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Synthesis and Characterization of Cyclic Oligomeric [*cis*-$Mo(CO)_4(Ph_2P(C_4H_2S)_2PPh_2)]_n$ and Model Complexes for the Edge and Corners in the Cyclic Oligomer

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Conducting organometallic polymers are an interesting class of materials because they combine the electronic properties of metals with the simpler processing requirements of organic polymers. In an approach to incorporating poly(thiophene) segments into controlled three-dimensional environments, we have synthesized 5,5′-bis(diphenylphosphino)-2,2′-bithiophene, $Ph_2P(C_4H_2S)_2PPh_2$, and have reacted this ligand with $Mo(CO)_4$(nbd) in a 1:1 ratio. The product of this reaction is a cyclic oligomer, as indicated by the presence of only *cis*-$Mo(CO)_4$ absorptions in the IR spectrum and the absence of resonances of free phosphines in the $^{31}P\{^1H\}$ NMR spectrum. Size exclusion chromatography of the polymer in THF gives an $\bar{M}_n$ value of 6.0×10^3 and $\bar{M}_w$ value of 9.7×10^3 for the polymer. To better understand the structural features of the polymer, model complexes for the edge, $Mo(CO)_5(Ph_2P(C_4H_2S)_2PPh_2)Mo(CO)_5$, and the corner, *cis*-$Mo(CO)_4(Ph_2P(C_4H_2S)_2H)_2$ and *cis*-$Mo(CO)_4(Ph_2PC_4H_2S)H)_2$, of the cyclic polymer have been prepared and characterized. X-ray crystal structures of $Ph_2P(C_4H_2S)_2PPh_2$ and the edge model have also been determined.

Introduction

Conducting polymers such as poly(acetylenes),[1] poly(pyrroles),[2] poly(thiophenes),[3] and fused-ring systems such as poly(isothianaphthenes)[4] have been studied intensely in recent years, due to their potential applications in electronics and optoelectronics. An area of considerable current interest is the development of materials that blend conducting polymers with inorganic elements via the incorporation of the conducting polymers into the ligands of transition-metal complexes. This process could allow the development of controlled nanostructures via metal-directed self-assembly,[5] and molecular recognition.[6−8] Such nanostructured materials could exhibit novel optoelectronic behavior,[9] and host−guest binding/inclusion complex phenomena for use as chemical sensors for a variety of materials.[6−8,10]

Poly(thiophenes) are of interest because they have nondegenerate ground states and thus exhibit different excitations responsible for conduction than do polymers with degenerate ground states such as poly(acetylenes).[9,11,12] Poly(thiophenes) have seen use in metal-containing films for use as thin-film transistors and molecular/ion-selective sieves.[8,13a−b] The electroluminescent behavior may be modified via similar techniques used for band gap control in other π-conjugated systems.[11,14] Coupling of poly(thiophenes) to transition metals has yielded materials with interesting linear and nonlinear optical behavior as well as electrochemical properties.[3,9]

One approach that has not been used to incorporate poly(thiophenes) into ligands for transition-metal com-

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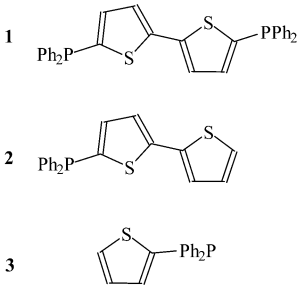

Figure 1. Phosphine−bithiophene and phosphine−thiophene ligands used in this study.

plexes is to substitute phosphines at the 5-carbons of the terminal thiophenes. Such substitutions have been used to prepare 2-phosphinothiophenes[15] that have been incorporated into transition-metal complexes via coordination of the phosphine and should work equally well with poly(thiophenes).[16] In this paper, we describe the synthesis of the simplest of the 5,5′-bis(phosphine)poly(thiophene) ligands, $Ph_2P(C_4H_2S)_2PPh_2$ (**1** in Figure 1), and an oligomeric complex of this ligand, $[cis\text{-}Mo(CO)_4(Ph_2P(C_4H_2S)_2PPh_2)]_n$ (**4**). To better understand the coordination environment of the ligand in the oligomeric complex, we have also synthesized and characterized complexes that model the edges, $Mo(CO)_5(Ph_2P(C_4H_2S)_2PPh_2)Mo(CO)_5$ (**5**), and the corners, *cis*-$Mo(CO)_4(Ph_2P(C_4H_2S)_2H)_2$ (**6**) and *cis*-$Mo(CO)_4(Ph_2PC_4H_3S)_2$ (**7**), of the oligomer.

