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Photochemically Reactive Polymers. Synthesis, Characterization, and Photochemistry of a Polyurea Containing a $Cp_2Mo_2(CO)_6$ Molecule along the Polymer Backbone and of Poly(ether urethane) Copolymers with $Cp_2Mo_2(CO)_6$ and $Cp_2Fe_2(CO)_4$ Molecules along the Polymer Backbone

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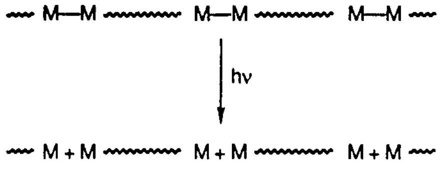
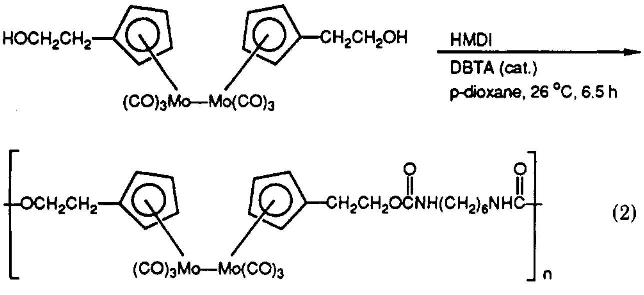
The synthesis of an oligomeric urea containing Mo–Mo bonds along the backbone is reported. Reaction of the organometallic "diamine" $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ with $OCN(CH_2)_6NCO$ (hexamethylene diisocyanate, HMDI) in an interfacial synthesis gave $[-NHCH_2CH_2C_5H_4(CO)_3Mo\text{–}Mo(CO)_3C_5H_4CH_2CH_2NHC(O)NH(CH_2)_6NHC(O)-]_n$. Similarly, poly(ether urethane) copolymers containing Mo–Mo or Fe–Fe bonds along the backbone were synthesized by reacting $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ or $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$ with Hypol 2000, a commercially available polyether capped with toluene diisocyanate end-groups. The polymers and oligomers were characterized by elemental analysis, by infrared, ^1H NMR, and electronic absorption spectroscopy, and by molecular weight. As an aid to the spectroscopic characterization of the polyurea, a model complex was synthesized by reacting $CH_3(CH_2)_5NCO$ with $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$. Because of the metal–metal bonds along the backbones, the polymers and oligomers are photochemically reactive, undergoing metal–metal-bond photolysis 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 $Cl(CO)_2FeC_5H_4\text{–}R\text{–}C_5H_4Fe(CO)_2Cl$ type products when the polymers 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 polymer fragmentation products 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 poly(ether urethanes) also occurred over several days 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 polymer fragmentation and the formation of metal oxide species in this solid-state reaction.

In two recent papers, we described the synthesis and characterization of photochemically reactive polyurethanes.[1,2] The polyurethanes are photoreactive because we incorporated metal–metal bonds along their backbones. When the polymers are irradiated, photolysis of the metal–metal bonds occurs with consequent fragmentation of the polymers:



(1)

The polymers were synthesized by reacting metal–metal bonded "diols" with diisocyanates, e.g.:[1]



(2)

In order to expand our repertoire of photoreactive polymers with metal–metal bonds along the backbone, we decided to synthesize a metal–metal-bonded "diamine". Diamines react with diacyl chlorides to make polyamides,[3–6] with diisocyanates to make polyureas,[3–7] and they can be used as curing agents for epoxies.[8] The reactions with diisocyanates and epoxies are especially attractive because these reactions do not require catalysts (which may react thermally with the metal–metal bonds) and they do not eliminate a small molecule that can react with the metal–metal bond. The reaction with diacyl chlorides is more problematic because of the HCl liberated in the reaction, but it may be useful if a nonnucleophilic base is used to neutralize the HCl.

This paper describes the synthesis of the $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ dimer and its interfacial polymerization with hexamethylene diisocyanate. The characterization and photochemistry of the resulting polyurea are also reported.

This paper also reports the synthesis of poly(ether urethane) copolymers containing metal–metal-bonded molecules along the backbone. In addition to increasing

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[1] Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1991**, *10*, 473–482.

[2] Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1991**, *10*, 1116–1123.

[3] Pittman, C. U., Jr.; Rausch, M. D. *Pure Appl. Chem.* **1986**, *58*, 617–622.

[4] Gonsalves, K.; Zhan-ru, Lin; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3862–3863.

[5] Gonsalves, K. E.; Lenz, R. W.; Rausch, M. D. *Appl. Organomet. Chem.* **1987**, 81–93.

[6] Stueben, K. C.; Barnabeo, A. E. In *Interfacial Synthesis*; Millich, F., Carraher, C. E., Jr., Eds.; Marcel Dekker: New York, 1977; Vol. II, Chapter 18.

[7] Sandler, S. R.; Karo, W. In *Polymer Syntheses*; Academic Press: New York, 1974; Vol. I, p 185.

[8] Stevens, M. P. In *Polymer Chemistry*; Addison-Wesley: Reading, MA, 1975; p 239.

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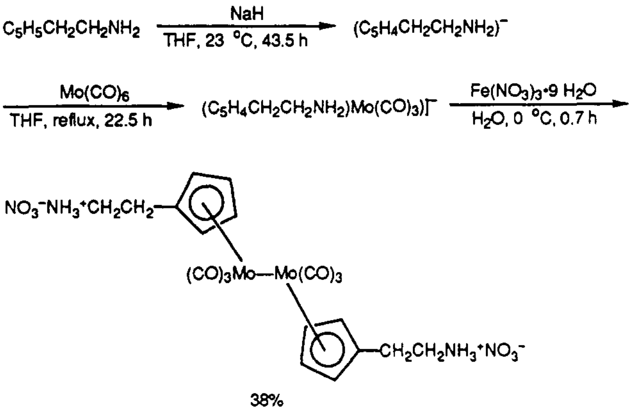
Scheme I. Synthesis of $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$



our repertoire of polymers, the synthesis of these copolymers demonstrates the feasibility of using prepolymers in the syntheses of metal–metal-bond-containing polymers.

Results and Discussion

Synthesis and Characterization of Complex 1, $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$. This dimer was selected for synthesis because the ammonium functionality is two methylene groups removed from the Cp ring. Previous work showed that the amine (or ammonium) group must be at least two methylene groups removed from the Cp ring to avoid any steric and electronic effects of the metal which may retard the polymerization reactions.[3,4,9,10] The reason the salt of the amine was synthesized instead of the free amine was that amines can disproportionate metal–metal dimers, e.g.:[11]

$$Cp_2Mo_2(CO)_6 + NR_3 \xrightarrow{h\nu} CpMo(CO)_3(NR_3)^+ + CpMo(CO)_3^- \quad (3)$$

By using the ammonium derivative, we thus sought to avoid intra- and intermolecular disproportionation reactions.

