the amine group is a part, disallow this. Thus, the observed N-H-Cl angle is only 138 (3)°.

Conclusions

A number of new five-coordinate ruthenium amide complexes have been prepared, all incorporating the tridentate $\mathrm{^-N(SiMe_2CH_2PPh_2)_2}$. The complex $\mathrm{RuCl(PPh_3)[N(SiMe_2CH_2PPh_2)_2]}$ (**1**) displays some unique reactivity patterns. Especially noteworthy is the conversion of the amide linkage of **1** to an amine via two distinct pathways: addition of $\mathrm{H_2}$ to produce the isomeric amine chlorides $\mathrm{RuCl(PPh_3)H[NH(SiMe_2CH_2PPh_2)_2]}$ (**2a**,**b**) and activation of an ortho C-H bond of the $\mathrm{PPh_3}$ unit to generate $\mathrm{RuCl(C_6H_4PPh_2)[NH(SiMe_2CH_2PPh_2)_2]}$ (**4**). The driving force for both of these reactions appears to be the formation of an intramolecular hydrogen bond between the amine N-H and the coordinated chloride. Attempts to introduce hydrocarbyl groups via metathesis of the chloride ligand of **1** with use of ortholithium or Grignard reagents were unsuccessful, resulting in the facile ortho metalation of the $\mathrm{PPh_3}$ group to generate $\mathrm{Ru(C_6H_4PPh_2)[N(SiMe_2CH_2PPh_2)_2]}$ (**3**).

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Supplementary Material Available: Complete tables of bond lengths and angles, calculated hydrogen atom parameters, anisotropic thermal parameters, and torsion angles (Tables V(S), VI(S), and VII-X) and a plot of the (O)$\mathrm{PPh_3}$ molecule (14 pages); a table of structure factors (Table XI) (59 pages). Ordering information is given on any current masthead page.

Photochemically Reactive Polymers: Synthesis and Characterization of Polyurethanes Containing $\mathrm{Cp_2Mo_2(CO)_6}$ or $\mathrm{Cp_2Fe_2(CO)_4}$ Molecules along the Polymer Backbone

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The syntheses of oligomeric urethanes containing Mo-Mo or Fe-Fe bonds along the backbone are reported. Reaction of the organometallic "diol" $\mathrm{(\eta^5\text{-}C_5H_4C(O)CH_2OH)_2Mo_2(CO)_6}$ with $\mathrm{OCN(CH_2)_6NCO}$ (hexamethylene diisocyanate; HMDI) gave $\mathrm{[-OCH_2C(O)C_5H_4(CO)_3Mo\text{-}Mo(CO)_3C_5H_4C(O)CH_2OC(O)NH(CH_2)_6NHC(O)-]_{\mathit{n}}}$ (n = 4-5). Similarly, reaction of $\mathrm{(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6}$ with HMDI gave $\mathrm{[-OCH_2CH_2C_5H_4(CO)_3Mo\text{-}Mo(CO)_3C_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)-]_{\mathit{n}}}$ (n = 6-8) and reaction of $\mathrm{(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4}$ with HMDI gave $\mathrm{[-OCH_2CH_2C_5H_4(CO)_2Fe\text{-}Fe(CO)_2C_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)-]_{\mathit{n}}}$ (n = 2-3). A copolymer with a lower density of metal-metal bonds along the backbone was synthesized by reacting $\mathrm{(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6}$ and $\mathrm{HO(CH_2)_4OH}$ with HMDI. The polyurethanes were characterized by elemental analysis, by infrared, ^{1}H NMR, and electronic absorption spectroscopy, and by molecular weight. With certain preparations, $\bar{M}_n$ values up to 16 000 ($n \simeq 20$) were obtained. As an aid to the spectroscopic characterization of the complexes, model complexes were synthesized by reacting *mono*isocyanates with the metal-metal bonded diols. For example, $\mathrm{[CH_3(CH_2)_5NHC(O)OCH_2CH_2C_5H_4(CO)_3Mo\text{-}Mo(CO)_3C_5H_4CH_2CH_2OC(O)NH(CH_2)_5CH_3]}$ was synthesized by reacting $\mathrm{(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6}$ with $\mathrm{CH_3(CH_2)_5NCO}$. Because of the metal-metal bonds along the backbone, the polyurethanes are photochemically reactive, undergoing metal-metal bond photolysis reactions similar to the $\mathrm{Cp_2Mo_2(CO)_6}$ and $\mathrm{Cp_2Fe_2(CO)_4}$ dimers.

Introduction

Reactive polymers are a major new area of polymer synthesis and technology. Such polymers can be used in a variety of technological applications. For example, recent reports describe the use of reactive polymers as catalysts,[1-9] ion-exchange resins,[10] selective chelating agents,[6,11-13] polymeric supports,[2-6,8,9] and permselective materials.[10] One subset of the reactive polymer area is the field of

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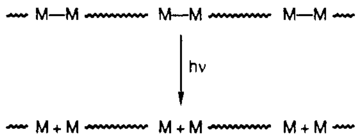
photochemically reactive polymers. These polymers are of considerable interest because they are potentially useful as degradable plastics, photoresists,[14-18] and precursors for ceramic materials.[14-16,19-21] In addition, they may find use in biomedical applications and in a host of other practical technologies.

We recently began a research program with the goal of synthesizing new types of photoreactive polymers. Our plan for making photochemically reactive polymers is to incorporate metal–metal bonds into the polymer backbone. The reason for doing this is that it is well-known that metal–metal bonds can be cleaved photochemically with visible light:[22,23]

$$L_nM-ML_n \xrightarrow{h\nu} 2ML_n \qquad (1)$$

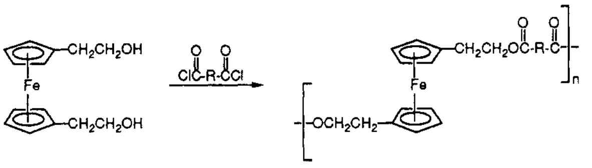
$$ML_n = CpMo(CO)_3\ (Cp = \eta^5\text{-}C_5H_5),\quad CpW(CO)_3,\ Mn(CO)_5,\ Re(CO)_5,\ CpFe(CO)_2$$

Incorporation of metal–metal bonds into a polymer should give a polymer that is similarly reactive:



(2)

Our syntheses of the metal–metal bond-containing polymers take advantage of the known chemistry of polymeric ferrocenes.[24-30] Ferrocenes form condensation polymers (e.g., eq 3) by the reaction of functional groups



(3)

on the Cp ligands with suitable difunctional molecules (Cp = η^5-C_5H_5). This polymerization strategy is quite general, and a number of organometallic polymers have been made from monomers containing functionalized Cp ligands.[24-30] However, no similarly constructed polymers have been reported that contain metal–metal bonds.

In this paper, we report the synthesis of polyurethanes containing either $Cp_2Mo_2(CO)_6$ or $Cp_2Fe_2(CO)_4$ units along the backbone. The photochemical reactions of these complexes in solution and in the solid state will be reported in a subsequent paper. A preliminary report describing the synthesis and photochemistry of one of the oligomers described herein has appeared.[31]

Experimental Section

Materials. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere by using standard Schlenk or vacuum line techniques or by using a Vacuum Atmospheres Co. glovebox. *All glassware used in the polymerization reactions was flame-dried under vacuum before use.*

Tetrahydrofuran (THF) was distilled under nitrogen from potassium benzophenone ketyl. Diethyl ether was distilled under nitrogen from sodium benzophenone ketyl. Hexane and pentane were distilled under nitrogen from sodium. *p*-Dioxane was distilled twice from sodium benzophenone ketyl under nitrogen. Hexamethylene diisocyanate (HMDI; 99.6%) was purchased from the Eastman Kodak Co. and distilled in vacuo (0.6 mmHg), collecting the fraction distilling at 75–76 °C. Hexyl isocyanate was purchased from Eastman Kodak and deoxygenated by purging with N_2 immediately before use. All isocyanates were stored at −18 °C. Dibutyltin diacetate (DBTA) was purchased from Aldrich and deoxygenated by purging with N_2 immediately before use. DBTA was stored in the refrigerator at 5 °C. 1,4-Butanediol was purchased from MCB, stored over type 4A molecular sieves, and distilled in vacuo (0.3 mmHg) through a 120-mm vigreux column, collecting the fraction distilling between 82 and 86 °C. Carbon tetrachloride was obtained from Fisher and distilled from P_2O_5 under nitrogen. Molybdenum hexacarbonyl was purchased from Pressure Chemical Co. and degassed under vacuum at room temperature immediately before use. Methyl glycolate was purchased from Eastman Kodak and used as received. 2-Methoxypropene was purchased from Aldrich and used as received. Pyridinium *p*-toluenesulfonate (PPTS) was prepared from pyridine and *p*-toluene sulfonic acid according to a literature procedure.[32]

Equipment. Infrared spectra were obtained with a Nicolet 5DXB FT-IR spectrometer. Electronic absorption spectra were obtained with a Beckman DU-7 recording spectrophotometer, and ^1H NMR were obtained on a GE QE-300 spectrometer at 300.15 MHz. Number-average molecular weights ($\bar{M}_n$) were obtained with a Perkin-Elmer Model 115 vapor pressure osmometer or a Knauer vapor pressure osmometer. Photochemical reactions were carried out with an Oriel 200-W high-pressure mercury arc lamp and a Corning CS 3-68 filter ($\lambda > 525$ nm). Elemental analyses were performed by E&R Microanalytical Laboratory, Inc. GPC data were obtained from Arro Labs.