Experimental Section

Materials. THF was dried by first allowing it to stand over $MgSO_4$ for at least 12 h, then by refluxing over CaH_2, and finally by distilling from Na/benzophenone and was used within a few hours. Other solvents were reagent grade and were degassed using high-purity (99.998%) nitrogen before use. Thiophene was distilled and stored over molecular sieves until use, while reagent grade bithiophene, chlorodiphenylphosphine, and 1.6 M *n*-butyllithium were of sufficient purity as received from the supplier (Aldrich). Literature methods were used to synthesize 2-(diphenylphosphino)thiophene (**3**),[15] $Mo(CO)_4(nbd)$,[16] and *cis*-$Mo(CO)_4(Ph_2PC_4H_3S)_2$ (**7**).[17]

Characterization. IR spectra of nitrogen-degassed dichloromethane solutions of the carbonyl complexes in an ICL 0.2 mm path length NaCl solution cell were recorded on a Nicolet Nexus 470 FT-IR spectrometer. Multinuclear $^{31}P\{^1H\}$ and ^1H NMR spectra were recorded on a Bruker ARX-300 NMR spectrometer. Chloroform-*d* solutions of the complexes were prepared under nitrogen. The $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% phosphoric acid (H_3PO_4) in a coaxial tube that also contained chloroform-*d*, and the ^1H NMR spectra were referenced to internal tetramethylsilane (TMS). Size exclusion chromatography was performed on a system utilizing a Waters 515 HPLC pump, a Waters 410 refractive index detector, a Linear UV/vis 205 absorbance detector, and a series of four columns (Styragel HT6E, HR5E, HT3, and HR2). This system employed a polystyrene calibration curve.

Molecular Modeling. Molecular modeling was performed using Spartan ‘02 for Windows. The dihedral angle containing the S−C−C−S atoms of the bithiophene was constrained from 180 to 0° in 10° increments and the strain energy recorded. This molecular mechanics method employed the MMFF force field parameters for minimization.[18]

5,5′-Bis(diphenylphosphino)-2,2′-bithiophene, $Ph_2P(C_4H_2S)_2PPh_2$ (1). A solution of 5.06 g (0.0304 mol) of 2,2′-bithiophene in 150 mL of THF was cooled in an acetone/dry ice slush bath as a mixture of 38.0 mL (0.0608 mol) of 1.6 M *n*-butyllithium in hexanes was added dropwise. When the addition was completed, 10.9 mL (0.0608 mol) of chlorodiphenylphosphine was added, and the reaction mixture was stirred for 60 min. Then, the solvent was removed under vacuum, and the dark solid residue was treated with 125 mL of degassed dichloromethane. This mixture was filtered to remove the lithium chloride, and the filtrate was evaporated to dryness under vacuum to yield a dark orange sticky solid. The solid was treated with 100 mL of degassed methanol, and the mixture was stirred for 5 h. Filtration then yielded 9.99 g (61.5%) of crude **1** as a light orange solid. ^1H NMR ($CDCl_3$): δ 7.27−7.34 (C_6H_5, m, 20H); 7.04−7.18 (C_4H_2S, m, 4H). ^{31}P NMR ($CDCl_3$): δ −18.50 (s).

5-(Diphenylphosphino)-2,2′-bithiophene, $Ph_2P(C_4H_2S)_2H$ (2). A solution of 1.98 g (0.0119 mol) of 2,2′-bithiophene in 25 mL of dry THF was cooled in an acetone/dry ice slush bath as a mixture of 7.45 mL (0.0119 mol) of 1.6 M *n*-butyllithium in hexanes and 12.55 mL of THF was added dropwise. During the addition, the color of the solution darkened to a deep green. Next, 2.21 mL (0.0123 mol) of chlorodiphenylphosphine was added to the solution. The reaction mixture was stirred for an additional 120 min, and then a few drops of degassed water were added to decompose any remaining bithiophenyllithium. The solvent was removed under vacuum to yield a viscous oily residue. The residue was treated with 30 mL of degassed dichloromethane, and the mixture was filtered through silica gel. The filtrate was evaporated to dryness under vacuum to yield crude **2** as a yellow oil in a yield of 45.9% (4.17 g). ^1H NMR ($CDCl_3$): δ 7.27−7.36 (C_6H_5, m, 10H); 6.89−6.91, 7.05−7.06 (C_4H_2S, m, 2H); 7.09−7.18 (C_4H_3S, m, 3H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −18.57 (s).

$[cis\text{-}Mo(CO)_4(Ph_2P(C_4H_2S)_2PPh_2)]_n$ (4). Solutions of 0.266 g (0.887 mmol) of $Mo(CO)_4(nbd)$ in 150 mL of degassed dichloromethane and 0.474 g (0.887 mmol) of bis(5,5′-diphenylphosphino)-2,2′-bithiophene (**1**) in 200 mL of degassed dichloromethane were added simultaneously and dropwise to 150 mL of degassed dichloromethane over a period of 5 h. When the addition was completed, the reaction mixture was stirred for 30 min, and then the solvent was removed under vacuum. The brown oily residue was dissolved into 60 mL of degassed dichloromethane, and this solution was filtered through 2 mm of silica gel in a sintered-glass funnel. The silica gel was then rinsed with two 15 mL portions of degassed dichloromethane. The filtrate and washes were combined to yield a golden yellow solution. This solution was heated under a stream of nitrogen to reduce volume to 20 mL, and then hexanes were added until the solution became saturated. Cooling of the solution to −5 °C yielded 0.414 g (62.8%) of analytically pure **4** as a pale yellow powder. ^1H NMR ($CDCl_3$): δ 7.17−7.24 (C_6H_5, m, 20H); 6.82−6.96 (C_4H_2S, m, 4H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.56 (s). Carbonyl IR (cm^{-1}): 2024 m, 1928 sh, 1908 s. SEC (THF-polystyrene calibration): $\bar{M}_n = 6.0 \times 10^3$ Da, $\bar{M}_w = 9.7 \times 10^3$ Da. Anal. Calcd: C, 58.23; H, 3.26. Found: C, 58.20; H, 3.40.

