Photochemically Reactive Polymers. Photochemical Reactions of Polyurethanes Containing $Cp_2Mo_2(CO)_6$ or $Cp_2Fe_2(CO)_4$ Molecules along the Polymer Backbone

Steve C. Tenhaeff and David R. Tyler*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

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The photochemistry of the $[-OCH_2C(O)C_5H_4(CO)_3Mo{-}Mo(CO)_3C_5H_4C(O)CH_2OC(O)NH(CH_2)_6NHC(O)-]_n$ (1), $[-OCH_2CH_2C_5H_4(CO)_3Mo{-}Mo(CO)_3C_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)-]_n$ (2), $[-(O(CH_2)_4OC(O)NH(CH_2)_6NHC(O))_m{-}OCH_2CH_2C_5H_4(CO)_3Mo{-}Mo(CO)_3C_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)-]_n$ (3), and $[-OCH_2CH_2C_5H_4(CO)_2Fe{-}Fe(CO)_2C_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)-]_n$ (4) oligomers was investigated. Because of the metal–metal bonds along the oligomer backbone, these polyurethanes are photochemically reactive, undergoing reactions similar to the $Cp_2Mo_2(CO)_6$ and $Cp_2Fe_2(CO)_4$ dimers. Irradiation leads to homolysis of the metal–metal bonds, as evidenced by formation of $Cl(CO)_3MoC_5H_4\text{-}R\text{-}C_5H_4Mo(CO)_3Cl$ or $Cl(CO)_2FeC_5H_4\text{-}R\text{-}C_5H_4Fe(CO)_2Cl$ ($R = CH_2CH_2OC(O)NH(CH_2)_6NHC(O)OCH_2CH_2$ or $C(O)CH_2OC(O)NH(CH_2)_6NHC(O)OCH_2C(O)$) when the oligomers are irradiated in the presence of CCl_4. In the presence of triethyl phosphite, disproportionation of the Mo–Mo and Fe–Fe bonded units occurred to give a fragmentation product containing $(C_5H_4R)Mo(CO)_3^-$ and $(C_5H_4R)Mo(CO)_2(P(OEt)_3)_2^+$ or $(C_5H_4R)Fe(CO)_2^-$ and $(C_5H_4R)Fe(CO)(P(OEt)_3)_2^+$ groups, respectively. Photochemical decomposition of the polyurethanes also occurred over several weeks to months in the solid state. Both light and oxygen are necessary for this decomposition in the solid state. It is proposed that cleavage of the metal–metal bonds leads to oligomer fragmentation and the formation of metal oxide species in these solid state reactions. Oligomer 2, containing the singly bonded $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ unit, was converted (photochemically or thermally) to a polymer containing triply bonded $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ groups.

We recently began a research program with the goal of synthesizing a new class of photochemically reactive polymers.[1-9] Our plan for making the photochemically reactive polymers is to incorporate metal–metal bonds into the polymer backbone. It is well-known that metal–metal bonds can be cleaved photochemically with visible light (eq 1),[10,11] and thus, incorporation of metal–metal bonds

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

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

into a polymer should give a polymer that is similarly reactive:

$$\sim\!\sim M{-}M\sim\!\sim\!\sim\!\sim M{-}M\sim\!\sim \xrightarrow{h\nu} \sim\!\sim M{\cdot}\ {\cdot}M\sim\!\sim\!\sim\!\sim M{\cdot}\ {\cdot}M\sim\!\sim \qquad (2)$$

In a recent paper,[12] we described the synthesis of several polyurethanes containing metal–metal bonded units along the backbone. (Oligomers 1–4; for ease of reference, refer to Tables I and II for the molecular formulas of the oligomers; $\bar{M}_n$ values for the various oligomers were ~5 000–17 000.[12]) To aid in our spectroscopic characterization and photochemical studies of the oligomers, we also synthesized model complexes for the oligomers[12] (complexes 5 and 6; again, refer to the tables for the molecular formulas of these species).

In this paper we describe the solution- and solid-state photochemistry of the oligomers and the model complexes. The work in solution focuses on the reactions of the oligomers with CCl_4 (a radical trap) and on the disproportionation reactions[13] of the metal–metal bonded units in the oligomers. Both types of reactions are common for regular metal–metal bonded complexes.[10,11,13] The solid-state studies focus on the photochemical reactions of the oligomers with molecular oxygen. A preliminary report on the photochemical reactions in solution has appeared.[14]

Experimental Section

Materials. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere with use of standard Schlenk or vacuum line techniques or a Vacuum Atmospheres Co. glovebox.

Tetrahydrofuran (THF) was distilled under nitrogen from potassium–benzophenone ketyl. Methylene chloride was distilled under N_2 from calcium hydride. *p*-Dioxane was distilled from sodium benzophenone under nitrogen. Carbon tetrachloride was obtained from Fisher, and distilled from P_2O_5 under nitrogen. Triethyl phosphite was purchased from Aldrich, and deoxygenated by purging with N_2 immediately before use.

Synthesis of the Oligomers and Starting Materials. Oligomers 1–4 and model complexes 5 and 6 were synthesized as previously described.[12]

Equipment. Infrared spectra were obtained with a Nicolet 5DXB FT-IR. Electronic absorption spectra were obtained with

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a Beckman DU-7 or Perkin-Elmer Lambda 6 recording spectrophotometer. ^1H NMR were obtained on a GE QE-300 spectrometer at 300.15 MHz. Photochemical reactions were carried out with an Oriel 200-W high-pressure mercury arc lamp and a Corning CS 3-68 ($\lambda > 525$ nm) or CS 3-66 ($\lambda > 560$ nm) filter. A 504-nm interference filter (Edmund Scientific Co.) was used in all of the quantum yield determinations, and a Beckman DU spectrophotometer was used to monitor the reactions. Fast-atom-bombardment spectra were obtained with a VG ZAB-2FHF mass spectrometer operating at an accelerating potential of 8 kV. Xenon was used with the atom gun operating with 1 mA emission current and 8 keV energy.