The $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ complex was synthesized by the overall route in Scheme I. The $C_5H_5CH_2CH_2NH_2$ for use in this scheme was synthesized from $C_5H_5CH_2CH_2OH$ using the method Grieco[12] reported for synthesizing acyclic diene amines. The synthesis is shown in Scheme II.

Scheme II. Synthesis of $C_5H_5CH_2CH_2NH_2$

$$C_5H_5CH_2CH_2OH \xrightarrow[\text{pyridine, 0 °C, 4 h}]{\text{TsCl}} \underset{91\%}{C_5H_5CH_2CH_2OTs} \quad (4)$$

$$C_5H_5CH_2CH_2OTs \xrightarrow[\text{DMSO, 0 °C, 18 h}]{\text{NaN}_3} \underset{87\%}{C_5H_5CH_2CH_2N_3} \quad (5)$$

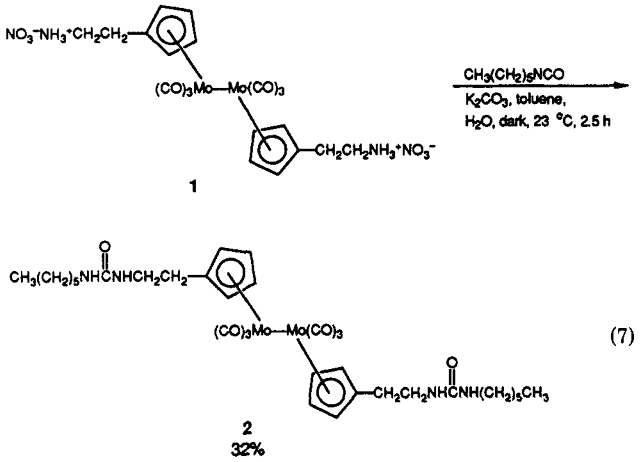
$$C_5H_5CH_2CH_2N_3 \xrightarrow[\text{Et}_2\text{O, 0°C, 2 h}]{\text{LiAlH}_4} \underset{17\%}{C_5H_5CH_2CH_2NH_2} \quad (6)$$

The ^1H NMR spectrum (DMSO-d_6), key IR (KBr) bands, and electronic spectrum for the $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ complex are reported in Table I.[13] Elemental analysis of the dimer was satisfactory.

The electronic absorption spectrum of the $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ complex (Table I) is similar to that of $Cp_2Mo_2(CO)_6$ and other related complexes. The bands at 386 and 496 nm are assigned to the metal–metal $\sigma \rightarrow \sigma^*$ and $d\pi \rightarrow \sigma^*$ transitions, respectively.[1,2]

Solubility Properties of the $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$ Complex. This dimer is only soluble in polar organic solvents such as DMSO and methanol. The solubility in methanol is approximately 7 g/L. It is also slightly soluble in water (1.2 g/L).

Synthesis and Characterization of a Urea Model Complex, $[(CO)_3MoC_5H_4CH_2CH_2NHC(O)NH(CH_2)_5CH_3]_2$ (2). As in our previous papers,[1,2] the polymers synthesized in this paper were spectroscopically characterized by comparison to "model" complexes. A urea model complex was synthesized by reacting complex 1 with hexyl isocyanate in an interfacial reaction (eq 7). The reaction conditions were very similar to those used to synthesize the polyurea in the next section.



(7)

The ^1H NMR, infrared, and electronic absorption spectroscopic data of this model complex are listed in Table I.

Synthesis and Characterization of a Polyurea: $[-NHCH_2CH_2C_5H_4(CO)_3Mo\text{-}Mo(CO)_3C_5H_4CH_2CH_2NHC(O)NH(CH_2)_6NHC(O)-]_n$. Complex 1 was reacted interfacially with HMDI to yield a polyurea, as shown in eq 8.

The polymer was analyzed by ^1H NMR (DMSO-d_6) and infrared spectroscopy (KBr). Key data are shown in Table

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[9] Trifan, D. W.; Backsai, R. *Tetrahedron Lett.* **1960**, *1*, 1–8.

[10] Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: New York, 1982; Vol. 8, p 1052.

[11] Philbin, C. E.; Stiegman, A. E.; Tenhaeff, S. C.; Tyler, D. R. *Inorg. Chem.* **1989**, *28*, 4414–4417.

[12] Grieco, P. A.; Galatsis, P.; Spohn, R. F. *Tetrahedron* **1986**, *42*, 11, 2847–2853.

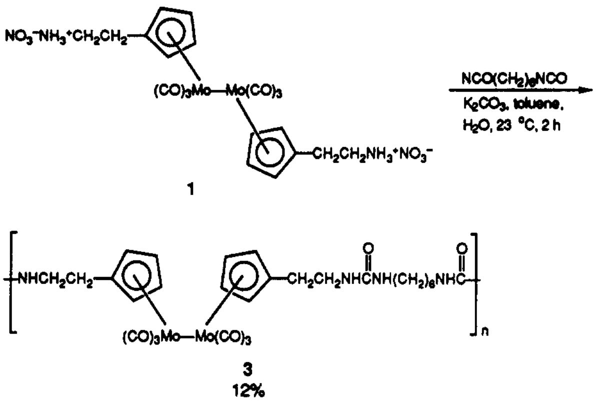
[13] The ^1H NMR resonance at δ 7.81 was confirmed as NH_3^+ protons by its disappearance upon treatment of the NMR sample with D_2O. The broad resonances of the C_5H_4 protons are attributed to the presence of both the anti and gauche conformation of the Cp rings in polar solvents.[14,15] Similar broad resonances are observed in other $(\eta^5\text{-}C_5H_4R)_2Mo_2(CO)_6$ complexes.[1,2]

[14] Adams, R. D.; Cotton, F. A. *Inorg. Chim. Acta* **1973**, *7*, 1, 153–156.

[15] Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.: Pergamon Press: New York, 1982; Vol. 3, p 1176.

[16] In addition, the percent nitrate was measured and determined to be 16.64%, which agrees reasonably well with the calculated amount of 17.66%. The FAB mass spectrum was obtained in glycerol. Isotopic clusters were observed at m/e = 576, 288, 260, 232, and 204, corresponding to a $(\eta^5\text{-}C_5H_4CH_2CH_2NH_2)_2Mo_2(CO)_6$ parent ion and a fragment of half this parent ion mass with the sequential loss of three CO ligands.[17]

[17] Bryan, R. F.; Greene, P. T.; Newlands, M. J.; Field, D. S. *J. Chem. Soc. A* **1970**, 3068–3074.



