Model Coordination Complexes for Designing Poly(terthiophene)/Rh(I) Hybrid Materials with Electrochemically Tunable Reactivities

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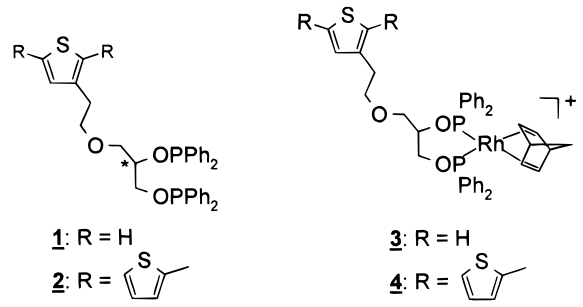
The synthesis and characterization of two chiral, redox-active Rh(I) bis(diphenylphosphinite) monomers, complexes **3** and **4**, are reported. Complex **4**, [(η^2-1,2- bis(diphenylphosphinite),4-oxo-6-(3′-α-terthiophene)Rh(I)(η^4-C_7H_8)]BF_4, can be electrochemically polymerized to form poly-**4**, and the η^4-C_7H_8 ligand can be hydrogenated in THF to form the metal-containing polymer **17**. Polymer **17** is proposed to consist of a poly(terthiophene) backbone with Rh(I) phenyl-bridged dimers acting as cross-linkers between neighboring polymer chains. This structural formulation for polymer **17** is based upon its electrochemistry and a comparison with the solution chemistry of monomer **4**. Significantly, this study discusses the importance of balancing polymerization potential, metal oxidation potential, and polymer ligating properties in the design of high surface area, polymeric, redox-switchable hemilabile ligands.

Introduction

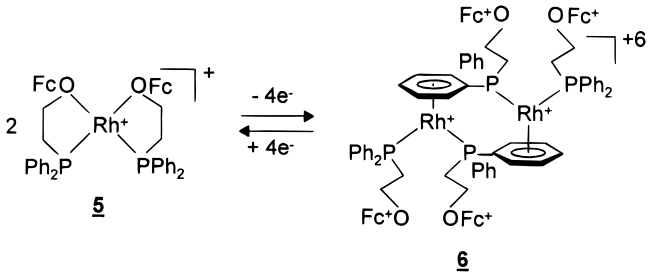
This paper reports the design, synthesis, and electrochemical behavior of thiophene- and terthiophene-based bis(diphenylphosphinite) ligands **1** and **2** and their complexes with Rh(I), **3** and **4** (Chart 1). These complexes incorporate a chiral carbon center and a catalytically active Rh(I) center into an electrochemically active conducting polymer matrix. These systems were targeted to probe the important factors in the design of polymeric, redox-switchable hemilabile ligands (RHLs).

RHLs are a class of ligands[1,2] intended to give electrochemical control over the coordination environment of a bound transition metal center.[3−8] For example, reversible electrochemical oxidation of the ferrocenyl groups in Rh(I)-RHL complex **5** results in the formation of the dimeric complex **6** (Scheme 1).[5] In this example, a 16-electron, square-planar metal complex and a 36-electron, piano-stool dimer can be electrochemically interconverted. Since the Rh centers in **5** and **6** have significantly different *steric* and *electronic* coordination environments, this type of reaction has implications in the design of new redox-active molecules and materials with electrochemically controllable catalytic[7] and small molecule uptake and release properties.[8]

Chart 1



Scheme 1



In addition to phosphinoether RHLs (as in **5**),[3,5,7,8] ligands based on redox-active phosphinothioethers[8] and phosphinoarenes[4,6] have been designed. In the case of phosphinoarenes, the arene is a labile group which can temporarily occupy three coordination sites on a Rh(I) center. In an attempt to extend our molecular RHL systems to polymeric structures, we have begun to explore the use of polymerizable heterocyclic ligands based on thiophenes, which are isoelectronic with arenes.

Thiophenes have several attributes which make them attractive materials for RHL design. First, they have

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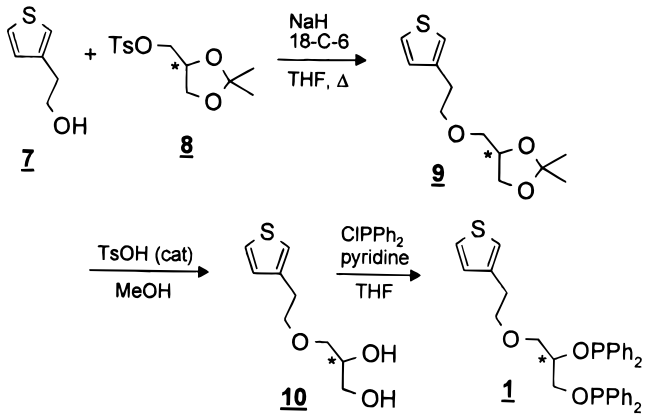
been shown to bind transition metals in a variety of ways:[9,10] η^1 through the sulfur heteroatom, η^2 and η^4 via the unsaturated carbon atoms, and η^5 via a π-interaction involving all atoms of the thiophene ring. The most common mode of binding is in an η^5 manner, and two crystallographically characterized Rh(I) η^5-thiophene complexes have been reported.[11,12] Graf et al. also have reported the preparation of Ru(II) and Os(II) η^5-oligothiophene complexes.[13,14]

Thiophenes and oligothiophenes can be electrochemically or chemically polymerized and deposited onto electrode surfaces as conducting polymer films,[15,16] and these conducting polymers can be reversibly oxidized to varying extents.[15−17] The rationale behind using polythiophenes in RHL materials is that the polymer's binding affinity for a metal center will depend on its extent of oxidation, which can be controlled electrochemically. This approach could lead to surface-confined, high surface area, polymeric RHL−metal complexes with electrochemically tunable stoichiometric and catalytic reactivities. Indeed, others have shown in complementary but fundamentally different work that a conducting polymer attached as a substitutionally inert ligand to a transition metal center allows one to alter the electronic characteristics of the metal as a function of polymer oxidation state.[18] In addition, several groups have recently reported conducting polymer/transition metal hybrid materials which demonstrate how metals can be used to tailor the electronic properties of a conducting polymer backbone.[19−22]

Toward the goal of designing tunable, conducting polymer-based transition metal complexes, this paper reports the synthesis and electrochemical behavior of thiophene- and terthiophene-based bis(diphenylphosphinite) ligands **1** and **2** and their complexes with Rh(I), **3** and **4** (Chart 1). Compound **4** can be used to prepare a redox-active conducting polymer with chiral, catalytically active Rh(I) centers covalently attached to the periphery of a redox-active polyterthiophene backbone. This paper explores the importance of balancing polymer oxidation potential, metal center oxidation potential, and competing modes of ligation in the design of polymeric, chiral RHLs. Although our ultimate goal has not been achieved, this work lays the foundation for the future design and synthesis of conducting polymer RHL complexes.