Synthesis of Methyl Glycolate Ketal. Methyl glycolate (15 mL, 195 mmol) and 2-methoxypropene (23.5 mL, 245 mmol) were added to a 50-mL round-bottom flask equipped with a magnetic stir bar. The reaction flask was immersed in an ice water bath, and a catalytic amount (0.04 mL) of concentrated HCl was added. The reaction mixture was stirred for 8 h at 0 °C. The mixture was then washed with 20 mL of a 5% aqueous $NaHCO_3$ solution and dried over K_2CO_3 for 12 h. The solution was filtered and then distilled twice in vacuo (13 mmHg), collecting the fraction distilling between 72 and 73 °C. Methyl glycolate ketal ($C_7H_{14}O_4$) was obtained in 25% yield (7.81 g, 0.048 mol). ^1H NMR ($CDCl_3$) δ, ppm 4.09 (s, 2 H, $C(O)CH_2$); 3.76 (s, 3 H, $CH_3OC(O)$); 3.22 (s, 3 H, OCH_3); 1.39 (s, 6 H, $C(CH_3)_2$).

Synthesis of Diol Complex 1, (η^5-$C_5H_4C(O)CH_2OH)_2Mo_2(CO)_6$. Metallic sodium (0.692 g, 30.1 mmol) and 75 mL of deoxygenated xylenes were added to a 500-mL Schlenk flask fitted

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with a reflux condenser and N_2 inlet. The xylene/Na mixture was refluxed under N_2 to make sodium sand. The sand was washed three times with THF, and then 150 mL of fresh THF was added followed by 3.4 mL (41 mmol) of freshly cracked, deoxygenated cyclopentadiene. The mixture was stirred until all of the sodium had reacted (about 4 h). (The solution at this point was light pink.) Methyl glycolate ketal (7.81 g, 48.0 mmol) was then added and the reaction mixture refluxed for 15 h under N_2. During this time, a white suspension formed. The reaction mixture was then cooled, and about 75 mL of THF was removed under vacuum. The remaining THF was cannula-filtered off, and the creamy-white residue was washed three times with ethyl ether and then dried in vacuo for 15 min. Yield: 5.4 g (24.8 mmol, 82%) of $Na^+[C_5H_4C(O)CH_2OC(CH_3)_2OCH_3]^-$. ^1H NMR (D_2O) δ, ppm 6.69 (br s, 2 H, C_5H_4); 6.21 (d, J = 21 Hz, 2 H, C_5H_4); 4.52 (s, 2 H, $C(O)CH_2$); 3.29 (s, 3 H, OCH_3); 1.45 (s, 6 H, $C(CH_3)_2$).

Fresh THF (150 mL) was added to $Na^+[C_5H_4C(O)CH_2OC(CH_3)_2OCH_3]^-$, followed by 5.00 g (18.9 mmol) of $Mo(CO)_6$, and the mixture was refluxed for 15 h. During this time, a clear, orange solution of $[(CO)_3MoC_5H_4C(O)CH_2OC(CH_3)_2OCH_3]^-$ resulted. ^1H NMR (D_2O) δ, ppm 5.97 (m, 2 H, C_5H_4); 5.41 (m, 2 H, C_5H_4); 4.59 (s, 2 H, $C(O)CH_2$); 3.26 (s, 3 H, OCH_3); 1.44 (s, 6 H, $C(CH_3)_2$). Once the reaction mixture was cooled to room temperature, a deoxygenated solution of 12.2 g (30.2 mmol) of $Fe(NO_3)_3{\cdot}9H_2O$ in 250 mL of water and 15 mL of acetic acid was cannulated into the reaction mixture and stirred for 1 h. The resulting purple, crystalline product was filtered onto a 150-mL medium glass-fritted Buchner funnel (in air), washed with water, methanol, and pentane, and then dried 4.5 h in vacuo (1 mmHg). Yield: 4.5 g (0.0074 mol, 78%) of 1. A 0.55-g portion was purified further by recrystallizing it from a mixture of 50 mL of THF and 20 mL of pentane. Anal. Calcd for $C_{20}H_{14}O_{10}M_2$: C, 39.62; H, 2.33. Found: C, 40.01; H, 2.16.

Synthesis of Cyclopentadienylethanol Ketal, $C_5H_5CH_2CH_2OC(CH_3)_2OCH_3$. Cyclopentadienylethanol (7.00 g, 64.0 mmol; prepared by the method of Schroder[33]) was added dropwise through the reflux condenser over 15 min to a 50-mL round-bottom flask containing a solution of 10 mL (104 mmol) of 2-methoxypropene and 0.08 g (0.3 mmol) of pyridinium *p*-toluenesulfonate (PPTS) at 0 °C. An additional 5 mL (52 mmol) of 2-methoxypropene was added through the reflux condenser. The reaction mixture was stirred for 1.25 h at 0 °C. Ethyl ether (30 mL) was then added, and the mixture was gravity-filtered through No. 1 Whatman paper into a 125-mL separatory funnel. The ether layer was washed twice with 20 mL of 10% salt water and then dried over 1 g of K_2CO_3 for 4 h. The ether and excess 2-methoxypropene were removed under vacuum to yield 9.9 g (54 mmol, 85%) of $C_5H_5CH_2CH_2OC(CH_3)_2OCH_3$. ^1H NMR ($CDCl_3$) δ, ppm 6.09–6.48 (br, 3 H, alkenyl); 3.55 (m, 2 H, OCH_2); 3.16 (m, 3 H, OCH_3); 2.94 (br, 2 H, allylic); 2.64 (m, 2 H, $C_5H_5CH_2$); 1.35 (s, 6 H, $C(CH_3)_2$).

Synthesis of Diol Complex 2, $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$. To a 500-mL Schlenk flask, fitted with a reflux condenser and N_2 inlet, were added 90 mL of THF and 1.093 g (47.5 mmol) of sodium sand. Cyclopentadienylethanol ketal (9.90 g, 54.0 mmol) was then added and the mixture stirred for 54 h at room temperature until all of the sodium had reacted. (The solution at this point is clear, light orange.) Degassed $Mo(CO)_6$ (10.8 g, 40.9 mmol) was then added and the mixture refluxed for 26 h. Once the reaction mixture was cooled, a deoxygenated mixture of 26.5 g (65.6 mmol) of $Fe(NO_3)_3{\cdot}9H_2O$ in 15 mL of acetic acid and 250 mL of distilled water was cannulated into the reaction mixture, and the mixture was stirred for 0.5 h in an ice bath. The resulting purple crystalline material was filtered (in air) onto a 150-mL medium glass-fritted Buchner funnel and washed with approximately 500 mL of distilled H_2O and then dried in vacuo (1 mmHg) for 12 h, yielding 9.76 g (83%) of 2. 2 was purified by recrystallizing once from a 70/30 (v/v) mixture of THF/hexane and once from THF (−30 °C) to yield 7.9 g (67%) of recrystallized product. Anal. Calcd for $C_{20}H_{18}O_8Mo_2$: C, 41.54; H, 3.14. Found: C, 41.76; H, 3.04.

Synthesis of Diol Complex 3, $(C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$. To a 250-mL Schlenk flask fitted with a reflux condenser, N_2 inlet, and magnetic stir bar was added 40 mL of diglyme and 7.57 g (0.042 mol) of deoxygenated cyclopentadienylethanol ketal in 5 mL of diglyme. Deoxygenated $Fe(CO)_5$ (4.5 mL, 0.034 mol) was then added, and the mixture was refluxed for 2.5 h until the yellow fumes of $Fe(CO)_5$ were absent, indicating no unreacted $Fe(CO)_5$. The reaction mixture was allowed to cool, then 180 mL of a deoxygenated solution of acetic acid in water (0.8 M) was added, and the resulting mixture was cannulated to a 500-mL Schlenk flask. Methylene chloride (60 mL) was added, the solution stirred for 15 min, and then the lower CH_2Cl_2 layer separated (under nitrogen). The original mixture was extracted with three 20–25-mL aliquots of CH_2Cl_2, combining all of the CH_2Cl_2 fractions. The volume of the CH_2Cl_2 solution was concentrated to approximately 40 mL, then 120 mL of hexane was added and mixed, and the solution was allowed to stand for 2.5 h. The CH_2Cl_2/hexane was cannulated from the red, oily residue, and the residue was redissolved in 60 mL of fresh CH_2Cl_2. The solution was dried over 2 g of K_2CO_3 for 1.5 h. The CH_2Cl_2 was cannulated from K_2CO_3, and the K_2CO_3 was rinsed with approximately 20 mL of CH_2Cl_2, combining the rinses with the CH_2Cl_2 fraction (80 mL total). Hexane (40 mL) was layered on top of the CH_2Cl_2 solution, and the solution was left to stand 17 h at room temperature in the dark and then was stored at −18 °C for 48 h. The resulting purple, crystalline material was washed with four 10–20-mL portions of hexane and then dried in vacuo for 18 h, yielding 2.34 g (31%) of crude dimer. The dimer was purified further by recrystallization from a mixture of 130 mL of CH_2Cl_2/75 mL of hexane and dried in vacuo for 2 days. Yield: 1.9 g (25%). Anal. Calcd for $C_{18}H_{18}O_6Fe_2$: C, 48.91; H, 4.10. Found: C, 49.14; H, 4.13.

