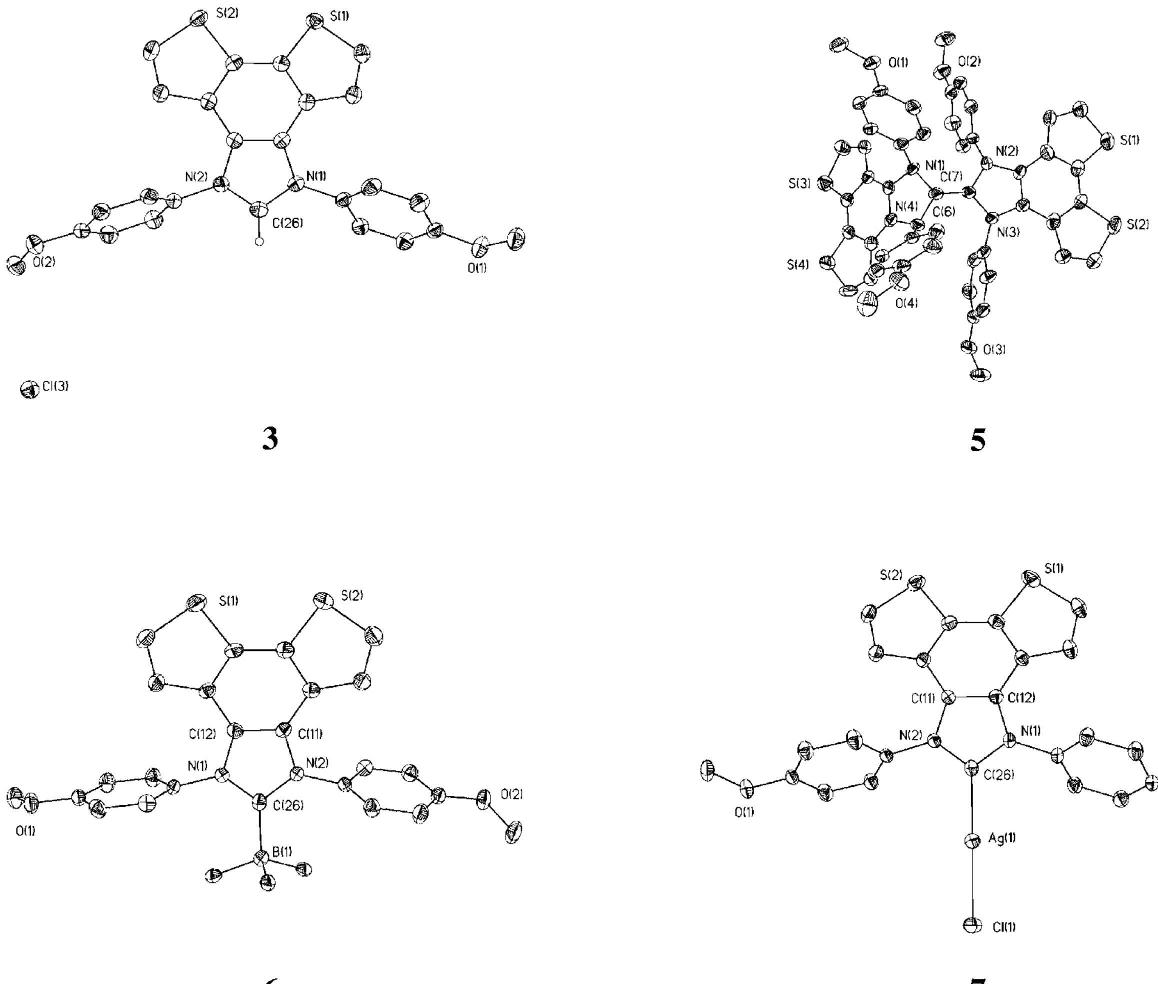
compd	λ_{abs}, nm	$\varepsilon_{\max}$, L mol^{-1} cm^{-1}	λ_{em}, nm
3	310	1.5×10^4	460
	323	1.6×10^4	
	427	4.4×10^3	
5	282	3.3×10^4	348
	308	2.5×10^4	362
	327	1.8×10^4	
	342	1.7×10^4	
6	307	1.7×10^4	336
	320	1.8×10^4	350, 364 (sh)
	334	1.8×10^4	
7	305	1.6×10^4	333
	318	1.7×10^4	347, 364 (sh)
	332	1.6×10^4	
9	293	1.5×10^4	
	308	1.3×10^4	
	344	1.2×10^4	
	397	2.6×10^3	
10	307	1.8×10^4	
	320	1.7×10^4	
	332	1.8×10^4	
	370	1.5×10^3	