Scheme 2



Results and Discussion

Ligand **1** was synthesized as outlined in Scheme 2. The first step was a Williamson ether reaction between 2-(3-thienyl)ethanol, **7**, and racemic tosyl solketal, **8**, in the presence of 18-crown-6 (18-C-6) to form the acetonide **9**. Compound **9** was stirred in methanol overnight with a catalytic amount of *p*-toluenesulfonic acid (TsOH) to yield the diol **10**, which was subsequently reacted with chlorodiphenylphosphine and pyridine in THF to yield ligand **1**.

Ligand **1** has several noteworthy features. First, it may chelate a metal center (e.g., Rh(I)) in a bidentate fashion to form a seven-membered bis(diphenylphosphinite) metallocycle. RajanBabu and co-workers have shown that chiral Rh(I) bis(diarylphosphinite) complexes are active catalysts for the hydrogenation of prochiral olefins,[23] and that Ni(0) bis(cyclooctadiene) complexes with this type of ligand are effective asymmetric olefin hydrocyanation catalysts.[24,25] Second, ligand **1** imparts chirality to the metal-chelating group. This chiral center is introduced via the tosyl solketal moiety, **8**, which is commercially available in both enantiomerically pure forms.[26] Finally, the thienyl moiety can often be electrochemically polymerized to form conducting films on an electrode surface.[15,16] Such films may be reversibly oxidized, forming charge-delocalized, electronically conducting materials.

Attempts to polymerize the free ligand **1** on a Au disk electrode in acetonitrile/0.1 M n-Bu_4NPF_6 solution, however, were not successful. During the electrochemical experiment a single, irreversible oxidation at 1100 mV (vs $FcH/[FcH]^+$) was observed, corresponding to oxidation of the thienyl group to a radical cation.[15] Surprisingly, no growth of conducting polymer was observed upon repeated cycling of the electrode between −250 and 1200 mV (vs $FcH/[FcH]^+$). Monomer concentrations ranging from 0.1 to 1.0 M were tested, all producing similar results.

The inhibited polymerization of **1** can be attributed to the presence of the nucleophilic phosphinite functionalities. These nucleophiles can attack and degrade

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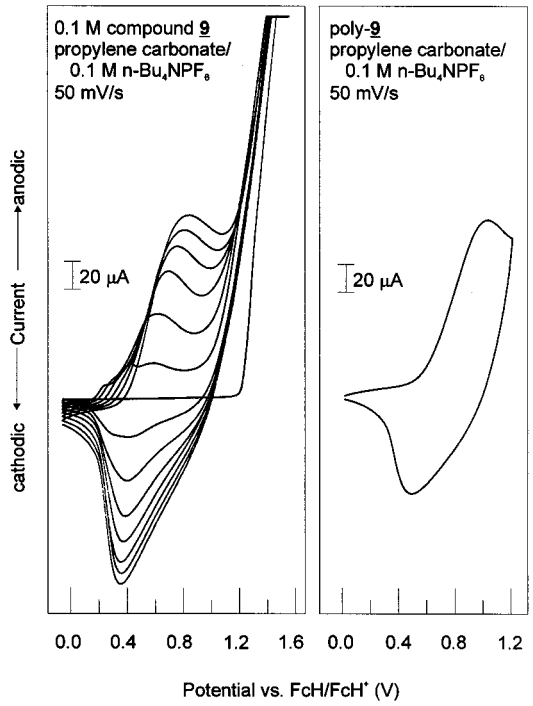
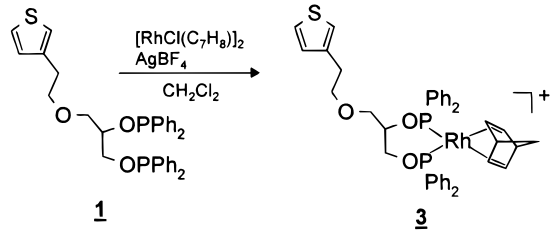


Figure 1. Polymerization of compound **9** in propylene carbonate/0.1 M n-Bu_4NPF_6. Monomer oxidation occurs at 1200 mV (vs FcH/FcH^+), and poly-**9** grows in at E_{pa} = 800 mV.

Scheme 3



1 **3**

the electrophilic radical cation generated upon oxidation of the thienyl moiety. This phenomenon has been observed by others, who noted that the presence of pyridine also inhibits the polymerization of thiophene.[15] The inhibitory effects of the phosphinite functionalities was confirmed by studying the oxidative electrochemistry of the acetonide precursor **9** in both the absence and the presence of $EtOPPh_2$. Without $EtOPPh_2$, compound **9** forms polymer films on a Au disk electrode by cycling between 0 and 1400 mV (vs $FcH/[FcH]^+$) in propylene carbonate/0.1 M n-Bu_4NPF_6 (Figure 1). Oxidation of the thienyl group occurs at 1200 mV (vs $FcH/[FcH]^+$), and upon repeated scanning, polythiophene grows in at E_{pa} = 800 mV and E_{pc} = 350 mV (vs $FcH/[FcH]^+$). Under identical conditions, addition of 2 equiv of $EtOPPh_2$ (approximately the same concentration of nucleophile in ligand **1**) completely inhibits the polymerization of **9**.

To tie up the nucleophilic phosphinite groups and incorporate a potentially catalytically active metal center into this system, ligand **1** was reacted with Rh(I) to from the *cis*-phosphinite, η^4-norbornadiene complex **3** (Scheme 3). Reaction of $[RhCl(C_7H_8)]_2$ and $AgBF_4$ in dichloromethane followed by filtration of the resulting AgCl precipitate and subsequent dropwise addition of ligand **1** in dichloromethane to the filtrate afforded complex **3** in high yield.