Synthesis of Model Complex 4, $[(CO)_3MoC_5H_4C(O)CH_2OC(O)NH(CH_2)_5CH_3]_2$. Dimer 1 (0.499 g, 0.824 mmol) was added to a 250-mL Schlenk flask fitted with a reflux condenser and N_2 inlet. Dried, deoxygenated THF (75 mL) was added, and the solution was refluxed for 10 min to dissolve the dimer. The solution was cannula-filtered into another 250-mL Schlenk flask containing 20 mL of THF, 0.05 mL (0.2 mmol) of DBTA, and 0.25 mL (1.8 mmol) of hexyl isocyanate. This solution was refluxed for 1.5 h, after which the volume of THF was reduced to approximately 25 mL. Dried, deoxygenated ethyl ether (70 mL) was added, and the solution was stored overnight in a freezer at −18 °C. The resulting red crystalline product was filtered, washed with diethyl ether at 0 °C, and then dried in vacuo overnight. Yield: 0.21 g (30%) of complex 4. The product (103 mg) was purified further by recrystallization from a mixture of 4 mL of THF and 2.5 mL of pentane. Anal. Calcd for $C_{34}H_{40}N_2O_{12}Mo_2$: C, 47.45; H, 4.69; N, 3.26. Found: C, 47.24; H, 4.64; N, 3.22. MW (vapor pressure osmometry (VPO) acetone solvent) 824 ± 40 g/mol; the calculated molecular weight is 861 g/mol.

Synthesis of Model Complex 5, $[(CO)_3MoC_5H_4CH_2CH_2OC(O)NH(CH_2)_5CH_3]_2$. Dimer 2 (0.8928 g, 1.544 mmol) and 30 mL of dried, deoxygenated *p*-dioxane were added to a 100-mL Schlenk flask fitted with a reflux condenser, magnetic stir bar, and N_2 inlet. The mixture was heated to 85 °C in a thermostated oil bath. Hexyl isocyanate (0.49 mL, 3.6 mmol) was then added, followed by 0.02 mL (0.08 mmol) of dibutyltin diacetate. The mixture was stirred for 2 h at 85 °C. Absolute ethanol (0.5 mL) was then added and the mixture stirred for 5 more min. The reaction mixture was cooled to room temperature and the volume reduced to approximately 10 mL under vacuum. The reaction mixture was then cannulated into 95 mL of dried, deoxygenated hexane and the mixture put in a refrigerator at 5 °C for 19 h. The hexane/*p*-dioxane solvent was then cannula-filtered from the resulting pink powder, and the crude product was washed with three 20-mL aliquots of hexane and dried 5 min in vacuo to remove the hexane. The product was dissolved in 10 mL of THF, 45 mL of hexane was layered on top, and the mixture was placed in a freezer at −18 °C for 72 h. The pink, powdery product was then filtered through a medium porosity glass frit in air, washed several times with hexane, and then dried in vacuo (0.1 mmHg) for 45 h, yielding 0.78 g (61%) of complex 5. The complex (50 mg) was recrystallized from 3 mL of diethyl ether (at −40 °C). Anal. Calcd for $C_{34}H_{44}N_2O_{10}Mo_2$: C, 49.06; H, 5.33; N, 3.36. Found: C, 49.21; H, 5.44; N, 3.64.

Synthesis of Model Complex 6, $(C_5H_4CH_2CH_2OC(O)NH(CH_2)_5CH_3)_2Fe_2(CO)_4$. To a 125-mL Schlenk flask fitted with

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a reflux condenser, N_2 inlet, and magnetic stir bar was added 0.2619 g (0.593 mmol) of **3** and 25 mL of *p*-dioxane. The mixture was stirred to dissolve the **3**, and then 0.20 mL (1.5 mmol) of hexyl isocyanate in 5 mL of *p*-dioxane was added, followed by 0.002 mL (0.008 mmol) of DBTA. The mixture was heated with stirring at 90 °C in a thermostated oil bath for 2.5 h. After the mixture was cooled, the *p*-dioxane was removed in vacuo. The residue was dissolved in 10 mL of THF, and then 40 mL of hexane was layered on top. This mixture was stored in a freezer at −18 °C for 16 h. The THF/hexane solvent was then cannula-filtered from the pink residue, and the residue was washed with hexane and then dried in vacuo. The THF/hexane filtrate was reduced in volume to 5 mL, and then 3 mL of THF plus 25 mL of hexane were added to it. The solution was stored at −18 °C for 20 h. The resulting red precipitate was filtered, washed with hexane, and dried in vacuo. The crude product fractions were combined into a 3-mL Schlenk tube, recrystallized twice by dissolving them in 3–4 mL CH_2Cl_2, and then layered in 16–20 mL of hexane, followed by storage for 1 week at −18 °C under N_2. The recrystallized product was dried in vacuo (0.02 mmHg) for 35 h. Yield: 0.153 g (37%). Anal. Calcd for $C_{32}H_{44}N_2O_8Fe_2$: C, 55.19; H, 6.37; N, 4.02. Found: C, 54.91; H, 6.60; N, 4.25.

Synthesis of Oligomer 7, [$-OCH_2C(O)C_5H_4(CO)_3Mo-Mo(CO)_3C_5H_4C(O)CH_2OC(O)NH(CH_2)_6NHC(O)-]_n$ (*n* = 4–5). To a 500-mL three-neck flask fitted with a reflux condenser, N_2 inlet, and magnetic stir bar were added 1.9463 g (3.2 mmol) of complex **1** and 200 mL of THF. The solution was brought to reflux, and a mixture of 0.52 mL (3.2 mmol) of HMDI and 0.08 mL (0.3 mmol) of DBTA in 18 mL of THF was added. The mixture was refluxed for an additional 3.5 h. (The completion of the reaction was determined by monitoring the disappearance of the isocyanate stretch at 2270 cm^{-1}.) After the mixture was cooled to room temperature, the reaction mixture was cannula-filtered into a 500-mL Schlenk flask and the volume reduced to approximately 100 mL under vacuum. This mixture was rapidly cannulated into 250 mL of pentane. The oligomer precipitated immediately as a red gummy material. The precipitate was allowed to settle for 15 min, washed with pentane, and dried in vacuo (1 mmHg) overnight. The oligomer was then ground up, washed with ethyl ether and pentane, and then dried in vacuo (1 mmHg) for 6 h. Yield: 1.63 g (66%) of red–purple powder. Anal. Calcd for $C_{28}H_{26}N_2O_{12}Mo_2{\cdot}0.24C_4H_{10}O{\cdot}0.19C_5H_{12}{\cdot}0.11C_4H_8O$: C, 44.79; H, 3.91; N, 3.44. Found: C, 44.61; H, 3.99; N, 3.77. $\bar{M}_n$ (VPO, acetone) 3500 g/mol.

Synthesis of Oligomer 8, [$-OCH_2CH_2C_5H_4Mo(CO)_3-Mo(CO)_3C_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)-]_n$. Method A. To a 50-mL three-neck flask fitted with a reflux condenser, N_2 inlet, and magnetic stir bar was added 0.7889 g (1.36 mmol) of **2** and 20 mL of *p*-dioxane. The mixture was heated with stirring to 75 °C in a thermostated oil bath. DBTA (0.04 mL, 0.02 mmol) was added, followed by 0.2314 g (1.38 mmol) of HMDI in 4 mL of *p*-dioxane, and the mixture was heated at 89 °C with stirring for 3 h. The reaction mixture was removed from the oil bath, 2 mL of deoxygenated absolute ethanol (dried over type 3A molecular sieves) was added, and the mixture was stirred for 15 more min. The mixture was then cannulated into 60 mL of hexane. The *p*-dioxane/hexane was cannula-filtered from the red, oily precipitate. THF (20 mL) was then added to dissolve the oligomer, and the solution was cannulated into 80 mL of hexane to precipitate the oligomer. The solution was filtered, and the red precipitate was dried in vacuo (0.02 mmHg) for 2 days, then ground up, washed with three 15-mL aliquots of hexane, and dried in vacuo (0.01 mmHg) for 21 h, yielding 0.72 g (71%) of **8**. A portion of the polymer was dried further at 45 °C in vacuo (0.005 mmHg) for 37 h and submitted for elemental analysis. Anal. Calcd for $C_{28}H_{30}N_2O_{10}Mo_2{\cdot}0.09C_6H_{14}{\cdot}0.025C_4H_8O{\cdot}0.025C_4H_8O_2$: C, 45.55; H, 4.21; N, 3.70. Found: C, 45.20; H, 4.14; N, 3.70. (Solvent amounts were determined by NMR.) $\bar{M}_n$ (VPO, *p*-dioxane) 4800 g/mol ($n \approx 6$).