[a] All UV−visible spectra were collected at a 5×10^5 M concentration in CH$_2$Cl$_2$, with the exception of compound **5**, which was measured with a 3.75×10^5 M solution in toluene.

Table 3. Crystal Data for Compounds 3, 5−7, and 9

	3	5	6	7	9
empirical formula	$C_{27}H_{23}N_2Cl_5O_2S_2$	$C_{50.8}H_{40.8}N_4O_4S_4$	$C_{43}H_{34}N_2O_2S_2$	$C_{26}H_{20}N_2AgClO_2S_2$	$C_{36}H_{31.5}N_2ClO_2RhS_2$
formula wt	648.84	947.55	684.64	586.88	726.61
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1$
a (Å)	9.2020(4)	10.3630(7)	20.285(4)	10.3668(4)	7.7079(5)
b (Å)	9.2504(4)	14.7130(11)	12.280(3)	17.3763(6)	20.6982(13)
c (Å)	17.1345(7)	16.9285(12)	28.040(6)	15.0656(5)	18.3693(12)
α (deg)	95.675(2)	93.514(2)	90.00	90.00	90.00
β (deg)	91.790(2)	96.846(2)	105.45(3)	103.229(2)	92.354(3)
γ (deg)	92.530(2)	99.525(2)	90.00	90.00	90.00
V (Å^3)	1449.03(11)	2518.7(3)	6832(2)	2639.30(16)	2928.2(3)
D_c (Mg m^{-3})	1.487	1.249	1.351	1.688	1.556
R1($I > 2\sigma(I)$)^a	0.0421	0.0690	0.0522	0.0261	0.1446
wR2(F^2)^a	0.1059	0.2094	0.1080	0.0607	0.3745

^{a}R1(F ($I > 2\sigma(I)$)) = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2(F^2 (all data)) = $[w(F_o^2 - F_c^2)^2]^{1/2}$; S(all data) = $[w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement.



3

5

6

7

Figure 3. Solid-state structures of compounds 3 and 5−7. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been removed for clarity. In compound 6, the phenyl groups have also been removed for clarity.

n−π* transitions from the phenyl and thiophene rings. Compounds 3 and 5−7 fluoresce when irradiated with light at 300 nm. Compound 3 fluoresces at the longest wavelength (460 nm), whereas compounds 5−7 had two fluorescent bands in the blue region, between 330 and 360 nm.

X-ray Crystallography. Single crystals of compounds 3 and 5−7 were grown by vapor diffusion using various solvent combinations, and their solid-state structures were determined by X-ray diffraction studies. The relevant crystallographic data and connectivities for compounds 3 and 5−7 are detailed in

Table 3 and Figure 3, respectively. Examination of the solid-state structures of compounds **3** and **5**−**7** revealed that the metrical parameters of the C_2N_2 ring are consistent with two C−N single bonds (1.386−1.405 Å; cf. 1.420 Å (av) in the free ligand **2**) and a C−C double bond (1.368−1.389 Å; cf. 1.382 Å (av) in the free ligand **2**). Upon coordination of the NHC to a metal center and in the NHC dimer, the metrical parameters of the C_2N_2 ring remain unchanged.