Photochemical Reactions with CCl_4. In a typical reaction, 0.01–0.03 g ((1.6–4) $\times 10^{-5}$ mol) of complex or oligomer was added to a 5-mL round-bottom flask fitted with a magnetic stir bar and rubber septum. THF (1–2 mL) was added in the dark to make a solution of approximately 15–20 mM concentration. A 10 mol excess of CCl_4 was then added to the solution. An aliquot of this solution was transferred to a 0.1-mm pathlength CaF_2 sealed IR cell, and an initial spectrum was obtained. The IR cell was then irradiated for 1–5-min intervals ($\lambda > 525$ nm). The spectrum was obtained after each photolysis interval.

Synthesis of Complex 8, $Cl(CO)_3MoC_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)CH_2CH_2OC_5H_4Mo(CO)_3Cl$. Oligomer 2 (0.154 g; 0.206 mmol) was added to a 30-mL Schlenk tube equipped with a magnetic stir bar. THF (4 mL) was added, and the mixture was stirred to dissolve the oligomer. Dried, deoxygenated CCl_4 (0.20 mL; 2.1 mmol) was syringed into the oligomer solution. The solution was photolyzed for 11 h, with stirring, with a 200-W high-pressure mercury arc lamp fitted with a Corning CS 3-68 filter ($\lambda > 525$ nm). The solvent was then removed under vacuum and the brown oily product purified by running it through a 200 × 10 mm column of 60–200 mesh silica gel with a 90% CH_2Cl_2/10% THF (v/v) solvent system. The orange fraction eluting with an R_f of 0.4 was isolated. Recrystallization from CH_2Cl_2/hexane, then ethyl ether, and then THF/hexane yielded 0.0182 g (11%) of product 8 as an orange oil. FAB mass spectrum (matrix = 2,2′-thiodiethanol): *m/e* 819 (molecular ion + H), 736 (molecular ion − 3CO). ^1H NMR (acetone-d_6) δ ppm 6.32 (br, 2 H, NH), 5.95 (br, 4 H, C_5H_4), 5.52 (br, 4 H, C_5H_4), 4.21 (t, J = 6.3 Hz, 4 H, $CH_2OC(O)$), 3.11 (quartet, J = 6.6 Hz, 4 H, CH_2N), 2.57 (t, J = 6.3 Hz, 4 H, $CpCH_2$), 1.50 (m, J = 6.0 Hz, 4 H), 1.33 (br, 4 H). FTIR (neat) cm^{-1}: 3339 (w), 3093 (vw), 2938 (w), 2861 (vw), 2052 (s), 1961 (vs), 1715 (ms), 1525 (w), 1251 (m).

Photochemical Reactions of Iron Complexes with $P(OEt)_3$. In order to obtain reproducible results, the following sample preparation must be carried out in a darkroom.[15] In a typical experiment, 10–30 mg (0.027–0.057 mmol) of complex or oligomer was weighed into a 10-mL round-bottom flask fitted with a magnetic stir bar and rubber septum. The flask was then purged with nitrogen gas. Methylene chloride (about 2 mL) was added and the mixture was stirred to dissolve the sample. A 0.2-mL aliquot was transferred to a 0.1-mm pathlength CaF_2 sealed IR cell, and an initial spectrum was obtained. Deoxygenated $P(OEt)_3$ (0.04–0.07 mL; 0.23–0.41 mmol) was then added and an aliquot transferred to an IR cell. The cell was irradiated for 2–10-min intervals ($\lambda > 560$ nm). The IR spectrum of the reaction solution was monitored after each irradiation period.

Photochemical Reactions of Molybdenum Complexes with $P(OEt)_3$. The following procedure was again carried out in the darkroom.[15] In a typical reaction, 10–20 mg (0.01–0.03 mmol) of complex or oligomer was weighed into a 5-mL round-bottom flask fitted with a magnetic stir bar and rubber septum. The flask was purged with nitrogen, and about 2 mL of THF was added in the dark to dissolve the sample. A 0.2-mL aliquot of this mixture was transferred to a 0.1-mm pathlength CaF_2 sealed IR cell, and an initial spectrum was obtained. Deoxygenated $P(OEt)_3$ (50 molar excess) was then added to the flask. An aliquot of this mixture was added to an IR cell. The cell was irradiated for 1–10-min intervals ($\lambda > 525$ nm). An infrared spectrum was obtained after each irradiation period. (The initial spectrum before irradiation was obtained in the absence of $P(OEt)_3$ because the quantum yield for the disproportionation reaction is so high that even traces of light will cause considerable disappearance of the Mo complex or oligomer. This aspect of the disproportionation reaction has been discussed previously.[15])

Quantum Yields. In a typical experiment, 1.6–10.0 mg (2.8 $\times 10^{-6}$ to 2.1 $\times 10^{-5}$ mol) of sample was weighed into a Pyrex cuvette containing a Teflon-coated stir bar. The cuvette and sample were evacuated and filled with N_2 three times, and then transferred to a darkroom. Deoxygenated 2 M CCl_4 in THF (4 mL) was syringed into the tube and the solution freeze–pump–thaw degassed three times on a high vacuum line ($<10^{-3}$ mmHg). The solution was irradiated with stirring at 504 nm for 1–15-min intervals, and the decrease in the absorbance at 508 nm ($d\pi \rightarrow \sigma^*$ transition; Mo complexes) or 514 nm (Fe complexes) measured on a Beckman DU spectrophotometer. Lamp intensities were measured by using Aberchrome 540 actinometry.[16]