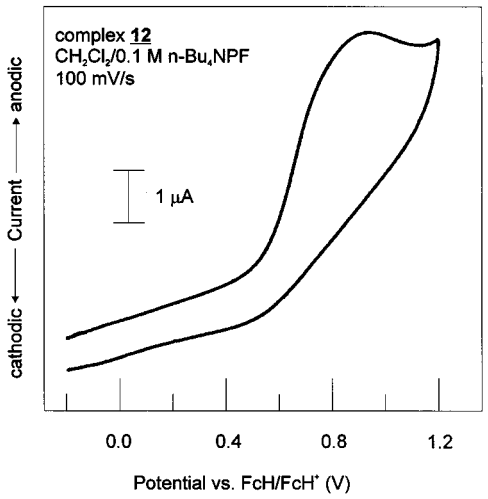
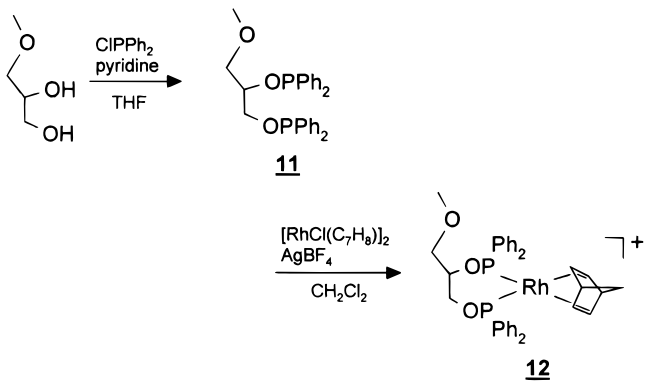


Figure 2. Electrochemistry of model complex **12**. Complex **12** exhibits an irreversible oxidation at E_{pa} = 900 mV (vs FcH/FcH^+) in CH_2Cl_2/0.1 M n-Bu_4NPF_6.

Scheme 4



Attempts to electrochemically polymerize complex **3** onto Au disk electrodes in acetonitrile/0.1 M n-Bu_4NPF_6 solvent were not successful, and two irreversible oxidations at E_{pa} = 900 mV and E_{pa} = 1200 mV (vs $FcH/[FcH]^+$) were observed. The second oxidation is assigned to generation of a thienyl radical cation (vide infra). The first oxidation tentatively was assigned to a Rh-centered oxidation. To confirm this assignment, model ligand **11** and its corresponding Rh(I) model complex **12** were synthesized (Scheme 4) and the electrochemistry of **12** was examined. Complex **12** shows an irreversible oxidation at 900 mV (vs $FcH/[FcH]^+$) in dichloromethane/0.1 M n-Bu_4NPF_6 (Figure 2) that is consistent with that observed for complex **3**.

One method for lowering the polymerization potential of an aromatic heterocycle is by increasing the conjugation length of the monomer.[27] Consistent with this strategy, the terthiophene-based ligand **2** was targeted. This ligand was synthesized as outlined in Scheme 5. The key steps in this synthesis were bromination of **7** using bromine in chloroform to form compound **13**. The alcohol functionality was protected by reaction of **13** with **8** to afford the acetonide **14**, which was coupled with 2-thienylmagnesiumbromide to make the terthiophene acetonide **15**. Compound **15** was deprotected to form the diol **16**, which was reacted with chlorodiphenyl-

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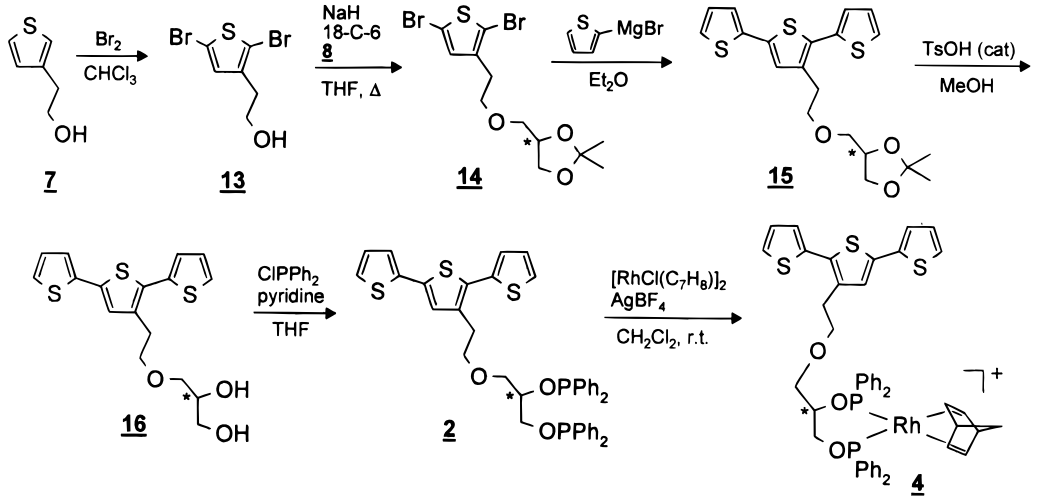
Scheme 5



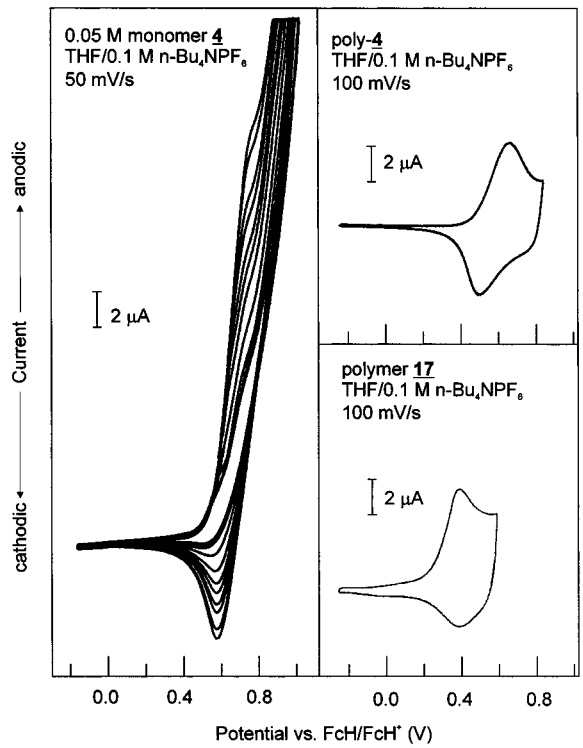
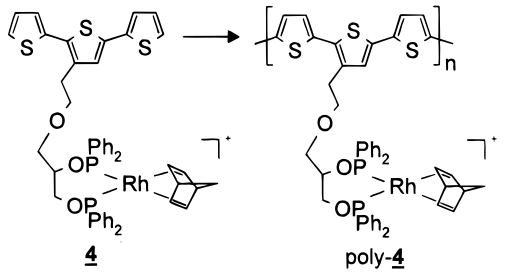