$(Mo(CO)_5)_2(\mu\text{-}Ph_2P(C_4H_2S)_2PPh_2)$ (5). A mixture of 0.326 g (1.23 mmol) of molybdenum hexacarbonyl and 0.137 g (1.23 mmol) of tetramethylamine *N*-oxide dihydrate in 20 mL of degassed acetonitrile was stirred at room temperature for 30 min. The solution was then added dropwise to a solution of 0.330 g (0.617 mmol) of bis(5,5′-diphenylphosphino)-2,2′-bithiophene (**1**) in 30 mL of a 2:1 acetonitrile/THF mixture. The solution was stirred for 2 h after the addition was completed and then filtered to remove the unreacted molybdenum carbonyl. The filtrate was evaporated to dryness, and the residue was recrystallized from a dichloromethane/

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Table 1. Data Collection Parameters for X-ray Structure Determination

	1	**5**
empirical formula	$C_{32}H_{24}P_2S_2$	$C_{43}H_{26}Cl_2Mo_2O_{10}P_2S_2$
formula wt	534.57	1091.48
temp, K	293(2)	293(2)
wavelength, Å	0.710 73	0.710 73
cryst syst, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a, Å	8.9841(18)	11.602(2)
b, Å	19.670(4)	15.688(3)
c, Å	8.8902(18)	26.980(5)
α, deg	90	90.97(3)
β, deg	117.97(3)	100.36(3)
γ, deg	90	109.00(3)
V, Å^3	1387.6(5)	4552.3(16)
Z; calcd density, Mg/m^3	2; 1.279	4; 1.593
abs coeff, mm^{-1}	0.327	0.885
F(000)	556	2176
cryst size, mm	0.80 × 0.40 × 0.30	0.06 × 0.52 × 0.18
θ range for data collecn, deg	2.07−27.47	2.15−22.48
limiting indices	$-11 \le h \le 10$, $-25 \le k \le 1$, $-1 \le l \le 11$	$-12 \le h \le 12$, $-16 \le k \le 1$, $-29 \le l \le 28$
no. of rflns collected/unique	4030/3178 (R(int) = 0.0392)	13 435/11 869 (R(int) = 0.0605)
θ, deg; completeness to θ, %	27.47; 100	22.48; 99.9
abs cor	empirical	empirical
max, min transmissn	0.4630, 0.4264	0.6743, 0.5296
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	3178/0/212	11 869/2/1100
GOF on F^2	0.998	0.997
final R indices ($I > 2\sigma(I)$)	R1 = 0.0458, wR2 = 0.1223	R1 = 0.0629, wR2 = 0.1453
R indices (all data)	R1 = 0.1292, wR2 = 0.1633	R1 = 0.1582, wR2 = 0.1776
extinction coeff	0.003(2)	0.000 00(12)
largest diff peak, hole, e Å^{-3}	0.286, −0.372	0.783, −0.604

methanol mixture to yield 0.423 g (68.1%) of **5** as green, prismatic crystals. ^{1}H{^{31}P} NMR (CDCl$_3$): δ 7.23 (dd, 2H); 7.31 (dd, 2H, $|^3J(\mathrm{H,H})| = 24.8$ Hz, $|^4J(\mathrm{H,H})| = 3.7$ Hz); 7.43−7.53 (C$_6$H$_5$, m, 20H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 26.63 (s). Carbonyl IR (cm^{-1}): 2074 m, 1988 w sh, 1948 s. Anal. Calcd: C, 47.32; H, 2.40. Found: C, 46.95; H, 2.35.

***cis*-Mo(CO)$_4$(Ph$_2$P(C$_4$H$_2$S)$_2$H)$_2$ (6).** A solution of 0.410 g (1.36 mmol) of Mo(CO)$_4$(nbd) in 100 mL of dichloromethane was added dropwise to a solution of 0.953 g (2.72 mmol) of 5-(diphenylphosphino)-2,2′-bithiophene (**2**) in 100 mL of degassed dichloromethane at room temperature. Then the solvent was then removed under vacuum to yield a pale yellow powder. Column chromatography on a silica gel column using a 1:4 dichloromethane/hexanes system followed by recrystallization from a dichloromethane/hexanes mixture yielded 0.353 g (28.6%) of analytically pure **6**. ^{1}H NMR (CDCl$_3$): δ 7.26−7.40 (C$_6$H$_5$, m, 10H); 6.98−7.23 (C$_4$H$_2$S−C$_4$H$_3$S, m, 5H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 27.31 (s). Carbonyl IR (cm^{-1}): 2023 m, 1923 sh, 1910 s, 1886 m. Anal. Calcd: C, 58.15; H, 3.33. Found: C, 57.88; H, 3.26.