Aging Studies in the Solid State. Films of oligomer 2 and copolymer 3 were prepared by dissolving 60 mg of the sample in 2–3 mL of dried, deoxygenated THF. Aliquots of the solution were pipetted onto four glass microscope slides inside the glove box. The THF was allowed to evaporate, and the films dried further by placing the slides in the vacuum chamber of the glove box for 13 h. One slide of each oligomer was placed on the south-facing window of the laboratory, one slide of each was wrapped in aluminum foil and stored in the dark in a desk drawer, one slide of each was taped on the inside of the glovebox window, and one slide of each was stored in the glove box in the dark, wrapped in aluminum foil. The electronic absorption spectrum of each slide was monitored periodically in the region from 650 to 250 nm. Films of oligomer 4 were prepared in a similar fashion by using a solution of 4 prepared by dissolving 140 mg in 5 mL of THF.

Generation of $[OCH_2CH_2C_5H_4(CO)_2Mo{\equiv}Mo(CO)_2C_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)]_n$. Thermal Method. Oligomer 2 (0.1203 g; 0.161 mmol) was added to a flame-dried 50-mL three-neck flask equipped with a reflux condenser, nitrogen inlet, and magnetic stir bar. *p*-Dioxane (20 mL) was added and the solution was refluxed for 8 h. The solution was monitored periodically by infrared spectroscopy, which showed the formation of the $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ unit in the product (Table III). The oligomer containing the $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ unit could be completely regenerated (as indicated by the intensities in the infrared spectrum) by bubbling CO through the reaction solution for about 20 min. The oligomer containing the $Mo{\equiv}Mo$ unit could be formed again by refluxing the reaction solution under nitrogen. The conversion from the Mo–Mo containing oligomer to the $Mo{\equiv}Mo$ containing oligomer and back again was repeated several times without degradation of the oligomer.

Generation of $[OCH_2CH_2C_5H_4(CO)_2Mo{\equiv}Mo(CO)_2C_5H_4CH_2CH_2OC(O)NH(CH_2)_6NHC(O)]_n$. Photochemical Method.[17] Oligomer 2 (0.0594 g; 7.96 $\times 10^{-5}$ mol) and *p*-dioxane (5 mL) were added to a 30-mL Schlenk tube, and the tube was deoxygenated with an Ar purge. The tube was immersed in a large beaker of water (for crude temperature control) and then irradiated ($\lambda > 330$ nm) for 25 h. An Ar (or N_2) purge was maintained throughout the irradiation. Periodic infrared spectroscopic monitoring of the reaction solution showed the formation of the triply bonded $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ unit. The oligomer containing the singly bonded $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ unit could be regenerated by bubbling CO through the reaction solution.

Results and Discussion

Reactions with CCl_4. Oligomers 1–4 reacted photochemically ($\lambda > 525$ nm) with CCl_4 in THF solution according to eqs 3–6, respectively. (Refer to the tables for the formulas of the oligomers and products.)

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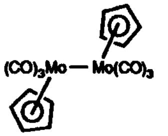
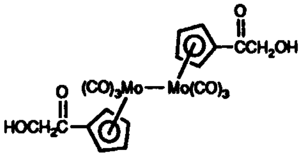
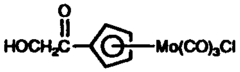
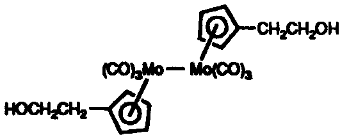
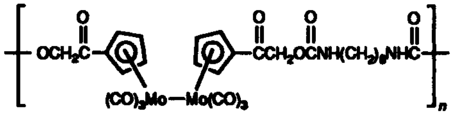
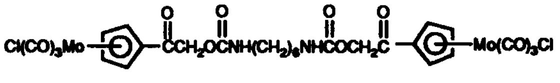
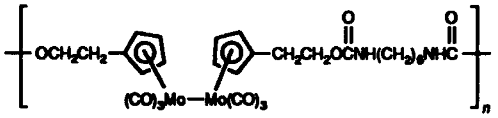
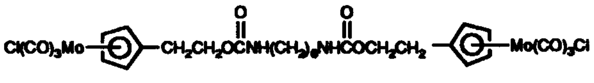
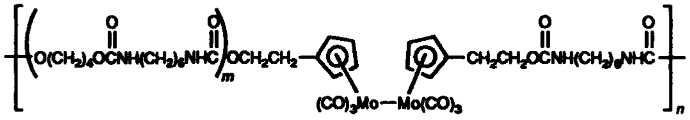
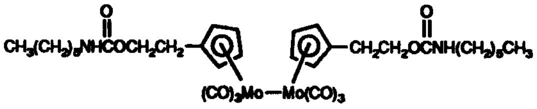
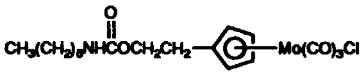
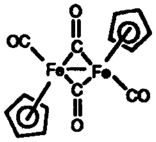
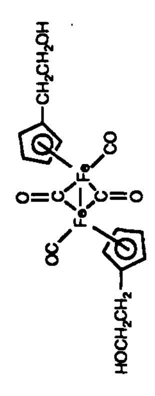
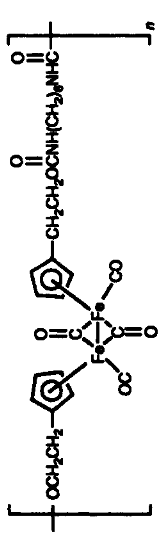
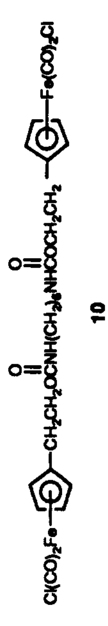
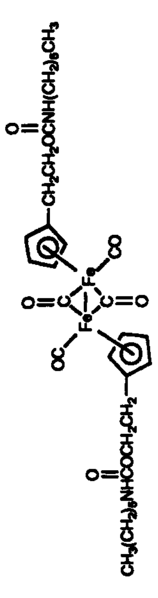
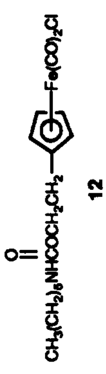
Table I. Quantum Yields and IR Data for the Products Formed in the Photochemical Reactions of the Dimers, Model Complexes, and Polymers with CCl_4 in THF