The NHC dimer **5** contains a shortened C−C double bond of 1.354(11) Å between the carbenic carbons C(7) and C(6). There is a slight contraction in the bond angle between N(3)−C(7)−N(2) and N(4)−C(6)−N(1) (107.9(6) and 108.2(6)°) in comparison to that found in the imidazolium salt (109.9(2) °). The sums of the bond angles around N(1) and N(4) ($\sum_{ang}$ = 339.2 and 339.6°) are congruous with a pyramidal geometry, whereas the geometry around N(2) and N(3) ($\sum_{ang}$ = 352.1 and 349.2°) is more consistent with a trigonal-planar arrangement.

Compound **6** crystallizes with two independent molecules in the asymmetric unit and consists of a four-coordinate boron(III) center with a C_3 propeller-like geometry about the boron atom ($\sum_{ang}$ = 332.8°). The C(6)−B(1) bond length is 1.658(4) Å, and a slight elongation in the C−N bonds (1.393(3) Å; cf. 1.378 Å (av)) in the imidazol-2-ylidene from **3** is observed, along with a contraction of the N−C−N bond angle (104.3(2)°; cf. 109.9(2)°).

Examination of the (NHC)AgCl complex **7** consists of a two-coordinate silver(I) ion in a linear environment with a C−Ag−Cl bond angle of 179.42(4)°. The C−Ag bond length is 2.082(1) Å, which is in accordance with other silver mono- or bis-carbene complexes. The Ag−Cl bond length is 2.335(4) Å and is within the range of other silver(I) chloride complexes reported. In the solid state, the silver complex is monomeric, with no evidence of argentophilic (Ag(I)···Ag(I)) interactions. All distances between Ag(I) centers are greater than 3.44 Å, the sum of twice the van der Waals radius of Ag(I).[34−41]

■ CONCLUSIONS

The successful synthesis of a novel imidazolium salt with a fused conjugated bithiophene backbone was carried out. The imidazolium salt was generated from a diamine precursor using a sealed pressure tube and was complete in less than 5 min. The NHC could be used as a ligand for both $BPPh_3$ and Ag(I) salts, in which rapid exchange was observed in solution between (NHC)AgCl and $(NHC)_2Ag$ due to the labile C−Ag bond. The Ag(I) salt was also used as a transfer reagent to synthesize the (NHC)Rh(COD)Cl complex, which was utilized in the synthesis of $(NHC)Rh(CO)_2Cl$. A comparison of the donor abilities of our NHC with a selection of those reported demonstrated that **4** is a stronger Lewis base than a five-membered NHC but weaker than the acyclic and six-membered NHCs. Upon examination of the photophysical properties, all of the compounds absorbed in the UV−visible region between 300 and 360 nm, whereas only compounds **3** and **5**−**7** fluoresced when excited with 300 nm light. Future work will encompass the extension of the thiophene backbone and further exploring its potential in fluorescent and polymeric materials. These modifications to the NHC ligand will bring to light the possibility of new reduced band gap polymers with a further bonus of facile addition and modification of a Lewis acid center onto the monomer or polymer backbone.

■ EXPERIMENTAL SECTION

General Procedures. All manipulations were performed under an N_2 atmosphere using standard Schlenk or glovebox techniques unless otherwise stated. Reagents were obtained from Sigma Aldrich and Alfa Aesar. $CDCl_3$ was dried over calcium hydride, distilled prior to use, and stored in the glovebox over 4 Å molecular sieves. All solvents were dried using an MBraun controlled-atmosphere solvent purification system and stored in Straus flasks under a N_2 atmosphere or over 4 Å molecular sieves in the glovebox. All NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer (^1H, 399.76 MHz; ^{13}C, 100.52 MHz; ^{11}B, 128.27 MHz) in $CDCl_3$ at room temperature unless otherwise stated. ^{11}B NMR spectra were recorded unlocked relative to an external standard ($Et_2O·BF_3$, δ_B 0.00). UV−visible absorption spectra were recorded over a range of 280−550 nm using a Varian Cary 300 spectrometer in CH_2Cl_2 or toluene. Emission spectra were recorded on a Fluorolog (QM-7/2005) instrument with a slit width of 0.5 nm in CH_2Cl_2 or toluene. X-ray diffraction data were collected on a Nonius Kappa CCD or a Bruker ApexII CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Single crystals were selected under Paratone-N, mounted on nylon loops, and immediately placed under a cold stream of N_2. Structures were solved by direct methods and refined using full-matrix least squares on F^2. Hydrogen atom positions were calculated. FT-IR spectra were collected on samples as a KBr pellet using a Bruker Tensor 27 spectrometer, with a resolution of 4 cm^{-1}. FT-Raman spectra were collected in flame-sealed capillary tubes on a Bruker RFS 100/s spectrometer with a resolution of 4 cm^{-1}. Decomposition/melting points were recorded in flame-sealed capillary tubes using a Gallenkamp Variable Heater. High-resolution mass spectra (HRMS) were collected using a Finnigan MAT 8200 instrument.