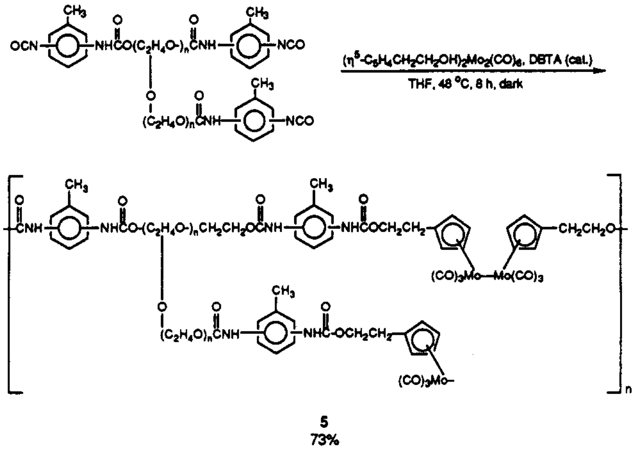
(8)

I. The ^{1}H NMR spectrum is consistent with the structure shown for the polymer (eq 8) and is similar to that of the model complex. The electronic absorption spectrum is similar to those of the model complex, 2, and dimer 1, indicating the presence of the Mo–Mo bond.

The molecular weight of the polymer was not determined because of its insolubility in almost all organic solvents. It is partially soluble in hot DMSO, but hot DMSO caused disproportionation (analogous to eq 3) to occur, resulting in low molecular weights. Polyureas are typically high-melting, insoluble polymers because of extensive interchain hydrogen bonding.[18]

Synthesis and Characterization of Poly(ether urethane) Copolymers with Mo–Mo Bonds along the Backbone. Poly(ether urethane) copolymers with Mo–Mo or Fe–Fe bonds along the backbone were synthesized by reacting $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ or $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$ with Hypol 2000 prepolymer. Hypol 2000 is a commercially available (W. R. Grace Co.) polyether prepolymer capped with toluene diisocyanate. Its exact composition is proprietary, but molecule 4 in Table I is an approximate structure of this prepolymer. It has an $\bar{M}_n$ of approximately 2000 g/mol. This prepolymer is in the form of a very viscous, light yellow liquid at room temperature. It has an equivalent weight of 625 g/equiv of isocyanate.[19]

Hypol 2000 was reacted with $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ according to eq 9. In this procedure, an amount of $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ and Hypol 2000 was weighed out so that there were equal numbers of –OH and –NCO groups. The reaction was carried out until no more –NCO reacted, as determined by measuring the intensity of the NCO IR stretch at 2274 cm^{-1}. The reaction was carried out in a darkened room because it was determined from earlier attempted syntheses that the polymer product is very photoreactive. After the reaction was complete (as indicated by no change in the intensity of the NCO IR band), absolute ethanol was added to react with any unreacted isocyanate groups. Following workup, the polymer was obtained in 73% yield as a red, gummy material.



(9)

The ^{1}H NMR, electronic absorption,[20] and infrared spectra of this polymer are found in Table I. Spectroscopic data for Hypol 2000 are also included in Table I for reference.

The $\bar{M}_n$ of the polymer was 8100 g/mol (VPO in THF).[21] An elemental analysis was not obtained on this copolymer because of the uncertainty about the Hypol 2000 structure.

The polymer resulting from reaction 9 should be an insoluble cross-linked elastomer if all the isocyanate groups have reacted. The cross-linking is due to the prepolymer having three NCO groups per chain. Totally cross-linked polymers are thermosets and are not soluble,[18,22] but this poly(ether urethane) is still soluble because not all the NCO groups reacted before ethanol was added to quench the reaction. By doing this, we were able to prevent the formation of a totally cross-linked polymer. This yielded a soluble polymer that we were able to characterize.

Synthesis and Characterization of Poly(ether urethane) Copolymers with Fe–Fe Bonds along the Backbone. Photoreactive polymers with Fe–Fe bonds along their backbones may have commercial uses as photodegradable packaging materials, as lithiographic materials,[23,24] or as a method to obtain thin films of iron oxide particles.[3,4] This prompted us to synthesize the Fe–Fe analogue of the poly(ether urethane) discussed above.[25]

The poly(ether urethane) was synthesized by reacting $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$ with Hypol 2000 prepolymer according to eq 10.

The ^{1}H NMR (acetone-d_6), infrared, and electronic absorption spectra for this polymer are listed in Table I along with that of $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$ for comparison. The ^{1}H NMR spectrum has resonances found in both Hypol 2000 and $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$.

The electronic absorption spectrum of polymer 6 is reported in Table I.[26] The spectrum is essentially identical

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(18) Saunders, J. H.; Frisch, K. C. In *Polyurethanes: Chemistry and Technology I. Chemistry*; *Interscience*: New York, 1962; Vol. XVI, Chapter 6.

(19) (a) Hypol 2000 Technical Data Sheet. W. R. Grace Co., Lexington, MA, 1990. (b) Wood, J. L. *J. Cell. Plast.* **1976**, 285–288.

(20) Because we do not know the exact composition of the Hypol 2000, and thus the repeating unit weight, an exact extinction coefficient cannot be calculated. However, because we measured an $\bar{M}_n$ value of 2000 g/mol for the Hypol prepolymer and because the equivalent weight is reported by the W. R. Grace Co. to be 625 g/mol, there must be three –NCO groups per Hypol chain. From this data, we calculated a weight per Mo–Mo bond of 1910 g/mol. Using this number and the electronic absorption data, extinction coefficients of 2100 M^{-1} cm^{-1} at 508 nm and 19 500 M^{-1} cm^{-1} at 391 nm were calculated (Table I). These extinction coefficients are typical for the other dimers, model complexes, and polymers.[1,2]

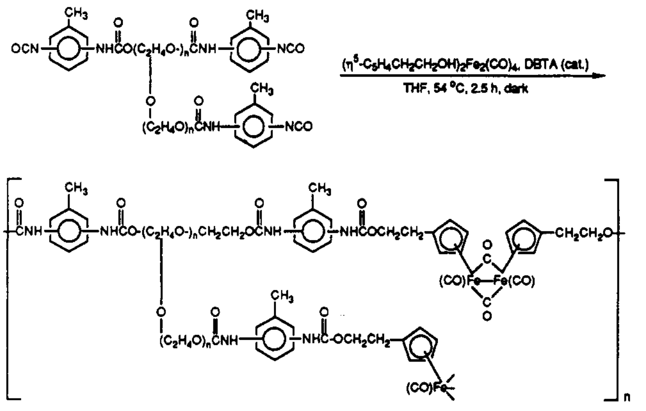
(21) This value was determined using the $(\eta^5\text{-}C_5H_4CH_2CH_2OC(O)NH(CH_2)_5CH_3)_2Mo_2(CO)_6$ model complex as a calibration standard instead of benzil (which was used with all of the other polymers). The reason the model complex was used is that its molecular weight was determined to be about half of its actual value when benzil was used as a standard. This may result from using THF as a solvent: extensive hydrogen bonding between the THF and the polymer could be causing nonideal solution behavior and thus low molecular weights.