		IR (THF) of product		
compound photolyzed	photolysis products	ν(C≡O), cm^{-1}	other bands, cm^{-1}	$\Phi_{504}{}^{a,b}$
	$CpMo(CO)_3Cl$	2051 (s) 1972 (vs)		0.47
		2058 (s) 1981 (vs)	ν(C=O, keto), 1703 (br, w)	
		2048 (s) 1969 (vs)		0.66
 1	 7	2059 (s) 1980 (vs)	ν(C=O, urethane), 1736 (m) ν(C=O, keto), 1711 (w) δ(N—H, amide II), 1540 (w)	
 2	 8	2049 (s) 1970 (vs)	ν(C=O, urethane), 1727 (m) δ(N—H, amide II), 1537 (w)	0.44
 3	 9	2049 (s) 1970 (vs)	ν(C=O, urethane), 1726 (s), 1684 (w) δ(N—H, amide II), 1539 (m)	
 5	 11	2049 (s) 1970 (vs)	ν(C=O, urethane), 1728 (m) δ(N—H, amide II), 1539 (w)	0.59
	$CpFe(CO)_2Cl$	2047 (s) 1999 (s)		0.21

		2043 (s) 1994 (s)		0.22
 4	 10	2044 (s) 1996 (s)	ν(C═O, urethane), 1726 (m) δ(N—H, amide II), 1539 (w)	0.14
 6	 12	2044 (s) 1998 (s)	ν(C═O, urethane), 1727 (s) δ(N—H, amide II), 1538 (w)	0.22

[a] Quantum yield (±7%) is that for disappearance of starting material. The reported values are the average of several measurements. [b] CCl_4 (2 M) in THF.

$$1 \xrightarrow[CCl_4]{h\nu} 7 \quad (3)$$

$$2 \xrightarrow[CCl_4]{h\nu} 8 \quad (4)$$

$$3 \xrightarrow[CCl_4]{h\nu} 9 \quad (5)$$

$$4 \xrightarrow[CCl_4]{h\nu} 10 \quad (6)$$

The reaction of 2 with CCl_4 (eq 4) was carried out in both an IR cell (Table I) and on a preparative scale. The product, 8, was isolated as an orange oil and purified by column chromatography. Although attempts to crystallize the oil from a variety of solvent combinations were unsuccessful, the product could be characterized by ^1H NMR, infrared, and FAB mass spectroscopy. The IR bands at 3339 (N—H stretch), 2938 and 2861 (CH_2, sp^3 stretch), 2052 and 1961 (C≡O stretch), 1715 (C═O stretch, amide I), 1525 (N—H bend, amide II), and 1251 cm^{-1} (C—N stretch, amide III) are consistent with the proposed structure for 8.[18] (Note that the $CpMo(CO)_3Cl$ complex has ν(C≡O) bands at 2051 and 1971 cm^{-1} (Table I).[19]) The ^1H NMR spectrum (see the Experimental Section) is similar to that of oligomer 2 with but two notable exceptions: the resonances for 8 are much narrower, and the complex pattern of four resonances for the C_5H_4 protons in 2 appears as two slightly broadened resonances at 5.51 and 5.95 ppm for 8. The simpler resonance pattern for the C_5H_4 protons results from the loss of conformational isomers, due to cleavage of the Mo–Mo bond in converting 2 to 8. An isotopic cluster centered around 819 was detected in the FAB mass spectrum (matrix = 2,2′-thiodiethanol). This cluster corresponds to a pseudo molecular ion of 8 (or to a pseudo molecular ion plus a hydrogen from the matrix). Isotopic clusters are typical for molybdenum compounds since there are seven isotopes of molybdenum. Another isotopic cluster about 736 corresponds to a pseudo molecular ion minus three CO ligands. Disappearance of the Mo–Mo bond is confirmed by the absence of the $\sigma \rightarrow \sigma^*$ (metal–metal bonding → metal–metal antibonding) transition in the electronic spectrum of product 8.[10,11,20]

Irradiation ($\lambda > 525$ nm) of model complex 5 in a mixture of THF and CCl_4 in an IR cell also resulted in homolysis of the Mo–Mo bond. The infrared spectrum of the product, 11, in the ν(C≡O) region shows bands at 2049 and 1970 cm^{-1}. As mentioned above, these bands are characteristic of the $CpMo(CO)_3Cl$ unit.[19] Irradiation of 5 is thus proposed to proceed as

$$5 \xrightarrow[CCl_4]{h\nu} 11 \quad (7)$$

The reactions of oligomer 1 (eq 3) and copolymer 3 (eq 5) with CCl_4 were carried out in a sealed IR cell, and the products (7 and 9; Table I) identified solely by their IR spectra. The disappearance of the $Cp_2Mo_2(CO)_6$ unit in the oligomer was indicated by the disappearance of bands at 2019 and 1923 cm^{-1} for 1 and 2009 and 1911 cm^{-1} for 3, while the formation of the $CpMo(CO)_3Cl$ unit was indicated by the appearance of bands at 2059 and 1980 (br) cm^{-1} (oligomer 1) and 2049 and 1970 cm^{-1} (oligomer 3) (Table I).[19] The band between 1970 and 1980 cm^{-1} in the product is broad and corresponds to the 1986 and 1962 cm^{-1} bands reported for $CpMo(CO)_3Cl$.[19]