Synthetic Procedures. *Compound **3**.* In a 10 mL pressure tube, triethyl orthoformate (6 mL), **2** (2.00 g, 4.60 mmol), and 4 M HCl in dioxane (2.30 mL, 9.20 mmol) were stirred at room temperature for 5 min. The reaction mixture was then heated to 145 °C for 2 min. The resulting orange powder was isolated by filtration and washed with Et_2O (3 × 5 mL). Yield: 72% (1.60 g, 3.38 mmol). Dec pt: 156−158 °C. ^1H NMR ($CDCl_3$, δ (ppm)): 10.44 (s, 1H, C*H*), 8.04 (d, 4H, aryl, $^3J_{HH}$ = 8.0 Hz), 7.48 (d, 2H, aryl, $^3J_{HH}$ = 5.2 Hz), 7.16 (d, 4H, aryl, $^3J_{HH}$ = 8.4 Hz), 6.79 (d, 2H, aryl, $^3J_{HH}$ = 5.6 Hz), 3.92 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ (ppm)): 161.6, 140.0, 134.6, 128.7, 127.2, 126.0, 125.4, 122.7, 120.2, 115.3, 55.7. FT-IR (cm^{-1} (ranked intensity)): 656.3 (10), 700.5 (14), 752.7 (8), 838.8 (3), 879.3 (6), 1027.0 (7), 1169.4 (2), 1257.7 (7), 1305.9 (11), 1366.4 (15), 1442.4 (13), 1507.9 (1), 1556.1 (4), 1609.1 (9), 3019.4 (12). FT-Raman (cm^{-1} (ranked intensity)): ν 659.0 (12), 796.7 (5), 1123.7 (13), 1238.1 (10), 1339.9 (8), 1363.6 (2), 1405.6 (3), 1433.6 (9), 1462.0 (6), 1491.5 (1), 1586.6 (4), 1608.3 (7), 3099.2 (11). HRMS: $[C_{25}H_{19}N_2O_2S_2]^+$ calcd (found) 443.5600 (443.8661). Anal. Calcd for $C_{25}H_{19}N_2O_2S_2Cl·0.5CH_2Cl_2$: C, 58.73; H, 3.87; N, 5.37; S, 12.61. Found: C, 58.74; H, 4.45; N, 5.50; S, 12.80.