Method B. To a 100-mL, three-neck flask fitted with a reflux condenser, N_2 inlet, magnetic stir bar, and thermometer were added 1.5342 g (2.65 mmol) of **2** and 28 mL of *p*-dioxane. The flask was wrapped in aluminum foil to protect it from light, and then 0.4461 g (2.65 mmol) of HMDI in 6 mL of *p*-dioxane was added. DBTA (0.034 mL, 0.13 mmol) was added, and the mixture was stirred at room temperature (approximately 26 °C) for 6.5 h. Absolute ethanol (0.04 mL, 0.7 mmol, dried over type 4A molecular sieves) was then added, and the mixture was stirred for 1 more h. The reaction mixture was then cannulated into approximately 75 mL of hexane, and the resulting mixture was stored in a refrigerator at 5 °C for 13.5 h. The hexane/dioxane was then decanted (under nitrogen by using a cannula) from the red, oily residue, and 30 mL of THF was added to redissolve the residue. Hexane (80 mL) was added and the mixture stored at 5 °C for 12 h. The THF/hexane was cannula-filtered from the red residue, and then the residue redissolved in 50 mL of THF. Hexane (100 mL) was added and the mixture stored for 2 h at 5 °C. The THF/hexane was cannula-filtered from the red, powdery polymer, and the polymer was washed with three 20-mL aliquots of hexane and then dried in vacuo (0.005 mmHg) at 45 °C for 37 h. Yield: 1.568 g (79%). $\bar{M}_n$ (VPO, $CHCl_3$) 6000 g/mol (*n* = 8).

Synthesis of Copolymer 9, [$-(O(CH_2)_4OC(O)NH(CH_2)_6NHC(O)-)_mOCH_2CH_2C_5H_4(CO)_3Mo-Mo(CO)_3C_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)-]_n$ (*n* = 2–3; *m* = 1). To a three-neck 250-mL round-bottom flask fitted with a reflux condenser, N_2 inlet, magnetic stir bar, thermometer, and 100-mL addition funnel was added 50 mL of *p*-dioxane and 0.7520 g (4.47 mmol) of HMDI. The mixture was heated, with stirring, at 85 °C in a thermostated oil bath. 1,4-Butanediol (0.2028 g, 2.25 mmol) and 0.05 mL (0.2 mmol) of DBTA in 18 mL of *p*-dioxane was then added dropwise from the addition funnel over 55 min. The reaction mixture was stirred an additional 55 min at 85 °C. Dimer **2** (1.2839 g, 2.22 mmol) in 20 mL of dried, deoxygenated *p*-dioxane was then rapidly added to the reaction mixture and the mixture heated at 88 °C for 1.5 h. Deoxygenated absolute ethanol (2 mL) was added, and the mixture stirred with heating for 15 min. After cooling for 0.5 h, the reaction mixture was cannulated into 250 mL of dried, deoxygenated hexane. The copolymer, **9**, precipitated immediately as a red powder. The solvent was removed from the copolymer by cannula filtration. The copolymer was washed with six 20-mL aliquots of hexane and then dried in vacuo (0.01 mmHg) at 50 °C for 15 h. Yield: 1.40 g (63%) of copolymer **9**. Anal. Calcd (based on ^1H NMR composition—see Table I) for $C_{43.92}H_{56.20}N_{4.28}O_{15.40}Mo_{2.28}{\cdot}0.03C_4H_8O_2{\cdot}0.10C_6H_{14}$: C, 47.85; H, 5.20; N, 5.35. Found: C, 47.48; H, 5.28; N, 5.49. $\bar{M}_n$ (VPO, $CHCl_3$) 2600 g/mol.

Synthesis of Oligomer 10, [$-OCH_2CH_2C_5H_4(CO)_2Fe-Fe(CO)_2C_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)-]_n$ (*n* = 2–3). To a three-neck 250-mL flask equipped with a reflux condenser, N_2 inlet, magnetic stir bar, and thermometer was added 0.7300 g (1.651 mmol) of **3** and 22 mL of *p*-dioxane. The mixture was heated to 80 °C with a thermostated oil bath, and then 0.2784 g (1.655 mmol) of HMDI in 2 mL of *p*-dioxane was added, followed by 0.002 mL (0.008 mmol) of DBTA. The HMDI vessel was rinsed with 6 mL of *p*-dioxane, and the rinses were added to the reaction vessel. The mixture was heated at 80 °C with stirring for 1.5 h. Deoxygenated absolute ethanol, 2 mL, was then added, and the mixture stirred for 6 min at 80 °C. After cooling, the reaction mixture was cannulated into 80–90 mL of hexane. An intermediate purple precipitate formed. The solution was immersed in an ice bath for 45 min, and then the hexane/dioxane was cannula-filtered from the oily product. THF (25 mL) was added to dissolve the oligomer, followed by addition of 100 mL of hexane to precipitate the oligomer. The mixture was stored at −18 °C overnight. The THF/hexane was cannula-filtered from the oligomer, and the oligomer was dried 0.5 h in vacuo. The oligomer was redissolved in 23 mL of THF and then precipitated with 125 mL of hexane. The resulting reddish-brown, powdery precipitate was washed with three 20-mL aliquots of hexane and dried in vacuo (0.001 mmHg) for 42 h. Yield: 0.80 g (79%). Anal. Calcd for $C_{26}H_{30}N_2O_8Fe_2{\cdot}0.09C_6H_{14}$: C, 51.56; H, 5.09; N, 4.54. Found: C, 51.90; H, 5.21; N, 4.65. $\bar{M}_n$ (VPO, $CHCl_3$) 1500 g/mol.

Synthesis of Polymer 11, [$-O(CH_2)_4OC(O)NH(CH_2)_6NHC(O)-]_n$. Polymer **11** was prepared by a modification of a literature method.[34] To a 50-mL three-neck flask fitted with a reflux condenser, N_2 inlet, and magnetic stir bar was added 20 mL of *p*-dioxane (distilled from P_2O_5 under N_2) and 0.6240 g (6.92 mmol) of 1,4-butanediol and 0.02 mL (0.08 mmol) DBTA. The

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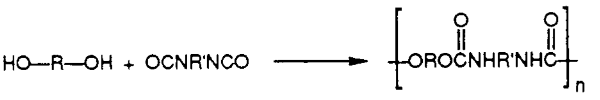
[34] Marvel, C. S.; Johnson, J. H. *J. Am. Chem. Soc.* **1950**, *72*, 1674–1677.

mixture was heated to 75 °C. HMDI (1.1649 g, 6.93 mmol) in 6 mL of *p*-dioxane was then added, and the mixture was heated to 88 °C with stirring for 3 h. During this time, a white precipitate formed. The reaction mixture was cooled for 15 min, 2 mL of deoxygenated absolute ethanol was added, and the reaction mixture was stirred for 0.5 h at room temperature. The reaction mixture was then poured into 60 mL of dried, deoxygenated hexane. The white precipitate was separated from the solvent by cannula filtration and then washed with 100 mL of a THF/hexane mixture (20/80) followed by washing with three 15–20-mL aliquots of hexane. The product was dried in vacuo (0.025 mmHg) for 17 h. Yield: 1.61 g (90%) of 8. Melting point 174–181 °C (lit. 175–176 °C).

Results and Discussion

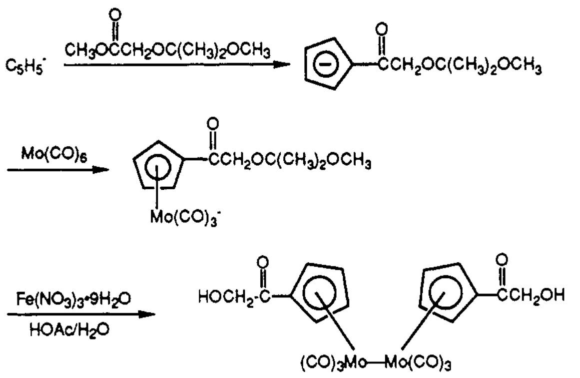
Synthetic Strategy. The introduction of metal–metal bonds into polymer backbones poses several synthetic problems not normally encountered in polymer synthesis. In general, these problems arise because metal–metal bonds are more reactive[35] than the bonds found in standard polymers; thus, under many standard polymerization reaction conditions, cleavage of the metal–metal bond would result. For example, metal–metal bonds react with acyl halides to form metal halide complexes. Thus, the synthesis of polyamides using metal–metal bonded "diamines" and diacyl chlorides would simply lead to metal–metal bond cleavage rather than polymerization. Likewise, metal–metal bonded complexes are incompatible with many Lewis bases because the Lewis bases cleave the metal–metal bonds in disproportionation reactions.[36] This type of reactivity thus rules out many condensation polymerization reactions in which bases are used to neutralize any acids produced. Similarly, it prevented us from using diamines in the synthesis of polyamides.