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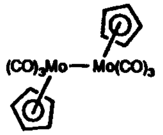
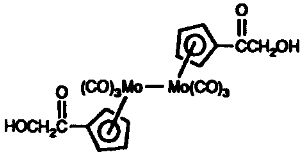
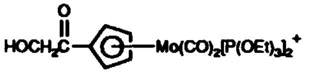
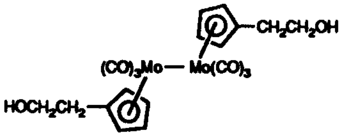
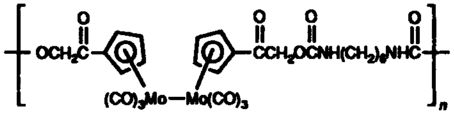
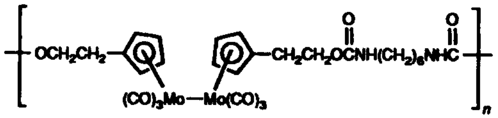
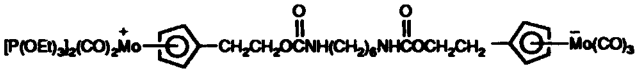
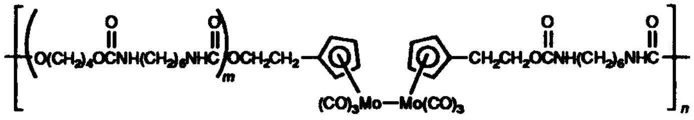
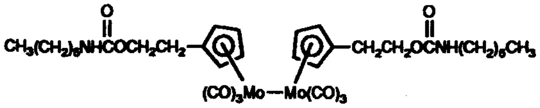
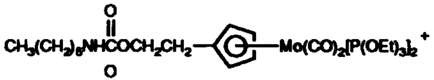
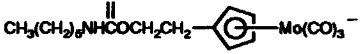
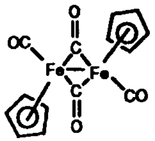
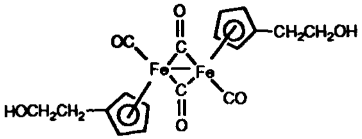
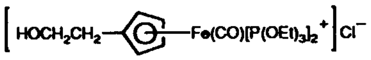
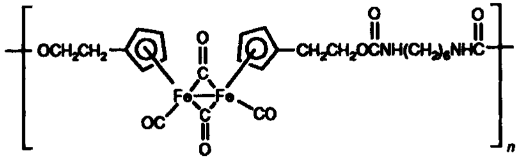
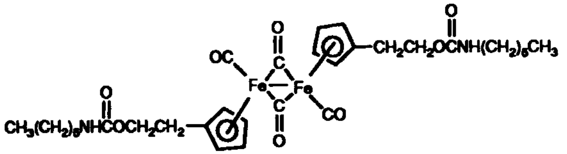
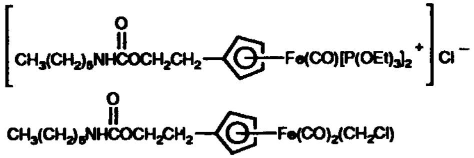
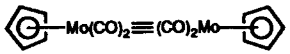
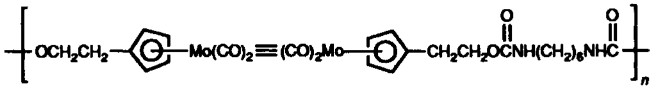
Table II. IR Data for the Products Formed in the Photochemical Reactions of the Dimers, Model Complexes, and Polymers with $P(OEt)_3$

compound photolyzed	photolysis products[a]	IR of product[b]	
		ν(C≡O), cm^{-1}	other bands, cm^{-1}
	$CpMo(CO)_2[P(OEt)_3]_2^+$ $CpMo(CO)_3^-$	1994 (m) 1919 (s) 1897 (s) 1784 (s)	
	 	1999 (w) 1926 (s) 1911 (vs) 1806 (vs)	ν(C═O, keto), 1706 (br, w) ν(C═O, keto) 1644 (br, w)
	 	1991 (w) 1916 (s) 1895 (m-s) 1782 (s)	
 1	 13	1999 (w) 1926 (s) 1910 (vs) 1805 (vs)	ν(C═O, urethane), 1734 (m) ν(C═O, keto), 1718 (vw) ν(C═O, keto) 1669 (br, vw) δ(N—H, amide II), 1543 (w)
 2	 14	1991 (w) 1917 (s) 1896 (s) 1785 (vs)	ν(C═O, urethane), 1724 (m) δ(N—H, amide II), 1537 (w)
 3	 15	1991 (w) 1917 (s) 1896 (s) 1784 (vs)	ν(C═O, urethane), 1724 (m), 1684 (w) δ(N—H, amide II), 1538 (w m)
 5	  16	1991 (w) 1917 (s) 1895 (s) 1783 (vs)	ν(C═O, urethane), 1722 (m) δ(N—H, amide II), 1533 (w)

	$[CpFe(CO)[P(OEt)_3]_2{}^+]Cl^-$ $CpFe(CO_2(CH_2Cl)$	1995 (s) 2022 (vs) 1966 (vs)	
	 	1988 (s) 2019 (w) 1941 (m)	
 **4**	 **17**	2017 (vs) 1989 (s) 1964 (vs)	ν(C=O, urethane), 1721 (m) δ(N—H, amide II), 1522 (w)
 **6**	 **18**	1989 (s) 2020 (vs) 1964 (vs)	ν(C=O, urethane), 1721 (s) δ(N—H, amide II), 1518 (m)

[a] Photolysis at λ > 525 nm for molybdenum compounds and at λ > 560 nm for iron compounds. [b] THF solvent for molybdenum compounds and CH_2Cl_2 for iron compounds.