*Compound **5**.* A 2 mL THF solution of LiHMDS (0.70 g, 0.42 mmol) was added to a 5 mL toluene solution of **3** (0.20 g, 0.42 mmol) at room temperature. The reaction mixture was stirred at room temperature for 2 h. Upon completion a white precipitate was removed by centrifugation and the resulting yellow solution was concentrated, yielding a yellow solid. Yield: 48% (0.09 g, 0.20 mmol), Mp: 147−150 °C. ^1H NMR (C_6D_6, δ (ppm)): 7.25 (d, 4H, aryl, $^3J_{HH}$ = 8.9), 6.87 (d, 2H, aryl, $^3J_{HH}$ = 5.5), 6.71 (d, 2H, aryl, $^3J_{HH}$ = 5.5), 6.71 (d, 2H, aryl, $^3J_{HH}$ = 5.5), 6.53 (d, 2H, aryl, $^3J_{HH}$ = 8.9), 3.22 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ (ppm)): 156.9, 138.7, 132.6, 129.1, 128.9, 128.1, 126.6, 124.9, 124.0, 121.8, 113.6, 54.5. FT-IR (cm^{-1} (ranked intensity): ν 551.4 (7), 599.3 (13), 634.3 (15), 730.5 (6), 820.6 (4), 856.3 (12), 1034.8 (3), 1104.9 (14), 1176.3 (5), 1246.4 (2), 1298.7 (8), 1366.9 (9), 1463.9 (10), 1505.5 (1), 1583.4 (11). HRMS: $[C_{50}H_{37}N_4O_4S_4]^+$ calcd (found) 885.1700 (885.1698). Anal. Calcd for $C_{50}H_{36}N_4O_4S_4$: C, 67.85; H, 4.10; N, 6.33; S, 14.40. Found: C, 67.10; H, 4.26; N, 5.98; S, 14.17.

*Compound **6**.* A 2 mL THF solution of LiHMDS (0.14 g, 0.63 mmol) was added dropwise to a 5 mL slurry of **3** (0.30 g, 0.63 mmol).

The reaction mixture was stirred for 10 min, after which a 3 mL solution of $B(C_6H_5)_3$ (0.15 g, 0.63 mmol) was added. The reaction mixture was stirred at room temperature for 1 h. The white precipitate was removed by centrifugation, and the resulting yellow solution was concentrated, yielding a yellow powder. Yield: 70% (0.30 g, 0.43 mmol). Mp: 136−138 °C. ^{1}H NMR ($CDCl_3$, δ (ppm)): 7.19 (d, 2H, aryl, $^3J_{HH}$ = 5.2 Hz), 7.07 (d, 6H, aryl, $^3J_{HH}$ = 6 Hz), 6.88 (m, 12H, aryl), 6.50 (d, 4H, aryl, $^3J_{HH}$ = 8.8 Hz), 5.88 (d, 2H, aryl, $^3J_{HH}$ = 5.2 Hz), 3.77 (s, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ (ppm)): 159.5, 135.8, 132.5, 129.6, 127.6, 127.5, 126.1, 125.6, 123.3, 123.1 120.7, 113.9, 55.4. ^{11}B{^{1}H} NMR ($CDCl_3$, δ (ppm)): δ −8.2 (br s). FT-IR (cm^{-1} (ranked intensity)): ν 644.4 (11), 706.4 (10), 732.4 (2), 821.7 (5), 897.8 (6), 1027.5 (4), 1107.1 (15), 1167.0 (8), 1251.5 (3), 1300.8 (7), 1361.6 (12), 1440.8 (14), 1510.4 (1), 3031 (13) cm^{-1}. HRMS: $[C_{43}H_{34}N_2O_2S_2BNa]^+$ calcd (found) 707.1974 (707.2006). Anal. Calcd for $C_{43}H_{34}N_2O_2S_2B$: C, 74.07; H, 5.13; N, 4.32; S, 9.89. Found: C, 74.53; H, 4.86; N, 4.05; S, 9.24.