X-ray Data Collection and Solution. Suitable single crystals of both **1** and **5** were glued on glass fibers with epoxy and aligned upon an Enraf-Nonius CAD4 single-crystal diffractometer under aerobic conditions. Standard peak search and automatic indexing routines followed by least-squares fits of 25 accurately centered reflections resulted in accurate unit cell parameters for each. The space groups of the crystals were assigned on the basis of systematic absences and intensity statistics. All data collections were carried out using the CAD4-PC software,[19] and details of the data collections are given in Table 1. The analytical scattering factors of the compounds were corrected for both $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion. All data were corrected for Lorentz and polarization effects, and when necessary, empirical absorption corrections were applied.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1

C3−C4	1.355(4)	C1−S1	1.724(3)
C3−C2	1.399(5)	C1−P1	1.804(3)
C2−C1	1.364(4)	P1−C15	1.825(3)
C4−C4′	1.449(6)	P1−C9	1.834(3)
C4−S1	1.722(3)		
C4−C3−C2	113.8(3)	C2−C1−P1	125.2(3)
C1−C2−C3	113.8(3)	S1−C1−P1	125.24(18)
C3−C4−C4′	129.7(4)	C1−P1−C15	103.54(15)
C3−C4−S1	110.0(2)	C1−P1−C9	101.36(14)
C4′-C4−S1	120.3(3)	C15−P1−C9	102.60(14)
C2−C1−S1	109.5(2)	C4−S1−C1	92.85(15)

All crystallographic calculations were performed with the Siemens SHELXTL-PC program package.[20] The Mo and P positions were located using the Patterson method, and the remainder of the non-hydrogen atoms were located in difference Fourier maps. Full-matrix refinements of the positional and anisotropic thermal parameters for all non-hydrogen atoms versus F^2 were carried out. All hydrogen atoms were placed in calculated positions with the appropriate molecular geometry and d(C−H) = 0.96 Å. The isotropic thermal parameter of each hydrogen atom was fixed equal to 1.2 times the U_{eq} value of the atom to which it was bound. Selected bond lengths and angles for **1** and **5** are given in Tables 2 and 3.

Results and Discussion

Ligand Syntheses and Characterization: The phosphine-substituted bithiophene ligands **1** and **2** were prepared as shown in Scheme 1. The reactions were run in a dry ice/acetone slush bath to minimize isomeric scrambling between the lithiated thiophenes and the phosphinothiophene. Generation of the lithiated thiophenes was rapid, and addition of the phosphine was carried out within 30 min of completion of the *n*-butyllithium addition. The ^{31}P{^{1}H} NMR spectra of the ligands were singlets, and the ^{1}H NMR spectra of the ligands contained only resonances for the phenyl and thiophenyl protons in the expected ratios. The NMR data indicated that the crude ligands were sufficiently pure for use in the syntheses of the complexes. Ligand **1** was recrystallized from a dichloromethane/hexanes solvent system to obtain the crystal of **1** that was used to determine its X-ray crystal structure.

Complex Syntheses. The *cis*-molybdenum tetracarbonyl complexes of ligands **1** and **2** were synthesized by the simultaneous additions of solutions of Mo(CO)$_4$(nbd) and the ligand into the solvent via pressure-equalizing dropping funnels, as shown in Scheme 2. These reactions were rapid and were completed within 30 min after the additions were completed. Because of the tendency of the liberated norbornadiene to polymerize, the solvent and norbornadiene were removed as soon as the reactions had reached completion. The edge model, **5**, was synthesized by the addition of **1** to 2 equiv of Mo(CO)$_5$(NCMe), as shown in Scheme 3.

Characterization: The edge (**5**) and corner (**6** and **7**) model complexes exhibited ^{31}P{^{1}H} NMR spectra, summarized in Table 4, that are similar to those of related Mo(CO)$_5$(phosphine) and *cis*-Mo(CO)$_4$(phosphine)$_2$

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[19] CAD4-PC Version 1.2; Enraf-Nonius, Delft, The Netherlands, 1988.

[20] Sheldrick, G. M. SHELXTL NT Version 6.12; Bruker AXS, Inc., Madison, WI, 2001.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 5