Table III. IR Data for $Mo{\equiv}Mo$ Species

compound	method of formation	IR (p-dioxane) ν(C≡O), cm^{-1}	IR (p-dioxane) other bands, cm^{-1}
	reflux $Cp_2Mo_2(CO)_6$ in *m*-xylene, Ar purge or irradiate $Cp_2Mo_2(CO)_6$ with broad-band UV, Ar purge	1889[a] 1859	
 **19**	reflux polymer 2 in *p*-dioxane (101 °C) under N_2	1885 (s) 1851 (s)	ν(C=O, urethane), 1725 (s) δ(N—H, amide II), 1533 (w m)
	irradiate polymer 2 (λ > 330 nm), Ar purge	1898 (s) 1851 (m)	ν(C=O, urethane), 1724 (s) δ(N—H, amide II), 1533 (w m)

[a] Isooctane solution.

Reaction of oligomer **4** and model complex **6** with CCl_4 (eqs 6 and 8) also resulted in homolysis of the metal–metal bond and formation of the chloride complexes **10** and **12**.[21]

$$6 \xrightarrow[CCl_4]{h\nu} 12 \qquad (8)$$

Spectroscopic data for the products of these reactions are found in Table I.

Reactions with $P(OEt)_3$. Irradiation ($\lambda > 525$ nm) of oligomer **1** and $P(OEt)_3$ in THF resulted in disproportionation of the Mo–Mo unit; products formed which contained the $(C_5H_4R)Mo(CO)_2[P(OEt)_3]_2^+$ and $(C_5H_4R)Mo(CO)_3^-$ moieties (eq 9).[13] (Statistically, 50%

$$1 \xrightarrow[P(OEt)_3]{h\nu} 13 \qquad (9)$$

of product **13** has one end group equal to $(C_5H_4R)Mo(CO)_2[P(OEt)_3]_2^+$ and the other equal to $(C_5H_4R)Mo(CO)_3^-$; 25% of product **13** has two $(C_5H_4R)Mo(CO)_2[P(OEt)_3]_2^+$ end groups; and 25% has two $(C_5H_4R)Mo(CO)_3^-$ end groups.) The reaction was monitored by infrared spectroscopy, which showed the appearance of bands at 1999 and 1926 cm^{-1} (attributed to the $(C_5H_4R)Mo^+(CO)_2[P(OEt)_3]_2$ moiety) and 1910 and 1805 cm^{-1} (attributed to the $(C_5H_4R)Mo(CO)_3^-$ moiety), and the disappearance of the 2019 and 1968 cm^{-1} bands of the $Cp_2Mo_2(CO)_6$ unit (Table II).[13] The infrared spectrum of the product is essentially identical with that of the disproportionation products obtained upon irradiation of the $(C_5H_4C(O)CH_2OH)_2Mo_2(CO)_6$ complex under identical conditions (1999, 1926, 1911, and 1806 cm^{-1}, see Table II). Also note the similarity of these spectra to the spectrum obtained by disproportionation of the $Cp_2Mo_2(CO)_6$ complex[13] (Table II). The only significant difference in all of the spectra is that the band at 1784 cm^{-1} for $CpMo(CO)_3^-$ occurs at 1805 cm^{-1} in the $(CO)_3Mo(C_5H_4C(O)CH_2O-)$ units generated by irradiation of **1**. The shift to higher energy in the anions containing the substituted Cp ligands is expected because an electron-withdrawing carbonyl group attached to the Cp ring reduces electron density on the molybdenum, resulting in less π-backbonding with the CO ligands.

Oligomers **2** and **3** also disproportionated photochemically ($\lambda > 525$ nm) with $P(OEt)_3$ in THF according to eqs 10 and 11. The products were identified by infrared

$$2 \xrightarrow[P(OEt)_3]{h\nu} 14 \qquad (10)$$

$$3 \xrightarrow[P(OEt)_3]{h\nu} 15 \qquad (11)$$

spectroscopy; bands at 1991 and 1917 cm^{-1} are assigned to $(C_5H_4R)Mo(CO)_2[P(OEt)_3]_2^+$ and the bands at 1896 and 1784 cm^{-1} are assigned to $(C_5H_4R)Mo(CO)_3^-$.[13] This spectrum agrees closely with spectra obtained by irradiating $Cp_2Mo_2(CO)_6$, $(C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$, or model complex **5** and $P(OEt)_3$ under similar conditions (Table II). As was the case in reaction 9, a statistical distribution of end groups is expected in products **14** and **15**: 50% of the product will have one $(C_5H_4R)Mo(CO)_2[P(OEt)_3]_2^+$ end group and one $(C_5H_4R)Mo(CO)_3^-$ end group; 25% will have two $(C_5H_4R)Mo(CO)_2[P(OEt)_3]_2^+$ end groups; and 25% will have two $(C_5H_4R)Mo(CO)_3^-$ end groups.