*Compound **7**.* A 5 mL CH_2Cl_2 solution of **3** (1.00 g, 2.10 mmol) was added dropwise to a 5 mL CH_2Cl_2 slurry of Ag_2O (0.24 g, 1.05 mmol). The reaction mixture was stirred at room temperature over 4 Å molecular sieves in the dark for 48 h. The yellow powder was isolated by filtration and washed with Et_2O (3 × 5 mL). Yield: 82% (1.22 g, 2.08 mmol). Dec pt: 195−197 °C. ^{1}H NMR ($CDCl_3$, δ (ppm)): 7.52 (d, 4H, aryl, $^3J_{HH}$ = 8.8 Hz), 7.38 (d, 2H, aryl, $^3J_{HH}$ = 5.6 Hz), 7.14 (d, 4H, aryl, $^3J_{HH}$ = 8.8 Hz), 6.67 (d, 2H, aryl, $^3J_{HH}$ = 5.6 Hz), 3.95 (s, 6H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ (ppm)): 160.9, 132.3, 131.3, 128.8, 127.8, 126.0, 123.6, 115.3, 55.8. FT-IR (cm^{-1} (ranked intensity)): ν 640.9 (12), 737.5 (4), 802.1 (9), 835.1 (3), 887.6 (6), 1027.0 (5), 1104.6 (11), 1164.5 (8), 1251.8 (2), 1301.2 (2), 1333.4 (15), 1441.9 (15), 1513.0 (1), 1607.4 (10), 3060.8 (12). FT-Raman (cm^{-1} (ranked intensity)): ν 640.8 (12), 737.5 (4), 802.1 (9), 835.1 (3), 887.6 (6), 1027.0 (5), 1104.6 (11), 1164.5 (8), 1251.8 (2), 1301.2 (7), 1333.4 (15), 1441.9 (14), 1513.0 (1), 1607.4 (10), 3060.8 (12). HRMS: $[C_{50}H_{36}N_4O_4S_4Ag]^+$ calcd (found) 991.0654 (991.0697). Anal. Calcd for $C_{50}H_{38}N_4O_4S_4Ag$: C, 51.16; H, 3.26; N, 4.77; S, 10.93. Found: C, 51.45; H, 2.77; N, 4.70; S, 10.74.

*Compound **9**.* A 10 mL toluene solution of compound **7** (0.12 g, 0.20 mmol) and $[Rh(cod)Cl]_2$ (0.10 g, 0.20 mmol) was heated to 120 °C in a pressure tube in the dark for 12 h. Upon completion the yellow reaction mixture was filtered to remove the salt and concentrated, yielding a yellow powder. Yield: 87% (0.12 g, 0.17 mmol). Dec pt: 164 °C. ^{1}H NMR ($CDCl_3$, δ (ppm)): 8.51 (dd, 2H, aryl, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.6), 7.44 (dd, 2H, aryl, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.6), 7.31 (d, 2H, thienyl, $^3J_{HH}$ = 5.5), 7.27 (dd, 2H, aryl, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.9), 7.12 (dd, 2H, aryl, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.9), 6.72 (d, 2H, thienyl, $^3J_{HH}$ = 5.5), 4.80 (t, 2H, COD, $^3J_{HH}$ = 2.96), 4.00 (s, 6H, CH_3), 3.04 (t, 2H, COD, $^3J_{HH}$ = 2.40), 1.87 (m, 2H, COD), 1.62 (m, 6H, COD). ^{13}C{^{1}H} NMR ($CDCl_3$, δ (ppm)): 159.9, 132.2, 131.6, 130.5, 128.5, 128.2, 125.3, 122.6, 120.8, 114.0, 98.1 ($^1J_{C-Rh}$ = 6.2), 68.0 ($^1J_{C-Rh}$ = 14.5), 55.7. ^{13}C{^{1}H} NMR ($CDCl_3$, δ (ppm)) at −50 °C: 191.3 ($^1J_{carbene-Rh}$ = 50.1). FT-IR (cm^{-1} (ranked intensity)): ν 557.9 (9), 640.5 (13), 702.9 (3), 736.3 (4), 802.0 (5), 835 (10), 887.0 (12), 1033.3 (7), 1170.4 (8), 1250.8 (2), 1302.8 (3), 1332.5 (6), 1440.5 (14), 1458.7 (15), 1513.1 (1). FT-Raman (cm^{-1} (ranked intensity)): ν 440.3 (3), 557.6 (13), 797.2 (6), 1119.9 (15), 1233.4 (14), 1284.5 (9), 1303.6 (12), 1361.9 (7), 1400.4 (4), 1464.8 (5), 1495.4 (2), 1587.1 (11), 1609.4 (8), 3103.3 (10). Anal. Calcd for $C_{33}H_{27}N_2O_2S_2ClRh$: C, 57.77; H, 3.97; N, 4.08; S, 9.35. Found: C, 56.65; H, 4.25; N, 3.78; S, 9.55 (in several attempts made for elemental analysis, the carbon was consistently high).