(22) Billmeyer, F. W. Jr. *Textbook of Polymer Science*, 2nd ed.; Wiley: New York, 1971; Chapter 16.

(23) West, R. *J. Organomet. Chem.* **1986**, *300*, 327–346.

(24) Hofer, D. C.; Miller, R. D.; Willson, C. G.; Neureuther, A. R. *SPIE, Proc. Int. Soc. Opt. Eng.* **1984**, *469*, 108–116.

(25) Gonsalves, K. E.; Rausch, M. D. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society; Washington, DC, 1988; Chapter 36.



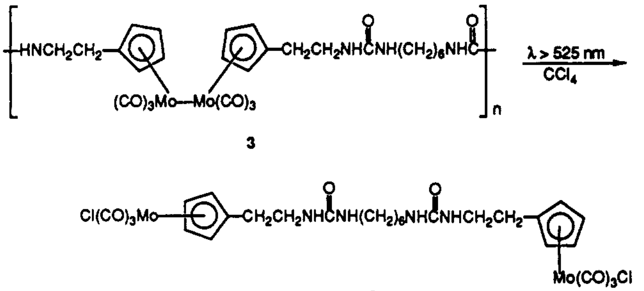
6
69%

(10)

to that of the (η^5-$C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$ and $Cp_2Fe_2(CO)_4$ dimers, indicating that the Fe–Fe unit is intact in this copolymer. The $\bar{M}_n$ (VPO) of polymer **6** was 3100 g/mol. Although this molecular weight seems low, films of the polymer could be cast from THF. The low $\bar{M}_n$ may also result from measurement errors because the urethane model complex used as the $\bar{M}_n$ calibration standard is slightly different in composition than this polymer.[27] The polymer may exhibit even more nonideal solution behavior than the model complex. Another reason the molecular weight of this polymer was low is that the reaction was quenched before all the NCO groups had reacted. This was done to prevent the polymer from cross-linking into an insoluble elastomer.[18,22]

As was the case with polymer **5**, an elemental analysis was not obtained on copolymer **6** because of the uncertainty about the Hypol 2000 structure.

Photochemical Reactions in Solution. The urea model complex, polyurea and poly(ether urethanes) reacted with CCl_4 to form M–M homolysis products. A sample reaction is shown in eq 11. The other polymers reacted analogously. Complete details and the spectroscopic characterization of the products are given in the supplementary material. Likewise, the model complexes, polyurea, and poly(ether urethanes) reacted with $P(OEt)_3$ to form disproportionation products. A sample reaction is shown in eq 12. Complete details are again given in the supplementary material. The quantum yields for the reaction of the poly(ether urethane) copolymers with CCl_4 in THF were measured [Φ(504 nm; polymer **5**) = 0.35; Φ(504 nm; polymer **6**) = 0.14]. These quantum yields are significantly lower than those for the corresponding reaction of the (η^5-$C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$ [Φ(504 nm) = 0.61] or the (η^5-$C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$ [Φ(504 nm) = 0.22] dimers with CCl_4,[2] possibly indicating a "cage effect". The quantum yield for the polyurea was not measured since this polymer is only soluble in DMSO, and DMSO reacts photochemically to disproportionate the Mo–Mo bond.[11]



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(11)

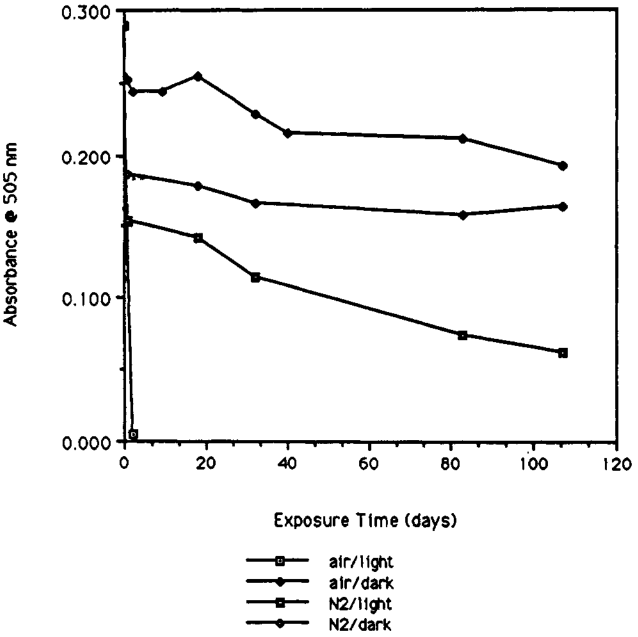
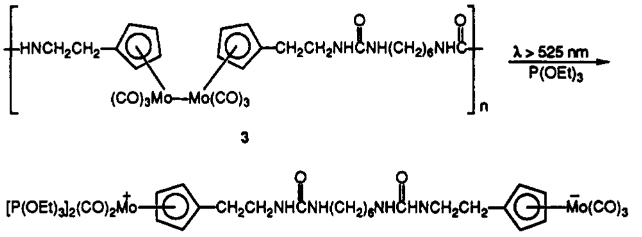


Figure 1. Plot of the absorbance at 506 nm vs time for a thin film of copolymer **5**. As indicated in the figure, one sample was exposed to air and light, one sample was kept in the dark in air, another sample was exposed to light but kept under nitrogen, and the last sample was kept in the dark under nitrogen. Complete details are found in the Experimental Section.