In order to avoid the problems above, we began our studies with polyurethanes. Polyurethanes were chosen as our first synthetic goal because they are synthesized in addition reactions of diisocyanates to diols (eq 4). No molecules are eliminated and therefore no Lewis bases or drying agents are required in the reaction mixture. Our strategy was to synthesize diols containing the $Cp_2Mo_2(CO)_6$ and $Cp_2Fe_2(CO)_4$ units and then react these with diisocyanates.



$$\mathrm{HO{-}R{-}OH + OCNR'NCO \longrightarrow \left[{-}OR O\overset{O}{\overset{\|}{C}}NHR'NH\overset{O}{\overset{\|}{C}}{-} \right]_n} \quad (4)$$

Synthesis of the Metal–Metal Bonded Diols. $(C_5H_4C(O)CH_2OH)_2Mo_2(CO)_6$, complex 1, was synthesized by the route outlined in eq 5. (*All of the metal–metal bonded complexes and polymers in this paper are shown in a gauche conformation. No implication as to the actual conformation is necessarily implied. The conformations are discussed further in the text below.*) Note that protection of the methyl glycolate OH group as a ketal was necessary to avoid reaction of this hydrogen with the cyclopentadienyl anion.

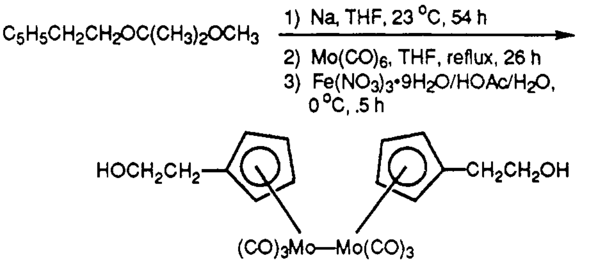


(5)

1
78%

Complex 1 crystallized from the aqueous THF solution as a bright red, crystalline material. The complex was characterized by IR, ^1H NMR, and electronic absorption spectroscopy (Table I). As indicated in Table I, the electronic spectrum of the complex is essentially identical with the spectrum of the $Cp_2Mo_2(CO)_6$ complex.[22] Respective assignment of the bands at 391 and 511 nm to the $\sigma \rightarrow \sigma^*$ and $d\pi \rightarrow \sigma^*$ transitions associated with the Mo–Mo bonds is therefore suggested.[22] The NMR spectrum of the complex is assigned in Table I. Note that the four proton resonances between 5.60 and 6.22 ppm in acetone-d_6 arise from the interaction of the protons on the two C_5 rings when the rings are in the gauche conformation. The intensity and number of these resonances is solvent dependent. For example, only two resonances are observed in $CDCl_3$ compared to four peaks in acetone-d_6. This solvent dependence is attributed to a change in the preferred conformation with the solvent polarity; a gauche conformation is preferred in polar solvents and a trans orientation of the rings is preferred in nonpolar solvents. The broad OH resonance at 4.17 ppm was verified by its disappearance upon addition of D_2O.

The $(C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ complex, **2**, was synthesized by reacting cyclopentadienylethanol (with the OH group protected as a ketal) with sodium and then refluxing the substituted cyclopentadienyl anion with $Mo(CO)_6$ in refluxing THF (eq 6). This method gave a much higher



(6)

2
67%

yield (67% recrystallized) than that previously reported.[37] Spectroscopic data for complex 2 are reported in Table I. Again, the complex pattern of broad resonances between 5.23 and 5.58 ppm arises from interaction of the two sets of C_5H_4 protons when the two rings are in the gauche conformation. The OH resonance at 3.86 ppm was verified by its disappearance upon treatment of the sample with D_2O. Complex 2 is much more soluble in THF than is complex 1 (0.35 M vs 0.02 M), making it more suitable for polymerization reactions.

The iron–iron diol, **3**, was synthesized by a modification of King's procedure for the synthesis of $Cp_2Fe_2(CO)_4$.[38] Cyclopentadienylethanol was again protected as a ketal by reacting it with 2-methoxypropene. This ligand was

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[35] The reactivity of metal–metal bonded carbonyl dimers can be attributed to the relative small bond dissociation energies of metal–metal bonds and to the fact that photolysis of the metal–metal bond occurs upon irradiation. See refs 22 and 23.

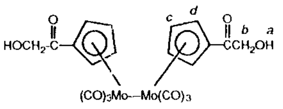
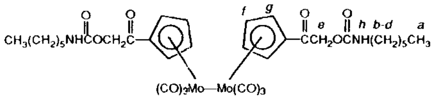
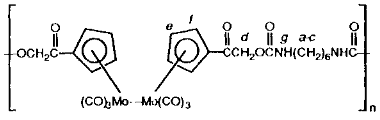
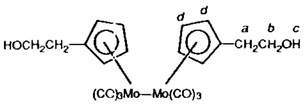
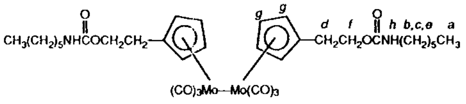
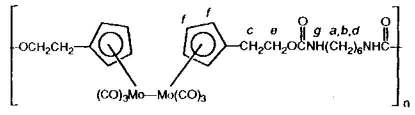
[36] Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217–240.

[37] Coolbaugh, T. S.; Coots, R. J.; Santarsiero, B. D.; Grubbs, R. H. *Inorg. Chim. Acta* **1985**, *98*, 99–105.

[38] King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, pp 114–115.

[39] Goldman, A. S.; Tyler, D. R. *Inorg. Chem.* **1987**, *26*, 253–258.

Table I. Infrared, ^{1}H NMR, and Electronic Absorption Spectroscopic Data for $Cp_2Mo_2(CO)_6$ and 1–8

	IR (KBr)			
compd	ν(C=O), cm^{-1}	other bands, cm^{-1}	^{1}H NMR (acetone-d_6), δ, ppm	λ, nm (ϵ) (THF)
$Cp_2Mo_2(CO)_6$	2012 (sh, w) 1954 (s) 1925 (m) 1901 (s) 1890 (s)		5.60, br, 5 H 5.44, br, 5 H	508 (1920) 388 (20690)
 1	2014 (w) 1955 (s) 1928 (s) 1898 (s)	ν(OH), 3482 (m) ν(C=O), 1682 (m) ν(CH_2, sp^3), 2938 (w), 2889 (w), 2861 (w)	a: 4.17, br, 2 H b: 4.59, d, J = 6.0 Hz, 4 H c, d: 5.60, br, 2.3 H 5.91, br, 2.2 H 6.05, br, 1.9 H 6.22, br, 2.0 H	511 (1730) 391 (17700)
 4	2021 (m) 1984 (s) 1929 (vs) 1902 (vs)	ν(N-H), 3381 (br, w) ν(C=O, urethane), 1728 (s) ν(C=O, keto), 1706 (s) ν(N—H, amide II), 1516 (m) ν(C—N, amide III), 1243 (m) ν(CH_2, sp^3), 2931 (m), 2861 (w)	a: 0.88, t, J = 6.3 Hz, 6 H b: 1.30, br, 12 H c: 1.51, m, J = 6.6 Hz, 4 H d: 3.13, q, J = 6.6 Hz, 4 H e: 4.99, s, 4 h f, g: 5.59, br, 1.8 H 5.91, br, 2.6 H 6.04, br, 1.7 H 6.23, br, 2.4 H h: 6.50, br, 2 H	511 (1870) 390 (16900)
 7	2021 (s) 1967 (vs) 1909 (vs)	ν(N—H), 3375 (m) ν(NCO), 2277 (vw) ν(C=O, urethane), 1724 (s) ν(C=O, keto), 1703 (s) δ(N-H, amide II), 1525 (m) ν(C—N, amide III), 1242 (s) ν(CH_2, sp^3), 2932 (m), 2861 (w)	a: 1.35, br, 4 H b: 1.50, br, 4 H c: 3.13, br, 4 H d: 4.98, s, 4 H e, f: 5.58, br, 1.5 H 5.89, br, 2.7 H 6.04, br, 1.4 H 6.23, br, 2.3 H g: 6.53, br, 2 H	504 (1820) 389 (16900)
 2	2008 (w) 1955 (s) 1940 (s) 1926 (s) 1905 (s) 1891 (s)	ν(OH), 3326 (br, w) ν(CH_2, sp^3), 2960, (vw), 2940 (vw), 2884 (vw)	a: 2.61, t, J = 6.3 Hz, 4 H b: 3.68, q, J = 6.3 Hz, 4 H c: 3.86, t, J = 5.1 Hz, 2 H d: 5.23–5.59, 3 br resonances, 8 H	508 (2080) 391 (17200)
 5	2010 (vw) 1963 (m) 1935 (s) 1902 (s) 1885 (s)	ν(N—H), 3299 (m) ν(C=O), 1707 (w), 1681 (m) δ(N—H, amide II), 1541 (m) ν(C—N, amide III), 1262 (m) ν(CH_2, sp^3), 2967 (w), 2949 (w), 2924 (w), 2872 (w), 2857 (w)	a: 0.87, t, J = 6.6 Hz, 6 H b: 1.28, br, 12 H c: 1.47, m, J = 6.6 Hz, 4 H d: 2.71, t, J = 6.3 Hz, 4 H e: 3.09, q, J = 6.6 Hz, 4 H f: 4.11, t, J = 6.3 Hz, 4 H g: 5.25–5.62, 3 br resonances, 8 H h: 6.25, br, 2 H	508 (1980) 392 (17400)
 8	2011 (ms) 1949 (s) 1885 (s)	ν(N—H), 3341 (wm) ν(C=O), 1697 (ms) δ(N—H, amide II), 1522 (m) ν(N—H, amide III), 1240 (m) ν(CH_2, sp^3), 2931 (m), 2861 (m)	a: 1.33, br, 4 H b: 1.48, br, 4 H c: 2.71, t, J = 5.7 Hz, 4 H d: 3.10, m, J = 6.0 Hz, 4 H e: 4.12, br, 4 H f: 5.25–5.61, 3 br resonances, 8 H g: 6.30, br, 2 H	508 (2070) 392 (17850)