P1−C1	1.831(10)	P3−C43	1.808(10)
P1−Mo1	2.513(3)	P3−Mo3	2.521(3)
P2−C8	1.840(9)	P4−C50	1.815(9)
P2−Mo2	2.537(3)	P4−Mo4	2.509(3)
Mo1−C33	2.017(13)	Mo3−C75	1.994(13)
Mo1−C34	2.043(13)	Mo3−C76	2.062(14)
Mo1−C35	2.020(16)	Mo3−C77	2.051(13)
Mo1−C36	2.067(15)	Mo3−C78	2.023(15)
Mo1−C37	2.036(13)	Mo3−C79	2.010(16)
Mo2−C38	1.962(12)	Mo4−C80	1.979(13)
Mo2−C39	2.047(14)	Mo4−C81	2.037(14)
Mo2−C40	2.055(14)	Mo4−C82	2.008(14)
Mo2−C41	2.029(15)	Mo4−C83	2.029(15)
Mo2−C42	2.077(14)	Mo4−C84	2.072(15)
C33−O1	1.126(13)	C75−O11	1.133(12)
C34−O2	1.124(13)	C76−O12	1.119(13)
C35−O3	1.138(15)	C77−O13	1.128(13)
C36−O4	1.095(14)	C78−O14	1.135(14)
C37−O5	1.137(13)	C79−O15	1.151(15)
C38−O6	1.155(13)	C80−O16	1.144(13)
C39−O7	1.118(13)	C81−O17	1.121(14)
C40−O8	1.140(13)	C82−O18	1.160(14)
C41−O9	1.162(14)	C83−O19	1.144(15)
C42−O10	1.097(14)	C84−O20	1.092(15)
C33−Mo1−C34	86.6(5)	C75−Mo3−C76	90.0(4)
C33−Mo1−C35	89.4(5)	C75−Mo3−C77	91.5(5)
C33−Mo1−C36	90.4(5)	C75−Mo3−C78	86.9(5)
C33−Mo1−C37	91.8(4)	C75−Mo3−C79	89.1(5)
C33−Mo1−P1	178.7(4)	C75−Mo3−P3	177.9(4)
P1−Mo1−C34	92.8(3)	P3−Mo3−C76	92.0(3)
P1−Mo1−C35	91.8(4)	P3−Mo3−C77	88.0(3)
P1−Mo1−C36	90.2(3)	P3−Mo3−C78	91.1(3)
P1−Mo1−C37	87.0(3)	P3−Mo3−C79	91.5(4)
C38−Mo2−C39	89.9(5)	C80−Mo4−C81	91.8(6)
C38−Mo2−C40	88.9(5)	C80−Mo4−C82	85.2(5)
C38−Mo2−C41	88.8(5)	C80−Mo4−C83	92.1(6)
C38−Mo2−C42	88.2(5)	C80−Mo4−C84	88.6(5)
C38−Mo2−P2	176.1(4)	C80−Mo4−P4	177.4(4)
P2−Mo2−C39	93.6(4)	P4−Mo4−C81	89.5(3)
P2−Mo2−C40	92.5(3)	P4−Mo4−C82	92.5(3)
P2−Mo2−C41	87.7(3)	P4−Mo4−C83	86.4(4)
P2−Mo2−C42	90.2(3)	P4−Mo4−C84	93.6(4)

complexes.[21,22] The ^{31}P NMR resonance of each of model complex was a sharp singlet ($\nu_{1/2}$: **5**, 5 Hz; **6**, 5 Hz; **7**, 6 Hz), indicating that the environments of the phosphorus nuclei in each complex were chemically equivalent on the time scale of the NMR experiment. The ^{31}P{^{1}H} NMR chemical shift of the edge model **5** was approximately 1 ppm downfield of those of the corner models **6**. This is consistent with the results from ^{31}P{^{1}H} NMR studies of Mo(CO)$_5$(phosphine) and *cis*-Mo(CO)$_4$(phosphine)$_2$ complexes containing the same phosphine ligands.[21,22] The ^{31}P{^{1}H} coordination chemical shift (δ(^{31}P{^{1}H} complex) − δ(^{31}P{^{1}H} free ligand)) is approximately 46 ppm for each of the complexes. Two factors contribute to coordination chemical shifts: a decrease in the electron density at the phosphorus nuclei due to donation of the electron pair to the molybdenum and a decrease in the electron density of the phosphorus due to a slight expansion of the substituent−phosphorus−substituent (SPS) angles, and hence the cone angles, upon coordination.[23] The very similar coordination chemical shifts of the three complexes suggest that the changes in the cone angles in the three ligands upon coordination are very similar.

The coordination geometries of the molybdenum carbonyl centers in the model complexes **5**−**7** were characterized using IR spectroscopy, and the frequencies of the infrared absorptions in the carbonyl region for the complexes are given in Table 5. The frequency of the higher energy A$_1$ absorption of each complex clearly indicates the coordination geometry of the complex (ν(A$_1$): Mo(CO)$_5$L, ∼2074 cm^{-1}; *cis*-Mo(CO)$_4$L$_2$, ∼2024 cm^{-1}).

The characterization data for the polymer **4**, obtained from the reaction of **1** and Mo(CO)$_4$(nbd), provides significant insight into the nature of this material. Size exclusion chromatography (SEC) of **4** gave an $\bar{M}_n$ value of 6.0 × 10^3 Da and an $\bar{M}_w$ of 9.7 × 10^3 Da, yielding a polydispersity of 1.61. The $\bar{M}_n$ suggests an oligomer with eight repeat units, i.e. [*cis*-Mo(CO)$_4$(Ph$_2$P(C$_4$H$_2$S)$_2$PPh$_2$)]$_8$; however, the polydispersity indicates that a number of polymeric species are present. Neither the $\bar{M}_n$ value nor the polydispersity is consistent with the formation of a cyclic tetramer.[5] It is important to note that the molecular weight values are based upon the use of a polystyrene calibration curve employing THF as solvent. Because SEC separates on the basis of hydrodynamic volume and the polymer most likely does not have the same swelling properties in THF as polystyrene, the molecular weight values determined by SEC may vary significantly from the absolute values. For example, McCullough has demonstrated that more rigid linear polymers, such as poly(alkylthiophenes), can have their molecular weights significantly overestimated through SEC.[24] Future studies are planned where increasingly larger edge and corner models of these polymers will be synthesized in order to develop SEC calibration curves specific to these polymers. This will require polymers spanning a range of molecular weights and the determination of their Mark−Houwink−Sakurada coefficients (from viscosity studies).