Figure 3. Polymerization of compound **4** in THF/0.1 M *n*-Bu_4NPF_6. Monomer oxidation occurs at 650 mV (vs FcH/FcH^+), and poly-**4** grows in at $E_{pa} = 610$ mV. Upon exposure of poly-**4** to H_2 in THF, polymer **17** is formed. Polymer **17** exhibits a −160-mV shift in E_{pa} compared to poly-**4**.

phosphine and pyridine in tetrahydrofuran (THF) to give ligand **2** as a light green oil. Ligand **2** was added dropwise to the product formed from the reaction between $[RhCl(C_7H_8)]_2$ and $AgBF_4$ in CH_2Cl_2 to obtain **4**, which was purified by recrystallization.

Complex **4** can be electrochemically polymerized in THF/0.1 M *n*-Bu_4NPF_6 to form poly-**4** by cycling an electrode between −200 and 900 mV (vs $FcH/[FcH]^+$) (Figure 3; Scheme 6). Poly-**4** grows in at $E_{pa} = 610$ mV (vs $FcH/[FcH]^+$), and its electrochemical behavior is similar to that observed for polymers of terthiophene acetonide **15** ($E_{pa} = 580$ mV (vs $FcH/[FcH]^+$)), suggesting that the electrochemical process is terthiophene-based. This potential is almost 300 mV below the Rh(I) oxidation of **12**, and Rh(I) oxidation apparently does not

Scheme 6



significantly interfere with terthiophene polymerization, unlike the monothiophene analogue **3** (vide infra).

Treatment of poly-**4** with H_2 (1 atm) in THF leads to a new polymer, **17**. Polymer **17** exhibits stable and reversible electrochemistry in THF/0.1 M *n*-Bu_4NPF_6, Figure 3. Thin films of polymer **17** exhibit significant negative shifts in E_{pa} and E_{pc} relative to poly-**4**, −160 and −60 mV, respectively. Upon scanning to higher potentials, a new, irreversible oxidation at $E_{pa} = 1200$ mV (vs $FcH/[FcH]^+$) is observed. Accessing this wave, which we attribute to Rh(I) oxidation, completely destroys the electrochemical response of polymer **17**.

To determine the ligand environment of the Rh in the hydrogenated polymer complex, the chemistry of monomer **4** was examined in solution. Monomer **4** can be reacted with H_2 in acetone-d_6 to form the solvento adduct **18** quantitatively by ^{31}P NMR (Scheme 7). No hydrides were detected by ^1H NMR. The presence of bound acetone-d_6 was confirmed by IR spectroscopy, which shows a $\nu_{CO} = 1696$ cm^{-1}. ($\nu_{CO} = 1703$ cm^{-1} for unbound acetone-d_6 in dichloromethane.)

When the solvent is removed from **18** and the product redissolved in weakly coordinating CD_2Cl_2, a new product, **19**, is obtained. The IR spectrum of **19** shows no bands in the region of 1696 cm^{-1}, indicating removal of the coordinated acetone ligand. Significantly, removal of CD_2Cl_2 from **19** and redissolution of the product in acetone-d_6 quantitatively regenerates complex **18** (Scheme 7).

In the absence of a coordinating solvent, two possibilities for the structure of **19** were considered: (1) a thiophene-bound, η^5-arene complex or (2) a phenyl-bridged dimer (Chart 2**)**. The ^1H spectrum of **19** shows several broad resonances, suggesting that multiple

Scheme 7

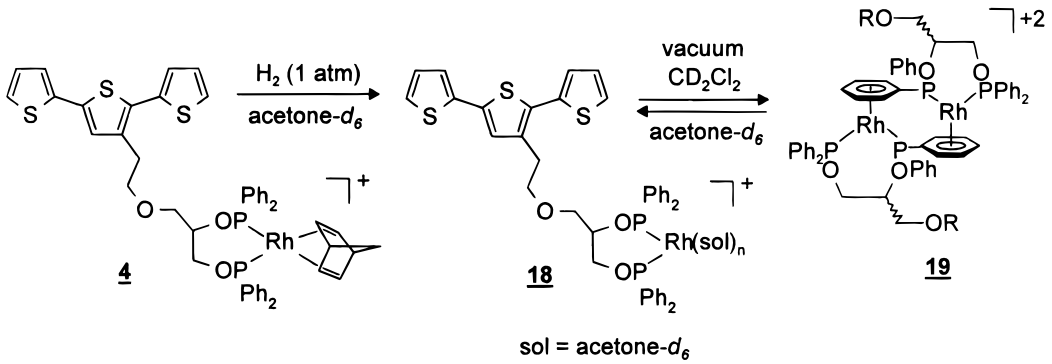
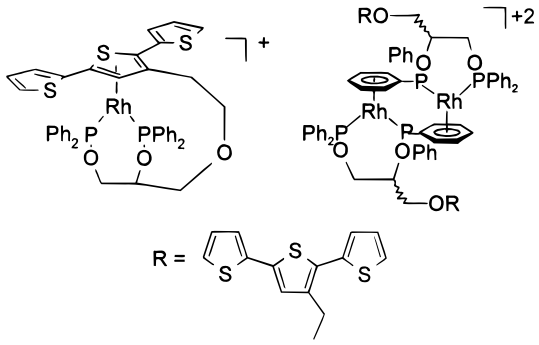


Chart 2



species exist in solution. In addition, the ^{31}P NMR also shows several multiplets in the 124−144 ppm region. Riley has reported that this spectral signature is characteristic of Rh phenyl-bridged dimers,[28] and on the basis of the reactivity of **19** coupled with the spectroscopy, we assign a phenyl-bridged dimer structure to **19**. The multiple species arise from structurally similar, but distinct, diastereomers resulting from the six chiral centers in each dimer.[29] This structural assignment is supported by molecular mass determination by vapor-phase osmometry[30] (M_{found} = 1785 g/mol, M_{calcd} = 1848 g/mol) and by comparing the ^{31}P NMR data for **19** with similar complexes reported in the literature.[5,28,29]