*Compound **10**.* A 25 mL flask was charged with a 10 mL CH_2Cl_2 solution of **9** (0.80 g, 0.12 mmol), and CO(g) was bubbled through for 2 h. Upon completion the reaction mixture was concentrated, yielding a yellow oil. The yellow oil was triturated with hexanes, precipitating a yellow solid. The hexanes were decanted off and the yellow solid dried in vacuo. Yield: 58% (0.045 g, 0.07 mmol). Dec pt: 158 °C. ^{1}H NMR ($CDCl_3$, δ (ppm)): 7.67 (br s, 4H, aryl), 7.36 (d, 2H, thienyl, $^3J_{HH}$ = 5.5), 7.18 (d, 4H, aryl, $^3J_{HH}$ = 9.0), 6.60 (d, 2H, thienyl, $^3J_{HH}$ = 5.5), 3.99 (s, 6H, CH_3); ^{13}C{^{1}H} NMR ($CDCl_3$ δ (ppm)): 160.6, 131.7, 130.7, 128.6, 125.8, 122.9, 120.5, 114.7, 55.6. ^{13}C{^{1}H} NMR ($CDCl_3$, δ (ppm)) at −50 °C: 185.4 ($^1J_{CO-Rh}$ = 55.0), 182.5 ($^1J_{C-Rh}$ = 75.4), 180.8 ($^1J_{CO-Rh}$ = 42.9). FT-IR (cm^{-1} (ranked intensity)): ν 588.9 (14), 640.8 (13), 701.9 (8), 731.6 (5), 805.0 (4), 835.0 (3), 889.5 (9), 1030.7 (6), 1106.9 (15), 1167.5 (12), 1251.4 (2), 1301.6 (11), 1512.8 (1), 1995.0 (10), 2074.7 (7). FT-Raman (cm^{-1} (ranked intensity)): ν 667.2 (9), 797.5 (6), 992.8 (11), 1122.9 (10), 1238.6 (5), 1286.9 (13), 1348.7 (3), 1367.4 (14), 1404.5 (1), 1466.6 (15), 1494.3 (2), 1610.5 (8), 1991.9 (7), 2076.3 (4). Anal. Calcd for $C_{27}H_{21}N_2O_2S_2RhCl$: C, 49.97; H, 2.90; N, 4.48; S, 10.26. Found: C, 50.43; H, 2.81; N, 4.19; S, 10.00.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Representative multinuclear NMR spectra, fluorescence and UV-vis spectra, and the IR spectrum for compound **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: pragogna@uwo.ca.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Rasmussen, S. C.; Schwiderski, R. L.; Mulholland, M. E. *Chem. Commun.* **2011**, *47*, 11394−11410.

(2) Skotheim, T. A.; Reynolds, J. R. *Handbook of Conducting Polymers*, 3rd ed.; CRC Press: Boca Raton, FL, 2007.

(3) Perepichka, I. F.; Perepichka, D. F. *Handbook of Thiophene-based Materials*; Wiley: Hoboken, NJ, 2009.

(4) Marshall, N.; Sontag, S. K.; Locklin, J. *Chem. Commun.* **2011**, *47*, 5681−5689.

(5) Roncali, J. *Mater. Chem.* **1999**, *9*, 1875.

(6) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93.

(7) Perepichka, I. F.; Perepickah, D. F. *Adv. Mater.* **2005**, *17*, 2281−2305.

(8) Wolf, M. O. *Adv. Mater.* **2001**, *13*, 545−553.

(9) Sauvage, J. P.; Kern, J. M.; Bidan, G.; Divisia-Blohorn, B.; Vidal, P. L. *New J. Chem.* **2002**, *26*, 1287−1290.