Oligomer **4** reacted photochemically ($\lambda > 560$ nm) with $P(OEt)_3$ in CH_2Cl_2 according to eq 12.[21] (The statistical

$$4 \xrightarrow[P(OEt)_3]{h\nu} 17 \qquad (12)$$

distribution of the $(C_5H_4R)Fe(CO)[P(OEt)_3]_2^+$ and $(C_5H_4R)Fe(CO)_2CH_2Cl$ groups is again expected.) The products were identified by infrared spectroscopy: A band at 1989 cm^{-1} is assigned to the $(C_5H_4R)Fe(CO)[P(OEt)_3]_2^+$ group, and the bands at 2017 and 1964 cm^{-1} are assigned to the $(C_5H_4R)Fe(CO)_2CH_2Cl$ group.[21] This spectrum agrees closely with the spectra obtained by irradiating $Cp_2Fe_2(CO)_4$ (Cp = η^5-C_5H_5) (eq 13) or model complex **6** (eq 14) and $P(OEt)_3$ under similar conditions (Table II). Note that in previous work we showed that the $CpFe(CO)_2CH_2Cl$ species forms by the reaction of $CpFe(CO)_2^-$ with CH_2Cl_2.[21,22]

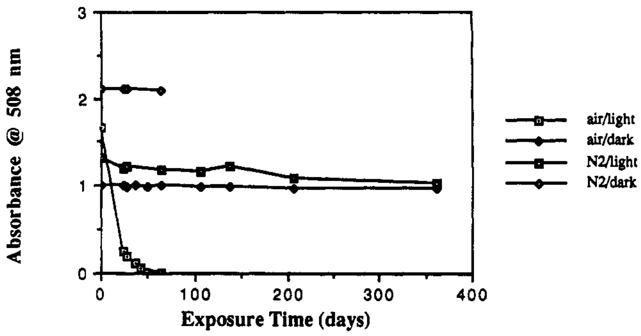


Figure 1. A plot of the absorbance at 508 nm vs time for four thin films of oligomer **2**. As indicated in the figure, one sample was exposed to air and light, one sample was kept in the dark in air, another sample was exposed to light but kept under nitrogen, and the last sample was kept in the dark under nitrogen. Complete details are found in the Experimental Section.

$$Cp_2Fe_2(CO)_4 + CH_2Cl_2 \xrightarrow[P(OEt)_3]{h\nu} CpFe(CO)(P(OEt)_3)_2^+ + CpFe(CO)_2CH_2Cl + Cl^- \qquad (13)$$

$$6 + CH_2Cl_2 \xrightarrow[P(OEt)_3]{h\nu} 18 \qquad (14)$$

Quantum Yields. The quantum yield data for photolysis of $Cp_2Mo_2(CO)_6$, $Cp_2Fe_2(CO)_4$, $(C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$, $(C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$, model complexes **5** and **6**, and oligomers **2** and **4** in 2 M CCl_4/THF are listed in Table I. Note that oligomer **2** has a significantly lower quantum yield for metal–metal bond homolysis than model complex **5** and $(C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$. Also, oligomer **4** has a much lower quantum yield for homolysis than $Cp_2Fe_2(CO)_4$, $(C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$, or model complex **6**. The lower quantum yields for oligomers **2** and **4** is expected because polymers frequently show lower fragmentation quantum yields than their monomeric counterparts due to less efficient cage escape of the bulkier polymer fragments.[1] One puzzling point, however, is the lower quantum yield for $Cp_2Mo_2(CO)_6$ photolysis (0.47) compared to model complex **5** and $(C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ (0.6). We have no explanation for why the quantum yield of the regular dimer is lower; further work is continuing on this point in our laboratory.

Solid-State Photochemical Studies. Films of homopolymers **2** and **4** and copolymer **3** were irradiated in the presence of oxygen and in the absence of oxygen. For each film and its dark reaction control, the absorbance of the

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

[22] Irradiation of $(C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$ and $P(OEt)_3$ under similar conditions gives a slightly different spectrum with a band at 1988 cm^{-1} assigned to $(C_5H_4R)Fe(CO)[P(OEt)_3]_2^+$ and bands at 2019 and 1941 cm^{-1} assigned to the $(C_5H_4R)Fe(CO)_2CH_2Cl$ end of the product (Table II). We can offer no explanation for the fact that the intensity of the 2019 cm^{-1} band is much smaller than that for the photolysis product of the $Cp_2Fe_2(CO)_4$ complex and that the band normally found at 1966 cm^{-1} is much lower in energy (1941 cm^{-1}) for the $(C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$ photolysis product.

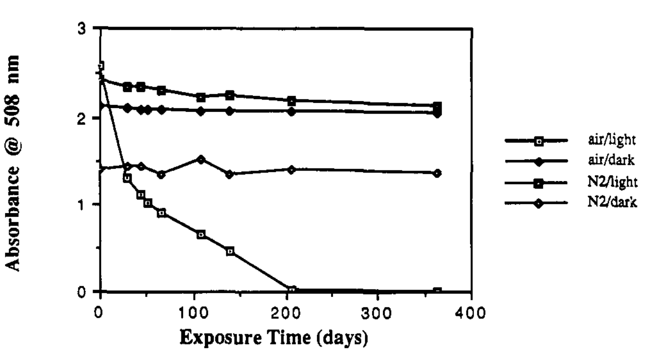

Figure 2. A plot of the absorbance at 508 nm vs time for four thin films of oligomer **3**. Four different sets of conditions were used, as described in the caption to Figure 1.