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(12)

Photochemical Reaction of Polymer 5 in the Solid State. Polymer **5** was cast as a film onto glass slides. One slide was exposed to sunlight in air, one was kept in the dark in air, one was stored in nitrogen in room light, and one was stored in nitrogen in the dark. As was the case with the polyurethanes we previously studied,[2] only the sample exposed to both air and light decomposed. (The sample turned color from red to green, indicating the formation of molybdenum oxides.) To quantitate the photodecomposition (or lack thereof), the absorbances of the $d\pi \rightarrow \sigma^*$ bands at 506 nm in the films were measured periodically and the results plotted as a function of time. As shown in Figure 1, the film exposed to air and sunlight decomposed rapidly compared to the other films. This

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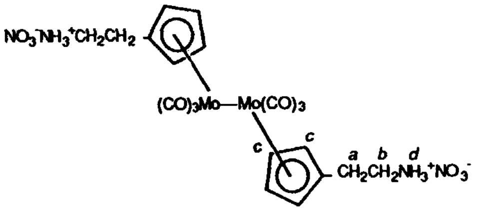
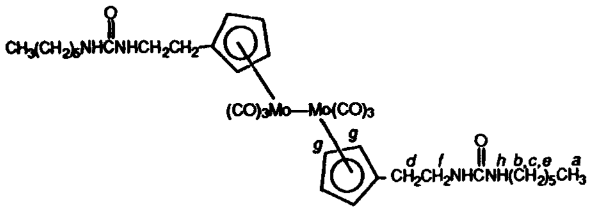
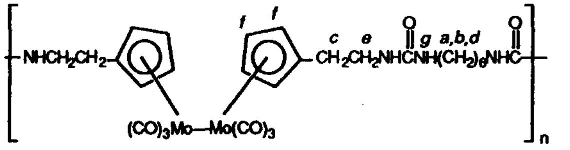
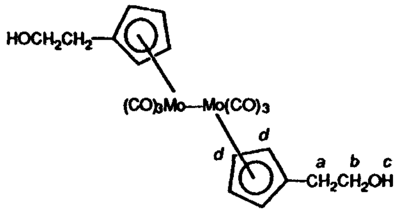
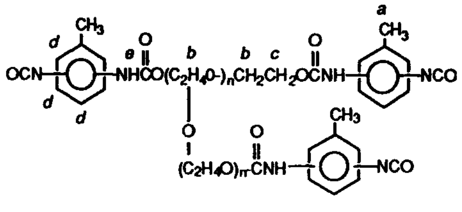
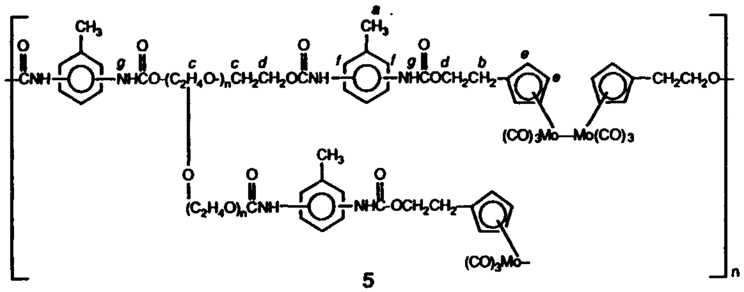
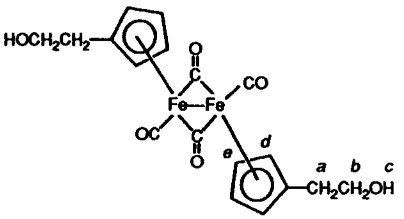
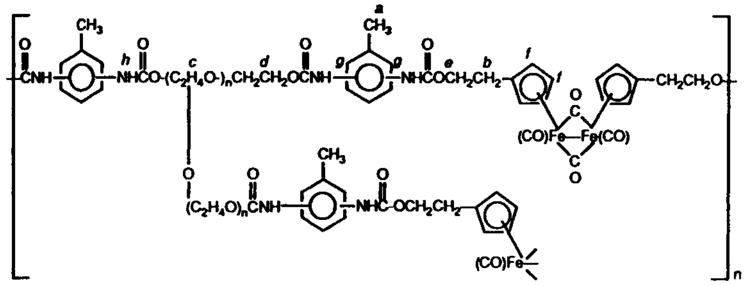
[26] Because the exact structure of the repeating unit is not known (because we do not know if there are any other types of polyethers present), the extinction coefficients at 510, 410, and 347 nm could not be determined. However, using our measured $\bar{M}_n$ value of 2000 g/mol and an equivalent weight of 625 g/equiv of NCO, a weight of 1775 g/mol per Fe–Fe was calculated. On the basis of this number and the measured absorbances, extinction coefficients of 490 M^{-1} cm^{-1} at 510 nm, 1640 M^{-1} cm^{-1} at 410 nm, and 8800 M^{-1} cm^{-1} at 347 nm were calculated.

[27] This value was determined using the (η^5-$C_5H_4CH_2CH_2OC(O)NH$-$(CH_2)_5CH_3)_2Fe_2(CO)_4$ model complex as a standard instead of benzil because the molecular weight of the model complex in THF came out low (410 g/mol (measured) vs 696 g/mol (theoretical)) when a benzil standard was used. The low values probably result from hydrogen bonding between the NH protons on the model complex and the oxygen of THF.

Table I. ^{1}H NMR, Electronic Absorption, and IR Spectrosopic Data for Dimers, Model Complexes, and Polymers Containing the $Cp_2Mo_2(CO)_6$ or the $Cp_2Fe_2(CO)_4$ Unit

compd	^{1}H NMR δ, ppm	λ, nm (ε)	IR (KBr), cm^{-1} ν(C=O)	IR (KBr), cm^{-1} other bands
$Cp_2Mo_2(CO)_6$	5.60 (broad, 5 H)^a	508 (1920)^b	2012 (sh, w)	
	5.44 (broad, 5 H)	388 (20690)	1954 (s)	
			1925 (m)	
			1901 (s)	
			1890 (s)	
 1	a: 2.65 (t, J = 6.9 Hz, 4 H)^c	496 (2040)^d	2009 (w)	ν(NH_3^+), 3104 (m), 3089 (m)
	b: 2.94 (t, J = 7.8 Hz, 4 H)	386 (17500)	1957 (s)	ν(CH_2, sp^3), 2986 (m)
	c: 5.29–5.72 (3 broad resonances, 8 H)		1953 (s)	δ(NH_3^+), 1617 (w)
	d: 7.81 (broad, 6 H)	505 (2040)^c 389 (20000)	1886 (s)	δ(NH_3^+), 1541 (m)
 2	a: 0.84 (t, J = 5.7 Hz, 6 H)^c	507 (2200)^b	2011 (w)	ν(NH), 3358 (broad & w)
	b: 1.22 (broad, 12 H)	392 (21000)	1961 (sh, s)	ν(C=O, 1627 (m)
	c: 1.30 (m, 4 H)		1940 (s)	δ(NH), 1574 (m)
	d: 2.41 (t, J = 5.7 Hz, 4 H)	498 (2100)^d	1920 (s)	ν(C—N), 1261 (w)
	e: 2.93 (quartet, J = 5.7 Hz, 4 H)	388 (19000)	1902 (s)	ν(CH_3, sp^3), 2957 (w)
	f: 3.08 (quartet, J = 5.7 Hz)			
	g: 5.21–5.58 (4 broad resonances, 8 H)			ν(CH_2, sp^3), 2928 (w)
	h: 5.81, 5.88 (2 broad resonances, 4 H)			
 3	a: 1.21 (broad, 4 H)^c	497 (1930)^d	2011 (m)	ν(N—H), 3326 (w)
	b: 1.31 (broad, 4 H)	386 (15900)	1949 (s)	ν(C=O), 1627 (m)
	c: 2.42 (broad, 4 H)		1891 (s)	δ(NH), 1565 (m)
	d: 2.94 (m, 4 H)			ν(C—N), 1252 (m)
	e: 3.08 (broad, 4 H)			ν(CH_2, sp^3), 2931 (m)
	f: 5.21–5.57 (4 broad resonances, 8 H)			ν(CH_2, sp^3), 2857 (m)
	g: 5.72, 5.85, 5.90 (broad, 4 H)			
	a: 2.61 (t, J = 6.3 Hz, 4 H)^a	508 (2250)^b	2008 (w)	ν(OH), 3326 (broad, w)
	b: 3.68 (quartet, J = 6.3 Hz, 4 H)	391 (21000)	1955 (s)	ν(CH_2, sp^3), 2960 (vw)
	c: 3.86 (t, J = 5.1 Hz, 2 H)		1940 (s)	ν(CH_2, sp^3), 2940 (vw)
	d: 5.23–5.59 (3 broad resonances, 8 H)		1926 (s)	ν(CH_2, sp^3), 2884 (vw)
			1905 (s)	
			1891 (s)	