The Rh centers of polymer **17** also are believed to exist in a dimeric structure. The possibility of Rh binding to the backbone of the conducting polymer is ruled out on the basis of the electrochemical behavior of polymer **17**. Graf et al. have shown that the metal fragments bound in an η^5 manner to oligothiophenes remove the bound ring from the oligothiophene system and raise the oxidation potential of the bound oligothiophene.[13,14] Therefore, one would expect that Rh binding to the conducting polymer backbone would raise the oxidation potential of polymer **17**, instead of lowering it as was observed. Therefore, we formulate polymer **17** as a cross-linked structure, where the Rh centers dimerize as in complex **19**. The degree of intra- versus interchain cross-linking is unknown. At this time, we do not understand why cross-linking would lead to negative shifts in the electrochemistry of polymer **17**.

Conclusion

Two new thienylalkylphosphinite ligands, **1** and **2**, and their corresponding Rh(I) complexes, **3** and **4**, have been synthesized and evaluated as candidates for conducting polymer-based RHLs. Although they do not yield the targeted materials, they do provide valuable insight into some of the factors that need to be considered when designing such materials. Monothiophene complex **3** cannot be electrochemically polymerized due to irreversible oxidation of the Rh(I) center, which occurs ~300 mV below thiophene oxidation and suppresses polymer formation. Extending the conjugation of the polymerizable unit using terthiophene (i.e., ligand **2** and complex **4**) brings the polymerization potential below that of the metal center, and poly-**4** can be readily grown by oxidative cycling. Hydrogenation of poly-**4** results in removal of the C_7H_8 ligand but gives the cross-linked polymer **17**, where the Rh(I) centers dimerize. This structure was assigned on the basis of the solution reactivity of complex **4** and the electrochemical behavior of polymer **17**.

Using these ligands and their corresponding Rh(I) complexes as templates, we have systematically determined the important factors which control the polymerization properties, electrochemistry, and coordination chemistry of this new class of thiophene-based monomer. Although in this system the Rh−thiophene interactions do not effectively compete with the Rh−arene interactions, this study lays the groundwork for designing terthiophene-based RHLs. Future work will be aimed at modifying the metal binding sites by exchanging the phosphinites for other substitutionally inert ligands such as phosphines or cyclopentadienyl groups and exploring other modes of terthiophene−metal binding.

Experimental Section

Materials and Methods. All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in an inert-atmosphere glovebox. Acetonitrile, dichloromethane, hexanes, and pentane were dried over calcium hydride. Tetrahydrofuran (THF) and diethyl ether were dried over sodium/benzophenone. All solvents were distilled under nitrogen and degassed prior to use. ^1H NMR spectra were recorded on a Varian Gemini 300-MHz FT NMR spectrometer, a Varian VXR 300-MHz spectrometer, or a Varian Unity 400-MHz FT NMR spectrometer. ^{31}P NMR spectra were recorded on a Varian Gemini 300-MHz spectrometer at 121 MHz and referenced versus the external standard 85% H_3PO_4. Electrochemical measurements were carried out on either a PINE AFRDE4 or a PINE AFRDE5 bipotentiostat/

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galvanostat using Au disk electrodes with a Pt mesh counter electrode and a $Ag/AgNO_3$ (0.01 M $AgNO_3$ in acetonitrile/0.1 M n-Bu_4NPF_6) reference electrode. All electrochemical data were referenced further versus the FcH/$[FcH]^+$ (Fc = (η^5-C_5H_5)-Fe(η^5-C_5H_4)) redox couple. Electron impact (EI) and fast atom bombardment (FAB) mass spectra were recorded using a Fisons VG 70-250 SE mass spectrometer. FT-IR spectra were recorded on a Nicolet 520SX spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification. 2-(3-Thienyl)ethanol (**7**), racemic tosyl solketal (**8**), pyridine, chlorodiphenylphosphine, racemic 3-methoxy-1,2-propanediol, 18-crown-6, sodium hydride, (1,1′-bis(diphenylphosphino)ferrocene)$PdCl_2$, *p*-toluenesulfonic acid, $[RhCl(C_7H_8)]_2$, and silver(I) tetraflouroborate were purchased from Aldrich Chemical Co. and used as received.

Syntheses. *$C_{12}H_{18}O_3S$ (**9**).* Dry sodium hydride (785 mg, 33 mmol) and 18-crown-6 (6.3 g, 24 mmol) were transferred to a 200-mL Schlenk flask which was fitted with a reflux condenser and evacuated to remove air. The flask was charged with dry N_2, and dry THF (30 mL) was then added, followed by **7** (2.9 mL, 26 mmol). After hydrogen evolution ceased, compound **8** (6.1 g, 22 mmol) in 30 mL of dry, degassed THF was added by cannula, and the reaction mixture was refluxed for 12 h. The organic layer was poured into 10 mL of water and diluted with 60 mL of diethyl ether. The organic layer was washed twice more with 10 mL of water and dried over magnesium sulfate, and the solvent was removed by rotary evaporation. Column chromatography on silica gel with 25% ether in pentane as the eluent gave **9** as a clear liquid (2.8 g, 11 mmol, 52%). ^{1}H NMR (acetone-d_6): δ 7.34 (dd, 1 H, 5-thienyl), 7.15 (dd, 1 H, 2-thienyl), 7.03 (dd, 1 H, 4-thienyl), 4.19 (m, 1 H, achiral ring H); 3.99 (dd, 1 H, achiral ring H); 3.7−3.6 (m, 3 H, chiral H and $ThCH_2CH_2O$), 3.51 (dd, 1 H, achiral nonring H), 3.43 (dd, 1 H, achiral nonring H), 2.88 (t, 2 H, $ThCH_2CH_2O$), 1.31 (s, 3 H, acetonide methyl), 1.26 (s, 3 H, acetonide methyl). HRMS(EI) [$M^+ - CH_3$] calcd for $C_{12}H_{18}O_3S$: 242.0977. Found: 242.0977.