(10) Jousselme, B.; Blanchard, P.; Ocafrain, M.; Allain, M.; Levillain, E.; Roncali, J. *J. Mater. Chem.* **2004**, *14*, 421−427.

(11) Hill, N. J.; Vargas-Baca, I.; Cowley, A. H. *Dalton Trans.* **2009**, 240−253.

(12) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612−3676.

(13) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290−1309.

(14) Jahnke, M. C.; Hahn, F. E. *Top. Organomet. Chem.* **2010**, *30*, 95−129.

(15) Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440−1449.

(16) Mercs, L.; Albrecht, M. *Chem. Soc. Rev.* **2010**, *39*, 1903−1912.

(17) Pugh, D.; Danopoulos, A. A. *Coord. Chem. Rev.* **2007**, *251*, 610−641.

(18) Wang, Y.; Robinson, G. H. *Dalton Trans.* **2012**, *41*, 337−345.

(19) Wang, Y.; Robinson, G. H. *Inorg. Chem.* **2011**, *50*, 12326−12337.

(20) Dutton, J. L.; Tuononen, H. M.; Ragogna, P. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 4409−4413.

(21) Cowley, A. H. *J. Organomet. Chem.* **2001**, *617−618*, 105−109.

(22) Murata, M.; Watanabe, T.; Nishihara, H. *J. Am. Chem. Soc.* **2003**, *125*, 12420−12421.

(23) Kingsborough, R. P.; Swagar, T. M. *J. Am. Chem. Soc.* **1999**, *121*, 8825−8834.

(24) Boydston, A. J.; Williams, K. A.; Bielawski, C. W. *J. Am. Chem. Soc.* **2005**, *127*, 12496−12497.

(25) Coady, D. J.; Khramov, D. M.; Norris, B. C.; Tennyson, A. G.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2009**, *48*, 5187−5190, S5187/1−S5187/52.

(26) Khramov, D. M.; Coady, D. J.; Bielawski, C. W. *Polym. Prepr.* **2008**, *49*, 139−140.

(27) Norris, B. C.; Bielawski, C. W. *Macromolecules* **2010**, *43*, 3591−3593.

(28) Mercs, L.; Neels, A.; Stoeckli-Evans, H.; Albrecht, M. *Dalton Trans.* **2009**, 7168−78.

(29) Zhou, H.; Zhang, W.-Z.; Wang, Y.-M.; Qu, J.-P.; Lu, X.-B. *Macromolecules* **2009**, *42*, 5419−5421.

(30) Powell, A. B.; Bielawski, C. W.; Cowley, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 18232−18233.

(31) Powell, A. B.; Bielawski, C. W.; Cowley, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 10184−10194.

(32) Monot, J.; Brahmi, M. M.; Ueng, S.-H.; Robert, C.; Desage-El, M. M.; Curran, D. P.; Malacria, M.; Fensterbank, L.; Lacote, E. *Org. Lett.* **2009**, *11*, 4914−4917.

(33) Newman, C. P.; Clarkson, G. J.; Rourke, J. P. *J. Organomet. Chem.* **2007**, *692*, 4962−4968.

(34) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972−975.

(35) Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 1256−1266.

(36) Scarborough, C. C.; Guzei, I. A.; Stahl, S. S. *Dalton Trans.* **2009**, 2284−2286.

(37) Dyker, C. A.; Lavallo, V.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int., Ed.* **2008**, *47*, 3206−3209.

(38) Lavallo, V.; Canac, Y.; DeHope, A.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 7236−7239.

(39) Bazinet, P.; Yap, G. P. A.; Richeson, D. S. *J. Am. Chem. Soc.* **2003**, *125*, 13314−13315.

(40) Türkment, H.; Çetinkaya, B. *J. Organomet. Chem.* **2006**, *691*, 3749−3759.

(41) de Frémont, P.; Scott, N. M.; Stevens, E. D.; Ramnial, T.; Lightbody, O. C.; Macdonald, C. L. B.; Clyburne, J. A. C.; Abernethy, C. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 6301−6309.