$d\pi \rightarrow \sigma^*$ transition[10,20] was monitored periodically over a period of several months. Figures 1 and 2 are plots of absorbance at 508 nm vs time for oligomers **2** and **3** under the various conditions. As shown in Figure 1, the film of oligomer **2**, exposed to sunlight in air, completely decomposed in 2 months. (The $\sigma \rightarrow \sigma^*$ band at 390 nm[10,20] was also absent, confirming that the Mo–Mo bond was not intact.) The color of the film on this slide changed from red to green. The copolymer **3** slide, exposed to exactly the same conditions, exhibited a 66% decrease in the absorbance at 508 nm after 2 months and had lost 99% of its original absorbance after 7 months and 100% after 1 year. Its color also changed from red to green. The copolymer **3** film was thicker than that of homopolymer **2**, and this fact probably accounts for the slower decomposition. The slides stored in the dark in air and in the glovebox under nitrogen showed only a slight loss of absorbance at 508 nm over a 1-year period. A duplicate experiment on oligomer **2** with four new slides gave similar results. From this data, we conclude that the decomposition of the oligomers requires both light and air (oxygen). (The small amount of reaction for those slides stored in the glovebox in the light is probably due to reactions with solvent vapors which are periodically introduced into the glovebox by various operations.) The green decomposition product has not yet been fully analyzed; however, infrared spectra (KBr pellet) showed the material contained no CO ligands, as indicated by the absence of any stretches in the region 1600–2200 cm^{-1}. Infrared spectra of **2** and **3** stored in the dark or in a nitrogen atmosphere for 1 year are virtually identical with the spectra of freshly prepared samples. We note that oxo complexes form in the reactions of $Cp_2Mo_2(CO)_6$ with O_2.[23]

Slides of the iron oligomer, **4**, exposed under similar conditions show the same behavior, i.e. the oligomer decomposed only when exposed to air and sunlight. These decomposition reactions were followed by infrared spectroscopy because the decomposition product has a strong bond in the UV which tails into the 520-nm region and obscures the oligomer band at 512 nm.

The data above suggest that oxygen is necessary for the solid-state photochemical reaction to occur. We propose that oxygen traps the metal radicals produced in the photolysis of the metal–metal bonds, thereby preventing radical recombination. If oxygen diffusion is rate-limiting then the relative rates of oligomer photochemical decomposition in the solid-state would reflect the oxygen diffusion rate. Work is continuing in our laboratory to measure the rate of oxygen diffusion into the polymer films and to determine if there is a correlation between this rate and the quantum yields.

Conversion of the $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ Unit to $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$. *Another characteristic photochemical reaction of the* $Cp_2Mo_2(CO)_6$ complex is stepwise loss of CO to form the triply bonded $Cp_2Mo_2(CO)_4$ complex.[17]

$$Cp_2Mo_2(CO)_6 \xrightarrow{h\nu} Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp + 2CO \quad (15)$$

Similar photochemical and thermal reactions were found to convert oligomer **2** to a new polymer containing triply bonded $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ units. Both the thermal and photochemical conversions were monitored by infrared spectroscopy which showed the disappearance of bands at 2010, 1952, and 1910 cm^{-1} of the $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ unit and the appearance of new bands at 1885 and 1851 cm^{-1}. These latter bands are attributed to the $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ unit by comparison to the known complex (Table III). (The disappearance of the $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ bands was complete in the thermal reaction. The disappearance was not complete in the photochemical reaction after 25 h. In the photochemical reaction, the product band at 1885 cm^{-1} appeared as a shoulder at 1898 cm^{-1} on the $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ band at 1910 cm^{-1}.) The $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ groups can be completely converted back to the singly bonded $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ units by purging the solution with CO at room temperature. The conversion between the singly and triply bonded forms of the polymer was cycled several times without apparent decomposition of the oligomer. Evidence for the absence of decomposition comes from the infrared and NMR spectra: The intensities of the urethane bands at 1725 and 1539 cm^{-1} remained unchanged throughout the cycling, and the ^1H NMR spectrum showed no new resonances after two cycles.

Conclusions. Polyurethanes containing $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ or $Cp(CO)_2Fe{-}Fe(CO)_2Cp$ units along the backbone are photochemically reactive, undergoing reactions similar to the $Cp_2Mo_2(CO)_6$ and $Cp_2Fe_2(CO)_4$ dimers. Reactions with CCl_4 established that photolysis of the metal–metal bond occurs upon excitation into the lowest energy excited states. In the presence of phosphites, disproportionation of the metal–metal bonded units occurred to give a product containing $(C_5H_4R)Mo(CO)_3^-$ and $(C_5H_4R)Mo(CO)_2(P(OR)_3)_2^+$ groups or $(C_5H_4R)Fe(CO)_2^-$ and $(C_5H_4R)Fe(CO)(P(OR)_3)_2^+$ groups. Photochemical decomposition of the polyurethanes also occurred over several weeks to months in the solid state. Both light and oxygen are necessary for this decomposition in the solid state. Oligomer **2**, *containing the singly bonded* $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ unit, was converted (photochemically or thermally) to a polymer containing triply bonded $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ groups. This reaction, which occurs by photochemical loss of CO in the $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ molecule, suggests that Mo–CO dissociation is also a primary photoprocess in polymers containing the $Cp(CO)_3Mo{-}Mo(CO)_3Cp$ unit.

Work is continuing in our laboratory on the preparation and photochemical reactivity of these and other metal–metal bond-containing polymers.

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[23] (a) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1964**, 1567–1572. (b) Cousins, M.; Green, M. L. H. *J. Chem. Soc. A* **1969**, 16–19. (c) Bottomley, F.; Ferris, E. C.; White, P. S. *Organometallics* **1990**, *9*, 1166–1171.