 Hypol 2000 4	a: 2.27 (s, 3 H)[a] b: 3.56 (s, 33 H), 3.70 (broad, 2 H) c: 4.14 (broad, 1 H), 4.23 (broad, 2 H) d: 7.18–7.46 (3 resonances, 3 H) e: 8.75 (broad, 1 H)			ν(N—H), 3296 (w)[f] ν((C=O), 1729 (s) δ(N—H, amide II), 1539 (s) ν(C—N, amide III), 1279 (m) ν(CH_2, sp^3), 2875 (s) ν(NCO), 2271 (vs) ν(C—C, aromatic), 1616 (m) ν(C—C, aromatic), 1595 (m) ν(C—O, ester), 1223 (s) ν(C—O, ether), 1110 (br, s)
 5	a: 2.21 (s, 5 H)[a] b: 2.79 (broad, b, 5 H) c: 3.56 (s, 60 H), 3.67 (b, 4 H) d: 4.15 (broad, 3 H), 4.23 (broad, 6 H) e: 5.26–5.61 (3 broad resonances, 8 H) f: 7.08–7.99 (4 resonances, 7 H) g: 7.88, 8.62 (broad, 3 H)	508 (2100)[b,g] 391 (19500)	2005 (m) 1949 (s) 1905 (s)	ν(N—H), 3300 (w)[f] ν(C=O), 1730 (m) δ(N—H, amide II), 1536 (w) ν(C—N, amide III), 1279 (vw) ν(CH_2, sp^3), 2875 (m) ν(C—C, aromatic), 1618 (vw) ν(C—C, aromatic), 1604 (w) ν(C—O, ester), 1229 (m) ν(C—O, ether), 1103 (br, m)
$Cp_2Fe_2(CO)_4$	4.94 (C_5H_5)[a]	511 (568)[b] 410 (1900) 345 (10100)	1973 (m) 1954 (s) 1933 (vs) 1907 (m) 1757 (vs)	
	a: 2.67 (t, J = 6.0 Hz, 4 H)[a] b: 3.77 (m, J = 5.4 Hz, 4 H) c: 3.86 (broad, 2 H) d: 4.66 (broad, 4 H) e: 4.84 (broad, 4 H)	512 (510)[b] 410 (1780) 347 (9260)	1958 (s) 1940 (s) 1914 (m) 1759 (vs) 1732 (m)	ν(OH), 3209 (m) ν(CH_2, sp^3), 2948 (w) ν(CH_2, sp^3), 2934 (w) ν(CH_2, sp^3), 2884 (w)
 6	a: 2.21 (s, 11 H)[a] b: 2.86 (broad, b, 3 H) c: 3.56 (s, 87 H), 3.67 (b, 5 H) d: 4.17 (broad, 2 H), 4.21 (broad, 9 H) e: 4.34 (t, J = 6.3 Hz, 3 H) f: 4.73, 4.87 (2 broad resonances, 8 H) g: 7.04–7.80 (2 resonances, 10 H) h: 7.88, 8.62 (broad, 2 H)	510 (490)[b,h] 410 (1640) 347 (8800)	1984 (s) 1943 (m) 1800 (w) 1771 (s)	ν(N—H), 3309 (w)[f] ν(C=O), 1730 (s) δ(N—H, amide II), 1536 (m) ν(C—N, amide III), 1279 (vw) ν(CH_2, sp^3), 2872 (m) ν(C—C, aromatic), 1618 (vw) ν(C—C, aromatic), 1601 (w) ν(C—O, ester), 1229 (s) ν(C—O, ether), 1103 (br, s)

[a] Acetone-d_6. [b] THF. [c] DMOS-d_6. [d] DMSO. [e] Methanol. [f] Spectrum obtained on film cast onto NaCl cell. [g] The extinction coefficient is per Mo–Mo unit, not per repeating unit. [h] The extinction coefficient is per Fe–Fe unit, not per repeating unit.

copolymer reacted approximately 9 times faster with air and light than the polyurethanes we reported in a previous paper.[1,2] We are currently investigating the reasons for the faster decomposition; we hypothesize that it may be due to more rapid oxygen diffusion through the copolymer film.

Summary. Polyureas and poly(ether urethane) copolymers 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 $P(OEt)_3$, disproportionation of the metal–metal-bonded units occurred. Photochemical decomposition of the poly(ether urethane) copolymer with Mo–Mo bonds along the backbone also occurred in the solid state. Both light and oxygen are necessary for this decomposition in the solid state. As was the case with the polyurethanes we previously synthesized,[1,2] it is reasonable to propose that oxygen is necessary to capture the metal radicals produced by photolysis of the metal–metal bonds.

Experimental Section

Materials. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk or vacuum line techniques or a Vacuum Atmospheres Co. glovebox (O_2 < 2 ppm). *All glassware used in the polymerization and model complex reactions with diisocyanates or isocyanates, respectively, was flame-dried under vacuum before use*, except for the interfacial reactions.

Materials were obtained and purified as previously described.[1,2] Cyclopentadienylethyl *p*-toluenesulfonate, $C_{14}H_{16}O_3S$, was prepared by the method of Tipson.[28] Cyclopentadienylethyl azide ($C_7H_9N_3$) and (cyclopentadienylethyl)amine ($C_7H_{11}N$) were prepared by the method of Grieco et al.[12] Hypol 2000 prepolymer was donated by the W. R. Grace Co. It was stored at 5 °C and deoxygenated with a nitrogen purge before use. Triethyl phosphite (Aldrich) was deoxygenated by purging with nitrogen immediately before use.