The ^{31}P{^{1}H} NMR and carbonyl IR spectral data for **4** are somewhat surprising. The ^{31}P{^{1}H} NMR spectrum of **4** exhibits only a sharp singlet ($\nu_{1/2}$ = 5 Hz) whose chemical shift is nearly identical with that of the corner model complex **6**. As is the case for the model complexes, the single ^{31}P{^{1}H} NMR resonance indicates that all of the environments of the phosphorus nuclei in the polymer are chemically equivalent on the time scale of the NMR experiment. The IR spectrum of **4** is also very similar to that the corner models **6** and **7**. The only formulation of **4** that is consistent with the ^{31}P{^{1}H} NMR and carbonyl IR spectral data and the SEC data is that the polymer is a cyclic oligomer containing only *cis*-Mo(CO)$_4$(Ph$_2$P(C$_4$H$_2$S)$_2$PPh$_2$) repeat units. This conclusion is supported by the elemental analysis of the complex, which is consistent with that calculated for the monomer unit.

X-ray Structures of 1 and 5. As discussed above, the characterization data for **4** indicate that the reaction of **1** and Mo(CO)$_4$(nbd) yields a mixture of cyclic oligomers because **1** coordinates only through the phosphines and the rigid nature of the bithiophene group in **1** prevents the phosphines from chelating. To better understand the structure of the oligomeric complex, the X-ray structures of the ligand **1** and the edge model

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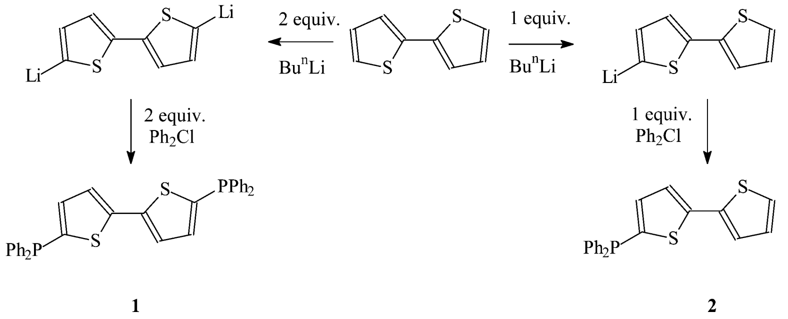
(21) Grim, S. O.; Wheatland, D. A.; McFarlane, W. *J. Am. Chem. Soc.* **1967**, *89*, 5573.

(22) Grim, S. O.; Wheatland, D. A. *Inorg. Chem.* **1969**, *8*, 1716.

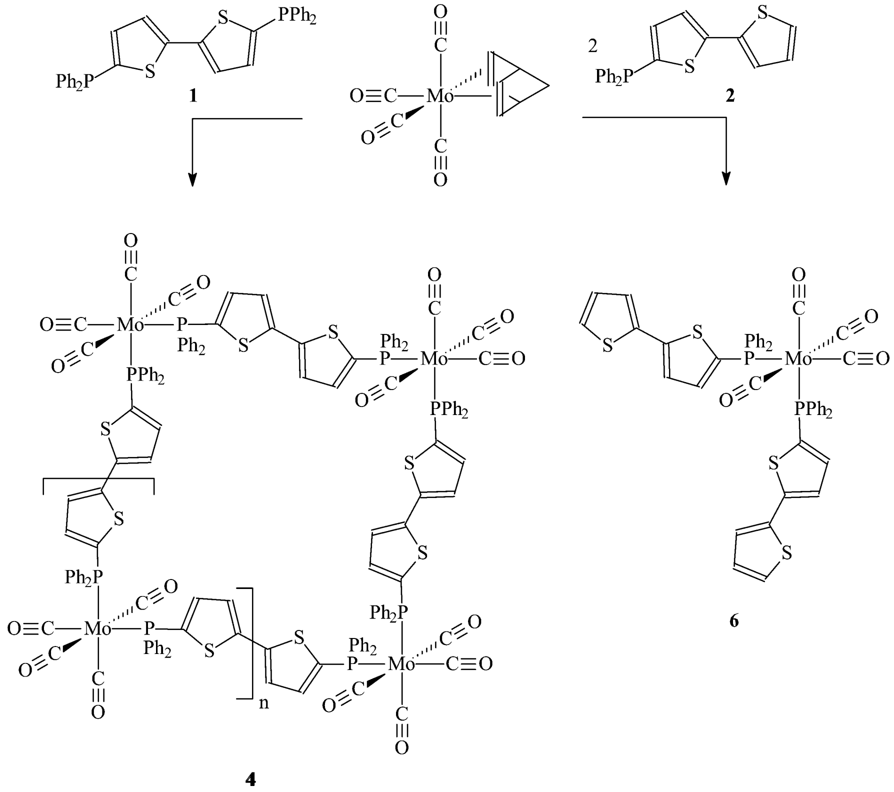
(23) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(24) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777−5785.