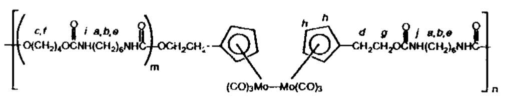
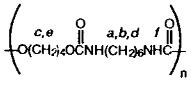
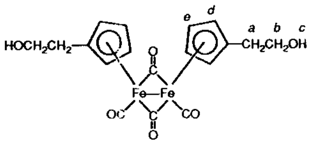
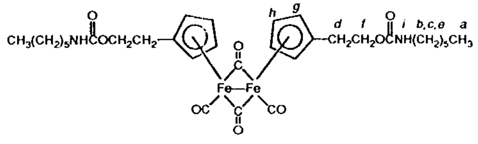
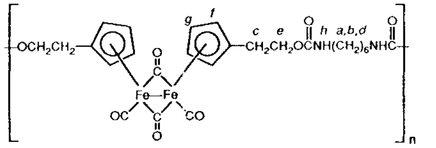
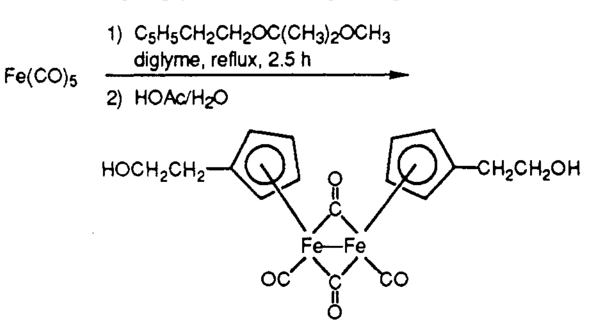
 9	2010 (m) 1947 (s) 1898 (s)	ν(N-H), 3325 (m) ν(C=O), 1687 (ms) δ(N—H, amide II), 1532 (ms) ν(C—N, amide III), 1258 (ms) ν(CH_2, sp^3), 2938 (m), 2861 (m)	a: 1.33, br, 8 H b: 1.49, br, 8 H c: 1.61, br, 4 H d: 2.71, t, J = 6.0 Hz, 4 H e: 3.10, m, J = 6.0 Hz, 8 H f: 4.00, br, 3.6 H g: 4.12, br, 4.1 H h: 5.26–5.62, 3 br resonances, 6 H i: 6.20, br, 1.2 H j: 6.31, br, 1.5 H	508 (2260) 391 (19 100)
 11		ν(N—H), 3325 (s) ν(C=), 1708 (s), 1687 (s) ν(N—H, amide II), 1539 (s) ν(C—N, amide III), 1265 (s) ν(CH_2, sp^3), 2966 (m), 2938 (m) 2868 (m)	a: 1.34, br, 4 H b: 1.49, br, 4 H c: 1.61, br, 4 H d: 3.10 m, J = 5.7 Hz, 4 H e: 4.00, br, 4 H f: 6.22, br, 1 H	

Table II. ^{1}H NMR, IR, and Electronic Absorption Spectra for $Cp_2Fe_2(CO)_4$, 3, 6, and 10

compound	IR (KBr), cm^{-1}			
	ν(C≡O), cm^{-1}	other bands, cm^{-1}	^{1}H NMR (acetone-d_6)	λ, (ε) (THF)
$Cp_2Fe_2(CO)_4$	1973 (m) 1954 (s) 1933 (vs) 1907 (m) 1757 (vs)		4.94 (C_5H_4)[a]	511 (568) 410 (1900) 345 (10 100)
 3	1958 (s) 1940 (s) 1914 (m) 1759 (vs) 1732 (m)	ν(OH), 3212 (m) ν(CH_2, sp^3), 2948 (w), 2934 (w), 2881 (w)	a: 2.67, t, J = 6.0 Hz, 4 H b: 3.77, m, J = 5.4 Hz, 4 H c: 3.86, br, 2 H d: 4.66, br, 4 H e: 4.84, br, 4 H	512 (510) 410 (1780) 347 (9260)
 6	1992 (w) 1949 (s) 1916 (vw) 1801 (vw) 1779 (m) 1768 (vs) 1744 (w)	ν(N—H), 3279 (m) ν(C=O), 1707 (m), 1680 (s) δ(N-H, amide II), 1555 (m) ν(C—N, amide III), 1270 (m) ν(CH_2, sp^3), 2951 (m), 2931 (m), 2860 (w)	a: 0.87, br, 6 H b: 1.28, br, 12 H c: 1.46, m, 4 H d: 2.77, t, J = 6.0 Hz, 4 H e: 3.09, q, J = 6.3 Hz, 4 H f: 4.19, t, J = 6.3 Hz, 4 H g: 4.71, br, 4 H h: 4.84, br, 4 H i: 6.26, br, 2 H	513 (550) 410 (1850) 346 (10 100)
 10	1988 (vs) 1945 (s) 1803 (m) 1768 (vs)	ν(N—H), 3336 (wm) ν(C=O), 1708 (br, s) δ(N—H, amide II), 1527 (m) ν(C—N, amide III), 1252 (m) ν(CH_2, sp^3), 2934 (wm), 2889 (w)	a: 1.32, br, 4 H b: 1.47, br, 4 H c: 2.78, t, J = 6.3 Hz, 4 H d: 3.11, q, J = 6.3 Hz, 4 H e: 4.21, t, J = 6.0 Hz, 4 H f: 4.73, br, 4 H g: 4.84, br, 4 H h: 6.29, br, 2 H	511 (520) 410 (1620) 347 (8940)

[a] See ref 39.

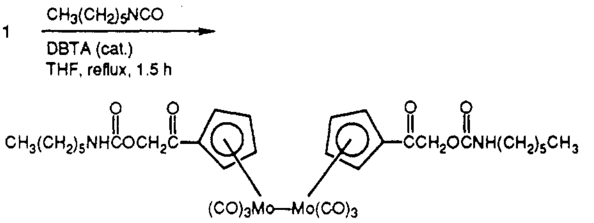
reacted with less than an equimolar amount of $Fe(CO)_5$ in refluxing diglyme according to eq 7. The relatively low yield (25%) probably results from using a relatively small excess of the ligand vs $Fe(CO)_5$. King's procedure uses a large excess of cyclopentadiene ligand, but we found that cyclopentadienylethanol polymerizes upon prolonged heating, and thus we avoided an excess of it. Also, the crude material is an oil which required several recrystallizations to obtain in pure, crystalline form. Spectroscopic data for complex 3 are presented in Table II. The infrared spectrum of the metal carbonyl region and the electronic absorption spectra are similar to that of $Cp_2Fe_2(CO)_4$ (Cp = η^5-C_5H_5) (Table II). The ^1H NMR is also consistent with that of the proposed structure.



(7)

3
25%

Synthesis and Characterization of the Model Complexes. As indicated in the Introduction, our plan for the synthesis of the polyurethanes was to react the metal–metal bond-containing diols (1–3) with diisocyanates. In order to spectroscopically characterize the polyurethanes, we synthesized "model complexes" by using the appropriate *mono*isocyanate. Model complex 4 was synthesized from 1 and hexylisocyanate according to eq 8 (yield 30%).