Equipment. Infrared spectra, electronic absorption spectra, ^1H NMR spectra, number average molecular weights, and fast-atom-bombardment mass spectra were obtained as previously described.[1,2]

Synthesis of Complex 3, $[(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+)_2Mo_2(CO)_6][NO_3^-]_2$. Sodium hydride dispersion (60%), 0.16 g (4.2 mmol of NaH), was added to a flame-dried 250-mL three-neck round-bottom flask fitted with a reflux condenser, nitrogen inlet, and magnetic stir bar. The NaH dispersion was washed three times with 10 mL of THF; then 50 mL of THF was added. (Cyclopentadienylethyl)amine, 0.54 g (4.9 mmol), in 10 mL of THF was added, and the solution was stirred at room temperature under nitrogen for 43.5 h. The solution was clear yellow. $Mo(CO)_6$, 1.05 g (4.0 mmol), was then added, and the solution was refluxed under nitrogen for 22.5 h. The solution is bright yellow at this point. The solution was cooled and concentrated to 10–15 mL in vacuo. The reaction was then cooled in an ice water bath, and 2.6 g (6.4 mmol) of $Fe(NO_3)_3{\cdot}9H_2O$ in 50 mL of deoxygenated (nitrogen-purged) deionized water was added, resulting in an immediate red precipitate. The aqueous solution was stirred in an ice water bath for 45 min and then filtered through a medium-porosity filter frit under nitrogen. The crude dimer was then washed four times with 10 mL of deoxygenated ice water, two times with 10 mL of deoxygenated 2-propanol, and four times with 10 mL of dried, deoxygenated ethyl ether and then dried in vacuo (5 mm) for 1 h. A total of 1.1925 g (1.7 mmol, 85%) of red, powdery, crude dimer was recovered. The dimer was purified by recrystallization from methanol/ethyl ether (2:1 by volume) and dried in vacuo (<0.001 mm) for 90 h. Yield: 0.5275 g (0.75 mmol), 38%. Anal. Calcd for $C_{20}H_{22}N_4O_{12}Mo_2$: C, 34.20; H, 3.16; N, 7.98. Found: C, 33.99; H, 3.15; N, 7.67. FAB mass spectrum (glycerol): *m/e* 576 $[(M - 2NO_3^- - H^+)^+$, 26%], 548 $[(M - 2NO_3^- - H^+)^+ - CO$, 4], 288 $[(M - 2NO_3^- - H^+)^+/2$, 72), 260 $[((M - 2NO_3^- - H^+)/2)^+ - CO$, 92], 232 $[((M - 2NO_3^- - H^+)/2)^+ - 2CO$, 55], 219 $[(M - 2NO_3^- - 5CO)^{2+}$, 10], 204 $[((M - 2NO_3^- - H^+)/2)^+ - 3CO$, 25].

Synthesis of Model Complex 2, $[(CO)_3MoC_5H_4CH_2CH_2NHC(O)NH(CH_2)_5CH_3]_2$. To a 50-mL three-neck flask fitted with a reflux condenser, nitrogen inlet, magnetic stir bar, addition funnel, and a thermometer were added 0.1867 g (0.266 mmol) of 1, 15 mL of deoxygenated water, and 15 mL of dried, deoxygenated toluene. The flask was covered with foil to exclude light from the reaction mixture. Approximately 0.20 mL (1.4 mmol) of hexyl isocyanate was syringed into the toluene layer. The reaction mixture was stirred, and then 10 mL of aqueous K_2CO_3 (0.036 M) was dripped into the reaction mixture over 5 min. The reaction mixture was then stirred for 2.5 h at room temperature. The resulting red precipitate was filtered (in air), washed with water, hexane, and ethyl ether and then dried in vacuo. The crude model complex was then recrystallized three times from THF and ethyl ether (3:1 by volume). Yield: 0.073 g (32%). Anal. Calcd for $C_{34}H_{46}N_4O_8Mo_2$: C, 49.16; H, 5.58; N, 6.75. Found: C, 48.87; H, 5.51; N, 6.54. FAB (3-nitrobenzyl alcohol): *m/e* 831 ($M,^+$ 4%), 775 ($M^+ - 2CO$, 3), 747 ($M^+ - 3CO$, 2), 663 ($M^+ - 6CO$, 9), 415 ($M^+/2$, 16), 387 ($M^+/2 - CO$, 44), 359 ($M^+/2 - 2CO$, 27), 331 ($M^+/2 - 3CO$, 37).

Synthesis of Polyurea 3, $[–NHCH_2CH_2C_5H_4(CO)_3Mo–Mo(CO)_3C_5H_4CH_2CH_2NHC(O)NH(CH_2)_6NHC(O)–]_n$. $(\eta^5\text{-}C_5H_4CH_2CH_2NH_3^+NO_3^-)_2Mo_2(CO)_6$, 0.4067 g (0.580 mmol), was added to a three-neck, 250 mL, round-bottom flask equipped with a magnetic stir bar, nitrogen inlet, and 50-mL addition funnel. The apparatus was evacuated and filled with nitrogen three times. Deoxygenated deionized water, 90 mL, was added (note that the dimer is not completely soluble in this amount of water), and then 40 mL of toluene was layered on top. HMDI, 0.1000 g (0.595 mmol), was syringed into the toluene layer. The reaction flask was covered with aluminum foil to protect it from light. Deoxygenated aqueous K_2CO_3 (50 mL, 0.039 M) was dripped into the stirring reaction mixture from the addition funnel over 10 min. The solution was then stirred at room temperature for 2 h. The red, insoluble residue was filtered (in air). The red residue was washed with water, methanol, and ethyl ether and then dried in vacuo (0.02 mmHg) for 39 h. Yield: 0.20 g (46%) of rust-colored, powdery polymer. The polymer was purified further by a Soxhlet extraction with methanol for 3 h. Purified yield: 0.05 g (12%). Anal. Calcd for $C_{28}H_{32}Mo_2N_4O_8$: C, 45.17; H, 4.33; N, 7.53. Found: C, 44.68; H, 4.48; N, 7.25.