*$C_9H_{14}O_3S$ (**10**).* This reaction was done in air. Compound **9** (1.30 g, 5.4 mmol) was dissolved in 5 mL of methanol, and *p*-toluenesulfonic acid (100 mg) was added to the reaction vessel. The reaction mixture was stirred for 16 h, and the solvent was removed by rotary evaporation. Column chromatography on silica gel with ether as the eluent gave **10** as a clear oil (983 mg, 4.7 mmol, 87%). ^{1}H NMR (acetone-d_6): δ 7.34 (dd, 1 H, 5-thienyl), 7.14 (dd, 1 H, 2-thienyl), 7.02 (dd, 1 H, 4-thienyl), 3.71 (m, 1 H, chiral H), 3.64 (t, 2 H, $ThCH_2CH_2O$), 3.4−3.6 (m, 4 H, achiral Hs), 2.86 (t, 2 H, $ThCH_2CH_2O$). HRMS(EI) [M^+] calcd for $C_9H_{14}O_3S$: 202.0664. Found: 202.0648.

*$C_{33}H_{32}O_3P_2S$ (**1**).* In a 25-mL Schlenk flask, compound **10** (494 mg, 2.45 mmol) was dissolved in 5 mL of dry THF. Dry pyridine (0.44 mL, 5.4 mmol) was syringed into the flask, followed by freshly distilled chlorodiphenylphosphine (0.88 mL, 4.9 mmol). The reaction mixture was stirred for 4 h, and the pyridinium chloride precipitate was then removed by filtration. Air-free column chromatography using silica gel (heated overnight at 250 °C under vacuum to remove water) with 25% ether in pentane as the eluent gave **1** as a clear oil (502 mg, 0.88 mmol, 36%). ^{1}H NMR (acetone-d_6): δ 7.3−7.6 (br, 21 H, phenyl H and 5-thienyl), 7.06 (dd, 1 H, 2-thienyl), 6.95 (dd, 1 H, 4-thienyl), 4.32 (m, 1 H, chiral H), 4.05 (m, 2 H, CH_2OP), 3.66 (m, 2 H, $ROCH_2CHOP$), 3.52 (m, 2 H, $ThCH_2CH_2O$), 2.73 (t, 2 H, $ThCH_2CH_2O$). ^{31}P {^{1}H} NMR (acetone-d_6): δ 116.6 (s); 114.2 (s). HRMS(FAB) [M^+] calcd for $C_{33}H_{32}O_3P_2S$: 570.1547. Found: 570.1527.

*$[C_{40}H_{40}O_3P_2SRh]BF_4$ (**3**).* $[RhCl(C_7H_8)]_2$ (150 mg, 0.32 mmol) and $AgBF_4$ (138 mg, 0.71 mmol) were added to a 50-mL round-bottom flask. The mixture was dissolved in 5 mL of dry dichloromethane and stirred for 1 h. The mixture was then filtered through Celite into a 50-mL Schlenk flask to remove AgCl and diluted with an additional 10 mL of dry dichloromethane. Ligand **1** (366 mg, 0.64 mmol) was dissolved in 5 mL of dry dichloromethane and added dropwise by pipet. After addition was complete, the solvent was removed in vacuo to afford crude **3**, which was purified by slow diffusion of pentane into a dichloromethane solution of **3**. Pure **3** was isolated as a red solid (472 mg, 0.55 mmol, 87%). ^{1}H NMR (acetone-d_6): δ 7.8−7.4 (br, 20 H, phenyl), 7.32(dd, 1 H, 5-thienyl), 7.07 (dd, 1 H, 2-thienyl), 6.94 (dd, 1 H, 3-thienyl), 5.29 (br, 4 H, NBD CH═CH), 4.87 (m, 1 H, chiral-H), 4.5−4.2 (m, 2 H, $ROCH_2CHOP$), 4.17 (br, 2H, NBD $CHCH_2$), 3.7−3.6 (m, 4 H, CH_2OP and $ThCH_2CH_2O$), 2.83 (t, 2 H, $ThCH_2CH_2O$), 1.71 (s, 2 H, NBD CH_2). ^{31}P {^{1}H} NMR (acetone-d_6): δ 133.5 (dd, J_{RhP} = 181, J_{PP} = 41), 131.4 (dd, J_{RhP} = 181, J_{PP} = 41). HRMS(FAB) [M^+]: Calcd. for $C_{40}H_{40}O_3P_2SRh^+$: 765.1228; Found: 765.1602.

*$C_{33}H_{32}O_3P_2S$ (**11**).* In a 25-mL Schlenk flask, racemic 3-methoxy-1,2-propanediol (200 mg, 1.88 mmol) was dissolved in 5 mL of dry pyridine. Freshly distilled chlorodiphenylphosphine (0.74 mL, 4.11 mmol) was syringed into the flask, and the reaction mixture was stirred for 4 h, after which the pyridinium chloride precipitate was removed by filtration. Air-free column chromatography using florisil (heated overnight at 250 °C under vacuum to remove water) with 2% ether in hexanes as the eluent gave **11** as a clear oil (61 mg, 0.13 mmol, 7%). ^{1}H NMR (acetone-d_6): δ 7.54−7.25 (br, 20 H, phenyls), 4.30 (m, 1 H, chiral H), 4.03 (m, 2 H, CH_2OP), 3.56 (m, 2 H, CH_2OMe), 3.19 (s, 3 H, methyl). ^{31}P {^{1}H} NMR (acetone-d_6): δ 116.5 (s), 114.4 (s). HRMS(EI) [M^+] calcd for $C_{28}H_{28}O_3P_2$: 474.1514. Found: 474.1528.