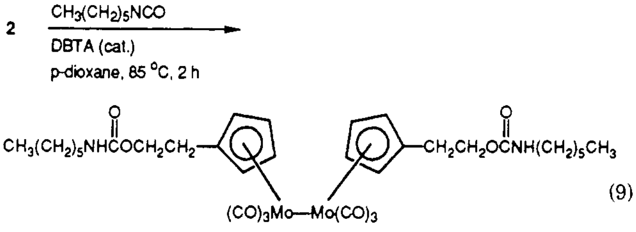
(8)

4
30%

The spectroscopic data (Table I) are consistent with the structure shown for 4. The ^1H NMR has the same pattern of C_5H_4 resonances as those of dimer 1. Of more importance, the complex has a broad resonance at 6.50 ppm, indicating a secondary amide proton,[40] and a singlet resonance at 4.99 ppm for the methylene protons α to the ethereal oxygen of the ester linkage. These latter proton resonances were at 4.59 ppm in 1. The 0.4 ppm downfield shift is consistent with the protons α to an alcohol group in 1 now being α to the ether oxygen of an ester linkage. The infrared spectrum of 4 showed the characteristic N–H stretch at 3381 cm^{-1} and the amide I, II, and III bands at 1728, 1516, and 1243 cm^{-1}, respectively.[41] The $\nu(C{\equiv}O)$ bands at 2021, 1984, 1929, and 1902 cm^{-1} are similar to those of $Cp_2Mo_2(CO)_6$[42] and complex 1. The electronic absorption spectrum indicates that the Mo–Mo bond is still intact [λ_{max} = 390 nm ($\sigma \rightarrow \sigma^*$) and λ_{max} = 511 nm ($d\pi \rightarrow \sigma^*$)]. The extinction coefficients at these wavelengths are also very similar to those for $Cp_2Mo_2(CO)_6$ and complex 1 (Table I).

The molecular weight of complex 4, determined by vapor pressure osmometry in acetone, was 824 g/mol. The calculated molecular weight is 861 g/mol.

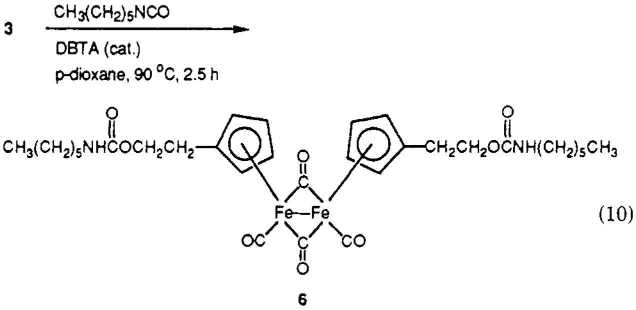
The model complex 5 was synthesized from dimer 2 and hexyl isocyanate according to eq 9. Complex 5 was characterized by elemental analysis and ^1H NMR, infrared, and electronic absorption spectroscopy (Table I). The ^1H NMR indicates a secondary amide proton resonance at 6.28 ppm, the same pattern of C_5H_4 resonances from 5.25 to 5.62 ppm as that of complex 2, and a triplet resonance at 4.11 ppm corresponding to the methylene protons α to the ethereal oxygen of the urethane linkage. The infrared spectrum is consistent with that of a urethane complex: there is an N–H stretch at 3299 cm^{-1}, amide I (carbonyl) stretches at 1707 and 1681 cm^{-1}, amide II bends at 1541 cm^{-1}, and amide III stretches at 1262 cm^{-1}. The $\nu(C{\equiv}O)$ stretches are similar to those of complex 2 and $Cp_2Mo_2(CO)_6$ (Table I). The presence of the Mo–Mo bond is again indicated by the two bands at 392 (17 400 M^{-1} cm^{-1}) and 508 nm (1980 M^{-1} cm^{-1}) in the electronic spectrum. Note that the extinction coefficients are very similar to those of 2 and $Cp_2Mo_2(CO)_6$.



(9)

5
61%

The iron diol dimer 3 was reacted with hexyl isocyanate according to eq 10 to make a model complex similar to oligomer 10. As shown in Table II, the infrared spectrum in the $\nu(C{\equiv}O)$ region is similar to that of dimer 3 and $Cp_2Fe_2(CO)_4$, with the exception of an additional weak band at 1992 cm^{-1} that is present only in complex 6. This weak band is attributable to molecules with Cp rings in the gauche conformation.[43] The electronic absorption spectrum is similar to 3, indicating the Fe–Fe bond is still intact, and the ^1H NMR is consistent with the structure shown.



(10)

6
37%

Synthesis of Oligomer 7. Polyurethanes were synthesized from 1–3 by using solution polycondensation reactions. Oligomer 7 was synthesized in refluxing THF

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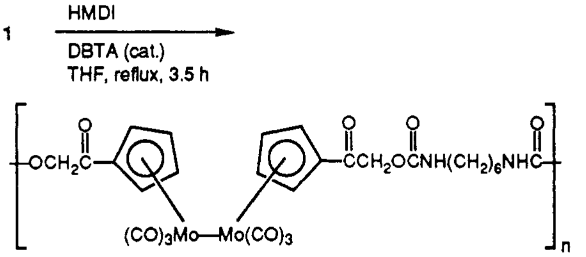
[40] Silverstein, R. M.; Bassler, G. C., Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 198.

[41] See ref 40, pp 125–126.

[42] Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246–4251.

[43] (a) Bryan, R. F.; Greene, P. T.; Newlands, M. J.; Field, D. S. *J. Chem. Soc. A* **1970**, 3068–3074. (b) Manning, A. R. *J. Chem. Soc. A* **1968**, 1319–1324. (c) Tenhaeff, S. C.; Tyler, D. R., manuscript in preparation.

according to eq 11. The oligomer was obtained in 66% yield as a red-purple crystalline powder. As shown in Table I, the spectroscopic data are similar to that of model complex 4.

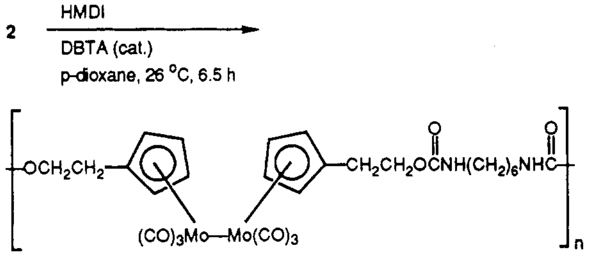


(11)

7
66%

The $\bar{M}_n$ of the oligomer, determined in acetone by VPO, was 3500 (n = 4-5). This low molecular weight might be attributable to (1) the unreactivity of the OH group on the Cp ring due to steric effects, (2) the low reaction temperature (67 °C), (3) the unbalanced reactant ratios resulting from errors in measuring small quantities,[44] and (4) the dilute reaction mixture required to dissolve dimer 1. Despite the low molecular weight of the polymer, brittle films of it could be cast onto glass slides from THF solutions. Attempts to cast films of model complex 3 were unsuccessful, a result we feel is an indication of the oligomeric nature of 7.

Synthesis of Oligomer 8. The insolubility of dimer 1 and its seemingly unreactive nature prompted us to synthesize dimer 2, which is much more soluble in THF than in 1 (0.35 M vs 0.02 M). Replacing the carbonyl group attached to the ring with a methylene group should also increase the reactivity of this dimer by increasing the nucleophilicity of the OH group.

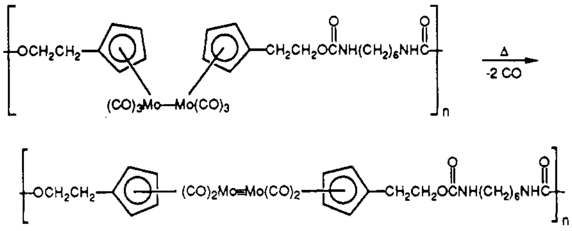


(12)