Scheme 1. Synthesis of Ligands Containing Phosphines and 2,2′-Bithiophenes



Scheme 2. Synthesis of the Cyclic Oligomeric Complexes and Corner Model Complexes



Scheme 3. Synthesis of the Edge Model Complex

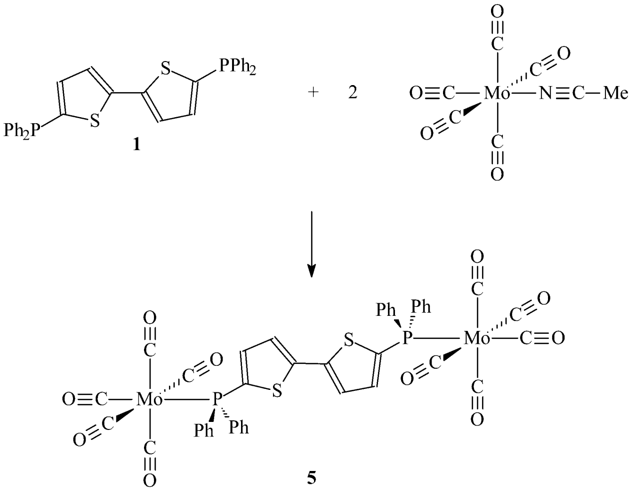


Table 4. ^{31}P{^{1}H} NMR Chemical Shifts

compd	chem shift (ppm)[a]	Δ(δ)[a]
1	−18.50	
2	−18.57	
3	−19.43	
4	27.56	46.06
5	26.64	45.14
6	27.31	45.88
7	26.61	46.04

[a] δ(^{31}P{^{1}H} complex) − δ(^{31}P{^{1}H} free ligand).

Table 5. IR Frequencies in the Carbonyl Region

	ν_{CO} (cm^{-1})	
compd	A$_1$	A$_1$, B$_1$, B$_2$
4	2024 m	1928 sh, 1908 s
5	2074 m	1988 w sh, 1948 s
6	2023 m	1923 sh, 1910 s, 1886 m
7	2023 m	1922 sh, 1911 s, 1886 m

complex **5** were determined. The structures of **1** and **5** are shown in Figures 2 and 3, respectively. The ligand **1** crystallizes in the centrosymmetric space group $P2_1/c$ with a center of symmetry at the center of the bond bridging the two thiophene rings. Coplanarity of the two thiophene rings is a necessary result from this centrosymmetric conformation and is confirmed by the 180° torsion angle about the carbon−carbon bond between the thiophene rings. This center of symmetry is also

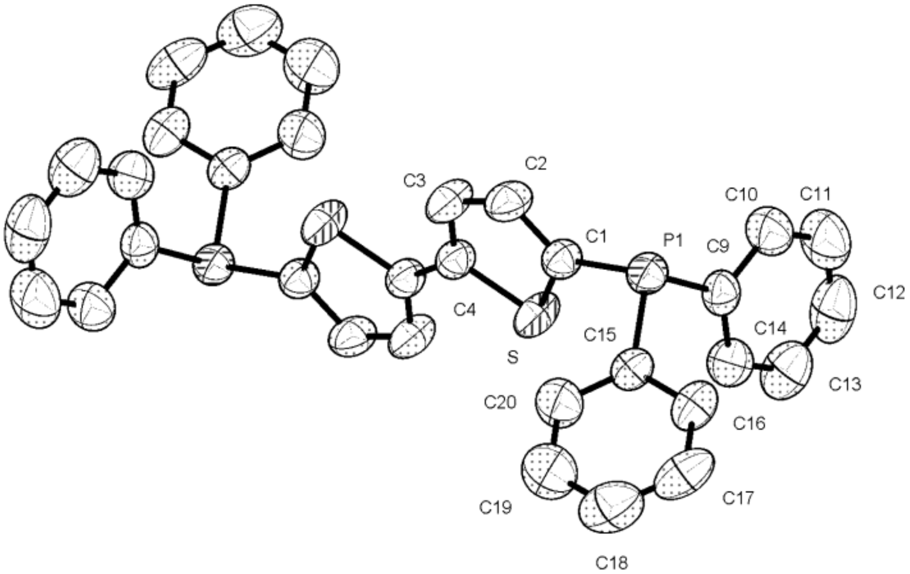


Figure 2. Molecular structure of **1**. Hydrogen atoms are omitted, and the atomic displacement ellipsoids are drawn at 50% probability.