*$[C_{40}H_{40}O_3P_2SRh]BF_4$ (**12**).* $[RhCl(C_7H_8)]_2$ (30 mg, 0.07 mmol) and $AgBF_4$ (28 mg, 0.14 mmol) were added to a 25-mL round-bottom flask. The mixture was dissolved in 2 mL of dry dichloromethane and stirred for 1 h. The mixture was then filtered through Celite into a 50-mL Schlenk flask to remove AgCl and diluted with an additional 10 mL of dry dichloromethane. Ligand **11** (61 mg, 0.13 mmol) dissolved in 2 mL of dry dichloromethane was added dropwise by pipet. After addition was complete, the solvent was removed in vacuo to afford crude **12**, which was purified by slow diffusion of diethyl ether into a dichloromethane solution of **12**. Pure **12** was isolated as a red solid (54 mg, 0.09 mmol, 72%). ^{1}H NMR (acetone-d_6): δ 7.72−7.42 (br, 20 H, phenyls), 5.29 (br, 4 H, NBD CH═CH), 4.87 (m, 1 H, chiral-H), 4.41−4.30 (m, 2 H, $MeOCH_2CHOP$), 4.17 (br, 2H, NBD $CHCH_2$), 3.55 (br, 2 H, CH_2OP), 3.26 (s, 3 H, methyl), 1.70 (s, 2 H, NBD CH_2). ^{31}P {^{1}H} NMR (acetone-d_6): δ 133.5 (dd, J_{RhP} = 181, J_{PP} = 41), 131.4 (dd, J_{RhP} = 181, J_{PP} = 41). HRMS(FAB) [M^+] calcd for $C_{35}H_{36}O_3P_2Rh^+$: 669.1195. Found: 669.1183.

*$C_6H_6Br_2OS$ (**13**).* This reaction was done in air. In a 250-mL round-bottom flask equipped with an addition funnel, **7** (10 mL, 89 mmol) was dissolved in 50-mL of chloroform. The reaction vessel was cooled in an ice/water bath, and bromine (9.5 mL, 184 mmol) dissolved in 50 mL of chloroform was added quickly through an addition funnel. After the mixture was stirred for 4 h, the excess bromine was consumed by adding a saturated, aqueous solution of sodium metabisulfite. The organic layer was washed twice with a saturated, aqueous solution of sodium bicarbonate and once with water and then dried over magnesium sulfate and removed by rotary evaporation. Column chromatography on silica gel with ether as the eluent gave **13** as a light brown liquid (24.9 g, 87 mmol, 98%). ^{1}H NMR (acetone-d_6): δ 7.12 (s, 1 H, thienyl H), 3.72 (t, 2 H, $ThCH_2CH_2O$), 2.74 (t, 2 H,$ThCH_2CH_2O$). HRMS(EI) [M^+] calcd for $C_6H_6OSBr_2$: 283.8506. Found: 283.8490.

*$C_{12}H_{16}Br_2O_3S$ (**14**).* Dry sodium hydride (1.0 g, 42 mmol) and 18-crown-6 (10.3 g, 39.0 mmol) were transferred to a 200-mL Schlenk flask fitted with a reflux condenser and evacuated to remove air. Dry THF (50 mL) was then added, followed by **13** (10 g, 35 mmol). After hydrogen evolution ceased, **8** (9.8 g, 35 mmol) in 50 mL of dry THF was added by cannula, and the reaction was refluxed for 12 h. The organic layer was poured into 10 mL of water and diluted with 100 mL of diethyl ether. The organic layer was washed twice more with 10 mL of water, dried over magnesium sulfate, and dried by rotary evaporation. Column chromatography on silica gel with 20% ether in pentane as the eluent gave **14** as a clear liquid (5.3 g, 13 mmol, 38%). ^{1}H NMR (acetone-d_6): δ 7.12 (s, 1 H, thienyl H), 4.18 (m, 1 H, achiral ring), 3.99 (dd, 1 H, achiral ring),

3.6−3.7 (m, 3 H chiral H, and $ThCH_2CH_2O$), 3.48 (m, 2 H, achiral nonring), 2.80 (t, 2 H, $ThCH_2CH_2O$), 1.31 (s, 3 H, acetonide methyl), 1.27 (s, 3 H, acetonide methyl). HRMS-(EI) [$M^+ - CH_3$] calcd for $C_{11}H_{13}O_3SBr_2$: 382.8952. Found: 382.8948.

*$C_{20}H_{22}O_3S_3$ (**15**).* (1,1′-Bis(diphenylphosphino)ferrocene)-$PdCl_2$ (135 mg, 0.18 mmol) was weighed into a 100-mL Schlenk flask which was fitted with a reflux condenser and addition funnel. The flask was evacuated and backfilled with dry nitrogen. Compound **14** (3.0 g, 7.4 mmol) was added by cannula in 30 mL of dry, degassed diethyl ether. The reaction mixture was cooled to −20 °C in an acetone/ice bath, and magnesium-2-bromothiophene (44 mmol) in 20 mL of dry diethyl ether was added by addition funnel over a 2-h period. The reaction mixture was then allowed to warm to room temperature and stir overnight. The following morning, the reaction was refluxed for 2 h. The excess Grignard reagent was consumed by the slow addition of water to the organic layer, followed by three successive washings with water. The organic layer was dried over magnesium sulfate, and the solvent was removed by rotary evaporation. Column chromatography on silica gel with 10% ether in hexanes as the eluent gave **15** as a yellow oil (2.1 g, 5.2 mmol, 71%). ^{1}H NMR (acetone-d_6): δ 7.53 (dd, 1 H, 5 or 5″ thienyl), 7.43 (dd, 1 H, 5 or 5″ thienyl), 7.2−7.3 (m, 3 H, 3, 3′, and 3″ thienyl), 7.14 (dd, 1 H, 4 or 4″ thienyl), 7.08 (d, 1 H, 4 or 4″ thienyl), 4.12 (m, 1 H, achiral ring H), 3.99 (dd, 1 H, achiral ring H), 3.6−3.8 (m, 3 H, chiral H and $ThCH_2CH_2O$), 3.50 (m, 2 H, achiral nonring), 2.82 (t, 2 H, $ThCH_2CH_2O$), 1.30 (s, 3 H, acetonide methyl), 1.26 (s, 3 H, acetonide methyl). HRMS(EI) [M^+] calcd for $C_{20}H_{22}O_3S_3$: 406.0731. Found: 406.0709.