8
71%

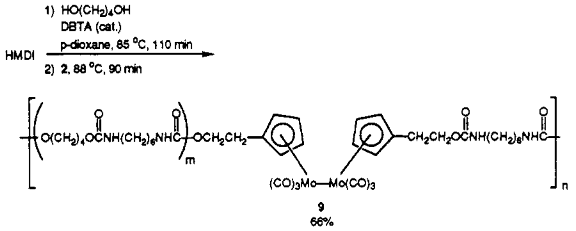
Polyurethane 8 was synthesized in 71% yield from 2 and HMDI according to eq 12. The structure of this oligomer was again determined by elemental analysis and infrared, ^{1}H NMR, and electronic absorption spectroscopy. The spectroscopic data (Table I) are nearly identical with that of model complex 5 with the exception of broader ^{1}H NMR resonances and IR bands. The $\bar{M}_n$ (VPO, CHCl$_3$) was determined to be 6000 ($n \approx 8$). In an alternate procedure, the polymer was synthesized by reacting 2 with HMDI for 3 h at 84 °C in p-dioxane ($\bar{M}_n$ in p-dioxane: 4800 g/mol; $n \approx 6$). Note that $\bar{M}_n$ was slightly larger ($\approx$1200 g/mol) for the room-temperature polymerization reaction; thermolysis of the Mo–Mo bond could lead to the decreased $\bar{M}_n$ value for the sample prepared at 84 °C. Molecular weight determination by gel permeation chromatography (THF solvent) on the sample prepared at 84 °C gave $\bar{M}_n$ = 1040 and $\bar{M}_w$ = 16 350 relative to polystyrene. Multiplying the $\bar{M}_n$ (as determined by VPO) by the $\bar{M}_w/\bar{M}_n$ ratio (determined by GPC) of 15.8 gives a calculated absolute $\bar{M}_w$ of 73 000. The molecular weight data indicate this polymer has a very broad distribution. The infrared spectrum (KBr) of oligomer 8 is similar to that of model complex 5 except that the urethane carbonyl stretch occurs as a broad band at 1701 cm^{-1} of medium intensity in the oligomer, whereas in the model complex it occurs as two sharp bands—one of weak intensity at 1707 cm^{-1} and one at 1681 cm^{-1} of medium intensity. Also, the amide II and amide III bends and stretches occur as broadened bands at lower energy in the oligomer than in the model complex (1522 and 1240 cm^{-1} vs 1541 and 1262 cm^{-1}, respectively). The most significant difference in the infrared spectrum is that the band at 2010 cm^{-1} is intense in the oligomer but quite weak in the model complex. This band is attributed to molecules with a gauche orientation of the Cp rings.[43] The larger amount of gauche conformation in the oligomer and its implication for polymer structure will be addressed in a subsequent paper.[43c]

The polymerization reaction was also done in refluxing p-dioxane (bp = 102 °C) in an attempt to increase the reaction rate and the molecular weight. An oligomer with $\bar{M}_n$ = 16 000 resulted (determined by VPO in dioxane), but the infrared spectrum of the oligomer indicated the formation of some Cp(CO)$_2$Mo$\equiv$Mo(CO)$_2$Cp units in the oligomer. (A ν(C$\equiv$O) stretch at 1850 cm^{-1} is assigned to the Cp$_2$Mo$_2$(CO)$_4$ complex.[45]) The Cp$_2$Mo$_2$(CO)$_4$ units form by thermally induced CO loss from Cp$_2$Mo$_2$(CO)$_6$[45] (eq 13). Although the formation of the triply bonded Mo$\equiv$Mo units may not be detrimental to the polymer, we wanted to avoid triple bond formation so as to simplify the interpretation of the photochemical reactions of the polymer. Therefore, the reaction in refluxing p-dioxane was not pursued further.



(13)

Polyurethane Copolymers. One of our long-term goals is to incorporate small numbers of metal–metal bonds into conventional carbon-backbone polymers. For that reason, we synthesized copolymer 9 by reacting a mixture of 2 and 1,4-butanediol with HMDI according to eq 14. In this synthesis, a mixture of 1,4-butanediol and DBTA were added dropwise to HMDI in p-dioxane to effectively add HMDI to both OH groups of 1,4-butanediol so that it would not polymerize. After all of the butanediol was added, an equimolar (to butanediol) amount of 2 was added, and the polymerization was continued. Theoret-



(14)

9
66%

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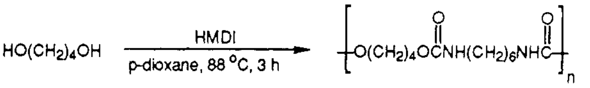
(44) Billmeyer, F. W., Jr. *Textbook of Polymer Science*, 3rd ed.; Wiley: New York, 1986; pp 38–39.

(45) Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85–94.

(46) The melting range was determined to be 174–181 °C, which agrees reasonably closely with the literature range of 175–176 °C.[34] The larger melting point range in our sample is probably due to entrapped solvents.

ically, this technique should give approximately alternating units of butanediol–HMDI and 2–HMDI.

The red copolymer, **9**, is less soluble in THF and *p*-dioxane than is homopolymer **8**. The infrared, ^{1}H NMR, and electronic absorption spectra are reported in Table I. The spectral data for a homopolymer of 1,4-butanediol and HMDI, **11**, are also reported in Table I to provide a reference in determining the composition of copolymer **9**. The $\bar{M}_n$ of 2600 indicates three repeating units, which would be approximately three butane diol/HMDI units and three **2**/HMDI units per chain. Polymer **11** was prepared in 90% yield by modification of a literature method[34] as shown in eq 15. The ^{1}H NMR and infrared spectra are reported in Table I.

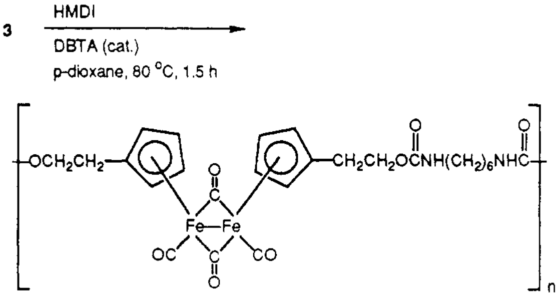


(15)

11
90%

The ^{1}H NMR spectrum of **9** has resonances that are present in both homopolymer **8** and homopolymer **11**. The ratio of the resonance integral at 4.13 ppm (CH$_2$OC(O) on organometallic fragment) to that of the resonance at 4.00 ppm (CH$_2$OC(O) on organic fragment) is 1.14:1. From this ratio, **9** appears to have 14% more **2** than 1,4-butanediol, even though equimolar amounts of each diol were used. To answer the question as to whether **9** is a copolymer or a blend, we compared the ^{1}H NMR of **9** to that of a 1:1 physical blend of homopolymer **8** and homopolymer **11**. Because **11** is virtually insoluble in acetone, the NMR spectrum of the blend showed an integral ratio of 5:1 for the 4.13 ppm (oligomer **8**) to 4.00 ppm (oligomer **8**) resonances. If **9** were a blend rather than a copolymer, the ratio of the 4.13 to 4.00 ppm resonance integrals would have been much higher. Also, microscopic examination (500×) of the copolymer indicated only one homogeneous phase.

The electronic absorption spectrum of polymer **9** is similar to that of the model complex **5** and oligomer **8** (Table I). (Note that the extinction coefficients in Table I are based on the repeating unit weight of the copolymer.) These data indicate that the Mo–Mo bond is still intact in the copolymer.

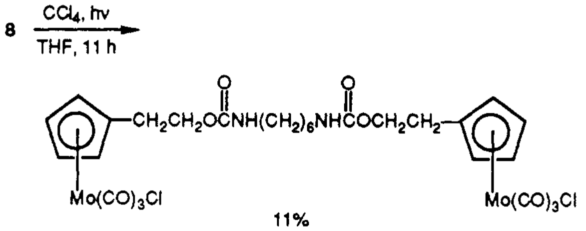


(16)

10
79%

Complex **10**, an oligomer with Fe–Fe bonds in the backbone, was synthesized by reacting diol **3** with HMDI (eq 16). The ^{1}H NMR of the oligomer was nearly identical with that of the model complex **6**, with the exception of the expected absence of the CH$_3$ proton resonance. The electronic absorption spectrum and the infrared spectrum in the ν(C$\equiv$O) region of oligomer **11** are also similar to model complex **6**. Also note that the amide I and amide III bands are broader and slightly lower in energy for the oligomer than in the model complex (Table II). The same differences were seen between model complex **2** and oligomer **8** in the molybdenum system. The most significant difference in the infrared spectrum is the strong absorbance at 1988 cm^{-1} for the oligomer compared to the weak absorbance at 1992 cm^{-1} in the model complex. (Dimer **3** exhibits only a very weak shoulder in this region). A similar band occurred in the oligomers containing Mo–Mo bonds. The band is attributable to molecules with a gauche conformation of the Cp rings, and it has implications for the polymer structure. A subsequent paper is in preparation to address this topic.[43c]

Photochemistry of the Oligomers. As stated in the Introduction, our motivation for synthesizing the oligomers above was to develop polymers that can be photochemically degraded. All three oligomers reported here are photochemically reactive, undergoing photochemical reactions in solution similar to the reactions of the Cp$_2$Mo$_2$(CO)$_6$ or Cp$_2$Fe$_2$(CO)$_4$ dimers, e.g., eq 17.[22] The oligomers are also reactive in the solid state. The photochemistry of these complexes will be discussed in detail in a forthcoming paper.[47]



(17)

11%

Acknowledgment is made to Amoco Chemical Co. for the support of this research. D.R.T. acknowledges the Alfred P. Sloan Foundation for a Fellowship.

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(47) Tenhaeff, S. C.; Tyler, D. R. *Organometallics*, in press.