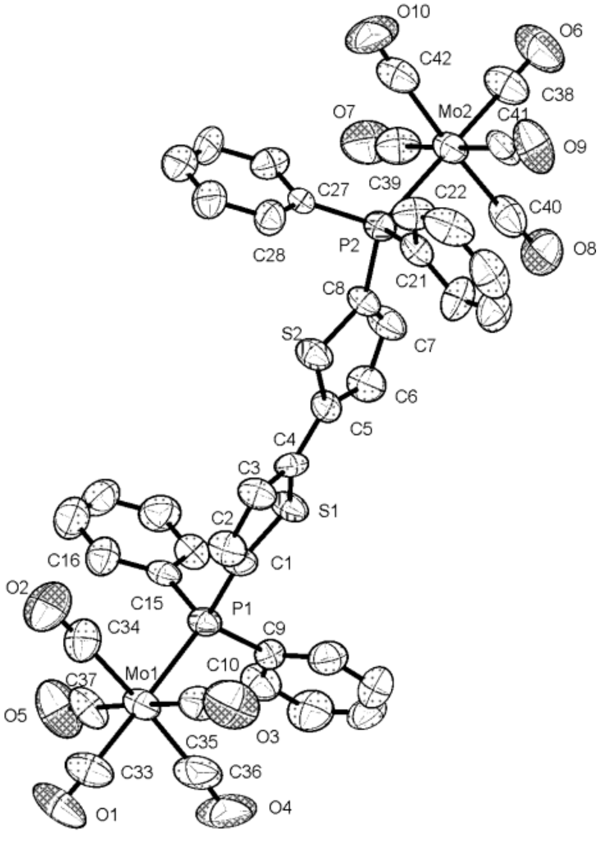


Figure 3. Molecular structure of one of the two molecules of **5** in the asymmetric unit. Hydrogen atoms are omitted, and the atomic displacement ellipsoids are drawn at 50% probability.

evidenced in the trans orientation of the sulfur atoms as well as the antiparallel orientation of the phosphorus lone pairs.

Coordination of $Mo(CO)_5$ groups to the phosphines in **5** disrupts the coplanarity of the two thiophene rings. The asymmetric unit in **5** consists of two independent molecules, giving two different examples of the model edge in the solid state. The two molecules have significantly different torsion angles about the carbon−carbon bond between the thiophene rings (molecule 1, $S_1-C_4-C_5-S_2$ torsion angle 163.5°; molecule 2, $S_3-C_{46}-C_{47}-S_4$ torsion angle 176.5°). The different degrees of rotation about the carbon−carbon bond between the two thiophene rings suggests that there is a relatively low barrier to rotation about this bond. Molecular modeling has shown that while the formation energy generally increases as the torsion angle moves from 180 to 0°, the energy difference between these two states is only about 1.4 kcal/mol.

The metal centers of this edge are slightly distorted octahedra. Examination of the molybdenum−carbonyl bond distances shows the general trend of a stronger, shorter Mo−C bond in the carbonyl opposite the coordinated phosphine. This behavior was expected, as phosphines are better σ-donors and weaker π-acceptors than carbonyls. This difference in bonding might also be expected to result in longer, weaker C−O bonds for the carbonyl opposite the coordinated phosphine. However, any differences in these bonds are obscured by differences due to crystal-packing forces in the solid-state crystal structure.[25]

The structures of **1** and **5** provide considerable insight into the reason that the reactions of **1** and $Mo(CO)_4$(nbd) yield mixtures of cyclic oligomers rather than only cyclic tetramers (molecular squares). There appear to be three requirements that must be met for the reaction of **1** and $Mo(CO)_4$(nbd) to yield a cyclic tetramer. These are as follows: (1) the thiophene rings in the bithiophene moiety must be coplanar, (2) the phosphorus lone pairs must have an antiparallel orientation, and (3) the bithiophene moieties forming opposite edges of the tetramer must have an identical orientation. The depiction of compound **4** in Scheme 2, with $n = 1$, shows the appropriate orientation. The centrosymmetric space group $P2_1/c$ of the ligand **1** enforces the first two conditions. However, even with coplanarity of the thiophene rings, there are 70 possible orientations of the ligands on the edges of the cyclic tetramer, but only 4 satisfy the third requirement, giving a 5.71% prob-

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(25) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432−4438.

ability of forming the cyclic tetramer.[26] The probability is certainly much lower than this because (1) the crystal structure of the edge model demonstrates that twisting around the C−C bond between the two thiophenes can also occur and (2) the $^{31}P\{^1H\}$ NMR data indicate that free rotation about the metal−phosphorus bonds is possible.

Conclusions

The development of novel organometallic polymers is an exciting area in current chemical research. Such polymers may serve as organometallic semiconducting materials that combine the electrical conductivity of metals with the light weight, corrosion resistance, and less demanding production requirements of organic materials. The phosphinothiophene ligands presented herein, and their molybdenum complexes, are the first results of our group's efforts in this area. The ease with which these complexes can be prepared suggest that it may be possible to use similar procedures to prepare a range of organometallic poly(thiophenes) in which both the length of the polythiophene and the nature of the metal center are varied.

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Supporting Information Available: Crystal structure data for **1** and **5**, including tables of atomic coordinates, *U* values, all bond lengths and angles, torsion angles, and hydrogen isotropic displacement parameters; crystallographic data are also available in electronic form as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) Each of the four ligands may be either cis or trans, yielding eight possible orientations. A combination of four orientations from a set of eight yields 70 possible orientations.