*$C_{17}H_{18}O_3S_3$ (**16**).* This reaction was done in air. Compound **15** (1.5 g, 3.7 mmol) was dissolved in 10 mL of methanol and *p*-toluenesulfonic acid (100 mg) added to the reaction vessel. The reaction mixture was stirred for 16 h, and the solvent was removed by rotary evaporation. Column chromatography on silica gel with ether as the eluent gave **16** as a yellow oil (1.2 g, 3.3 mmol, 90%). ^{1}H NMR (acetone-d_6): δ 7.52 (dd, 1 H, 5 or 5″ thienyl), 7.41 (dd, 1 H, 5 or 5″ thienyl), 7.2−7.3 (m, 3 H, 3, 3′, and 3″ thienyl), 7.13 (dd, 1 H, 4 or 4″ thienyl), 7.07 (dd, 1 H, 4 or 4″ thienyl), 3.7−3.8 (m, 3 H, chiral H and $ThCH_2CH_2O$), 3.4−3.7 (m, 4 H, achiral H's), 3.00 (t, 2 H, $ThCH_2CH_2O$). HRMS(EI) [M^+] calcd for $C_{17}H_{18}O_3S_3$: 366.0418. Found: 366.0420.

*$C_{41}H_{36}O_3P_2S_3$ (**2**).* In a 25-mL Schlenk flask, **16** (711 mg, 1.94 mmol) was dissolved in 5 mL of dry THF. Dry pyridine (0.35 mL, 4.3 mmol) was syringed into the flask, followed by freshly distilled chlorodiphenylphosphine (0.70 mL, 3.9 mmol). The reaction mixture was stirred for 4 h; the pyridinium chloride precipitate was then removed by filtration. Air-free column chromatography on silica gel (heated overnight at 250 °C under vacuum to remove water) using 25% ether in pentane as the eluent gave **2** as a green oil (564 mg, 0.77 mmol, 40%). ^{1}H NMR (acetone-d_6): δ 7.0−7.6 (br, 27 H, phenyls and thienyl H), 4.33 (m, 1 H, chiral H), 4.06 (m, 2 H, CH_2OP), 3.5−3.7 (m, 4 H, $ROCH_2CHOP$ and $ThCH_2CH_2O$), 2.87 (t, 2 H, $ThCH_2CH_2O$). ^{31}P {^{1}H} NMR (acetone-d_6): δ 116.5 (s), 113.7 (s). HRMS(EI) [M^+] calcd for $C_{41}H_{36}O_3P_2S_3$: 734.130. Found: 734.128.

*$[C_{48}H_{44}O_3P_2S_3Rh]BF_4$ (**4**).* $[RhCl(C_7H_8)]_2$ (121 mg, 0.26 mmol) and $AgBF_4$ (114 mg, 0.58 mmol) were added to a 50-mL round-bottom flask. The mixture was dissolved in 5 mL of dry dichloromethane and stirred for 1 h. The mixture was then filtered through Celite into a 50-mL Schlenk flask to remove AgCl and diluted with an additional 10 mL of dry dichloromethane. Ligand **2** (386 mg, 0.53 mmol) dissolved in 5 mL of dry dichloromethane was added dropwise by pipet. After addition was complete, the solvent was removed in vacuo to afford crude **4**, which was purified by slow diffusion of diethyl ether into a dichloromethane solution of **4**. Pure **4** was isolated as a red solid (525 mg, 0.52 mmol, 97%). ^{1}H NMR (acetone-d_6): δ 7.7−7.4 (br, 22 H, phenyls, 5 and 5″ thienyl), 7.0−7.3 (m, 5 H, 3, 3′, 3″, 4, and 4″ thienyl), 5.27 (br, 4 H, NBD C*H*=C*H*), 4.82 (m, 1 H, chiral H), 4.2−4.5 (m, 2 H, $ROCH_2CHOP$), 4.15 (br, 2H, NBD $CHCH_2$), 3.8−3.6 (m, 4 H, CH_2OP and $ThCH_2CH_2O$), 2.98 (t, 2 H, $ThCH_2CH_2O$), 1.67 (s, 2 H, NBD CH_2). ^{31}P {^{1}H} NMR (acetone-d_6): δ 133.7 (dd, J_{RhP} = 181, J_{PP} = 41), 131.2 (dd, J_{RhP} = 181, J_{PP} = 41). HRMS-(FAB) [M^+] calcd for $C_{48}H_{44}O_3P_2S_3Rh^+$: 929.0983. Found: 929.0941.

Hydrogenation of **4** *in acetone-d_6 (**18**).* The crystalline product **4** (∼15 mg) was dissolved in acetone-d_6 and transferred into a J-Young air-free NMR tube. Hydrogen gas (1 atm) was admitted, and the solution was allowed to stand under active hydrogen overnight. The starting material hydrogenates cleanly to product **18** under these conditions. ^{1}H NMR (acetone-d_6): δ 7.0−7.8 (br, 27 H, phenyl and thienyl), 5.18 (br, 1 H, chiral H), 4.68 (br, 1 H, CH_2OP), 4.25 (m, 1 H, CH_2-OP), 3.6−3.8 (m, 4 H, $ROCH_2CHOP$ and $ThCH_2CH_2O$), 3.01 (t, 2 H, $ThCH_2CH_2O$). ^{31}P {^{1}H} NMR (acetone-d_6): δ 145.5 (dd, J_{RhP} = 218, J_{PP} = 61); 143.7 (dd, J_{RhP} = 218, J_{PP} = 61).

Vapor-Phase Osmometry of 19. The apparatus and theory behind this experiment are described in ref 27. The experimental molecular mass was determined by the relationship $M_x = [(m_x)(M_s)(V_s)]/[(m_s)(V_x)]$, where M_x = molecular mass of the unknown, m_x = mass of the unknown used in the experiment, V_x = final volume of the unknown solution, M_s = molecular mass of the standard, m_s = mass of the standard used in the experiment, and V_s = final volume of the standard solution.

The entire setup was done air-free inside a glovebox. Compound **19** (m_x = 40 mg) was dissolved in 1.06 mL of dichloromethane and transferred to one bulb of the apparatus. In the other bulb, the decamethyl ferrocene standard (m_s = 12 mg, M_s = 326.31 g/mol) was dissolved in 1.02 mL of dichloromethane. The entire apparatus was then freeze/pump/thawed three times to remove all gases. After 7 days, the solutions had equilibrated and the volume of liquid in each bulb was measured. The final measured volumes were V_x = 0.78 mL and V_s = 1.28 mL, giving: M_x = [(40 mg)(326.31 g/mol)(1.28 mL)]/[(12 mg)(0.78 mL)] = 1785 g/mol.

During the experiment, some precipitation of **19** was observed, but upon completion, 35 mg of **19** was recovered. ^{1}H and ^{31}P NMR in acetone-d_6 showed pure **18**, indicating little decomposition of **19** during the experiment.

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