Synthesis of Copolymer 5, $[–OCH_2CH_2C_5H_4(CO)_3Mo–Mo(CO)_3C_5H_4CH_2CH_2OC(O)NHC_7H_6NHC(O)O(C_2H_4O)_m–CH_2CH_2OC(O)NHC_7H_6NHC(O)–]_n$. Hypol 2000 polyether prepolymer, 1.6879 g (2.70 mequiv of NCO), was dissolved in 30 mL of THF and then cannulated into a flame-dried 250 mL, three-neck round-bottom flask fitted with a reflux condenser, nitrogen inlet, thermometer, and magnetic stir bar. The solution was deoxygenated with a nitrogen purge. In the dark, the solution was heated with stirring to 50 °C in a thermostated oil bath. $(C_5H_4CH_2CH_2OH)_2Mo_2(CO)_6$, 0.7787 g (2.69 mequiv of OH), in 20 mL of THF was then cannulated into the Hypol/THF solution. The dimer was rinsed into the reaction solution with about 15 mL of THF. DBTA, 0.02 mL (0.08 mmol), was added, and the solution was stirred at 48 °C for 8 h until no further depletion of NCO was observed by periodic IR analysis (NCO stretch at 2275 cm^{-1}). The reaction solution was cooled to 37 °C, then 0.1 mL of absolute ethanol was added, and the solution was stirred for 35 min. The polymer was then reprecipitated several times from THF with hexane. The red, gummy precipitate was filtered, washed with hexane, and then dried in vacuo (0.3 mmHg) for 46 h, yielding 1.799 g (73%) of red, spongy polymer. ^1H NMR ($CDCl_3$): δ, ppm 7.77 (br, 1 H, NH), 7.36, 7.16, 7.06 (3 br resonances, 6 H, aromatic), 6.52 (br, 3 H, NH), 5.30 (br, 4 H, C_5H_4), 5.16 (br, 4 H, C_5H_4), 4.28 (br, 10 H, $–CH_2OC(O)$), 3.63 (s, 87 H, $(–C_2H_4O)_n–$), 2.78 (br, 4 H, $C_5H_4CH_2$), 2.18 (s, 7 H, $–CH_3$). $\bar{M}_n$ (VPO, THF): 8100 g/mol.

Synthesis of Copolymer 6, $[–OCH_2CH_2C_5H_4(CO)_2Fe–Fe(CO)_2C_5H_4CH_2CH_2OC(O)NHC_7H_6NHC(O)O(C_2H_4O)_m–CH_2CH_2OC(O)NHC_7H_6NHC(O)–]_n$. Hypol 2000 prepolymer, 1.6356 g (0.00262 equiv of NCO), was dissolved in 25 mL of THF and the solution deoxygenated with a nitrogen purge. The solution

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[28] Tipson, S. *J. Org. Chem.* **1944**, *9*, 235–241.

was then cannulated into a flame-dried, three-neck, 250-mL round-bottom flask fitted with a reflux condenser, nitrogen inlet, magnetic stir bar, and a thermometer. In the dark, the solution was stirred and brought to 50 °C with a thermostated oil bath. A solution of $(\eta^5\text{-}C_5H_4CH_2CH_2OH)_2Fe_2(CO)_4$, 0.5785 g (0.00262 equiv of OH), and DBTA, 0.02 mL (0.08 mmol), in 20 mL of THF was then cannulated (under nitrogen) into the Hypol solution (total volume of THF ≈45 mL). The solution was stirred at 54 °C for 2.5 h until all the Hypol 2000 had reacted (determined by monitoring the decrease in the intensity of the NCO stretch at 2275 cm^{-1}). Absolute ethanol (dried over type 4-Å molecular sieves), 0.2 mL (3.4 mmol), was then added by syringe, and the solution was stirred for 15 min. The polymer was then reprecipitated several times from THF with hexane. The THF/hexane mixture was cannula-filtered from the polymer, and the polymer flask was covered with foil and dried in vacuo (~2 mmHg) for 20.5 h, yielding 1.519 g (69%) of red, gummy polymer. The polymer was transferred to and stored in an amber vial in the glovebox. ^1H NMR ($CDCl_3$): δ, ppm 7.74 (br, 2 H, NH), 7.16, 7.04 (2 br resonances, 4 H, aromatic), 6.55 (br, 3 H, NH), 4.63, 4.54 (2 br resonances, 8 H, C_5H_4), 4.34, 4.29 (br, 8 H, $-CH_2OC(O)$), 4.16 (br, 2 H), 3.62 (s, 79 H, $-(C_2H_4O-)_n$), 2.81 (br, 4 H, $C_5H_4CH_2$), 2.16 (s, 7 H, $-CH_3$). $\bar{M}_n$ (VPO, THF) = 3100 g/mol.

Photochemical Reactions. Photochemical reactions and quantum yield measurements were carried out as previously described.[1,2]

Acknowledgment is made to Amoco Chemical Co. and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. W. R. Grace Co. is acknowledged for a sample of the Hypol 2000 prepolymer.

Registry No. 1, 138815-35-7; (1)($NCO(CH_2)_6NCO$) (copolymer), 138834-50-1; **2**, 138815-36-8; **5** (copolymer), 138815-37-9; 6 (copolymer), 138876-19-4; CCl_4, 56-23-5; $C_5H_5(CH_2)_2NH_2$, 138816-65-6; $Mo(CO)_6$, 13939-06-5; triethyl phosphite, 122-52-1.

Supplementary Material Available: Textual presentation of complete experimental details for the synthesis of the cyclopentadienylethyl *p*-toluenesulfonate, cyclopentadienylethyl azide, and (cyclopentadienylethyl)amine and tables with spectroscopic data describing the photochemical reaction products of complexes 2, 3, 5, and 6 with CCl_4 and $P(OEt)_3$ (11 pages). Ordering information is given on any current masthead page.

Clusters Containing Ynamine Ligands. 5. Coordination and Transformations of an Ynamine Ligand in a Dimanganese Complex. Synthesis and Structural Characterization of $Mn_2(CO)_8[\mu\text{-}MeC_2NEt_2]$, $Mn_2(CO)_8[\mu\text{-}H_2CCC(H)NEt_2]$, $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C_3H_3NEt_2]$, and $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}C_3H_3NEt_2]$

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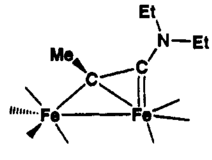
Received October 2, 1991

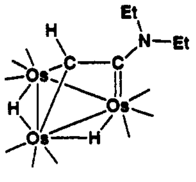
The complex $Mn_2(CO)_8(\mu\text{-}MeC_2NEt_2)$ (1), obtained from the photoreaction of $Mn_2(CO)_{10}$ with MeC_2NEt_2, has been structurally characterized and shown to contain an ynamine ligand asymmetrically bridging the two mutually bonded manganese atoms. The new isomer $Mn_2(CO)_8(\mu\text{-}H_2CCCHNEt_2)$ (2) was isolated in very low yield (0.7%) from this reaction. Compound 2, a second isomer, $Mn_2(CO)_8[\mu\text{-}\eta^2\text{-}C_3H_3NEt_2]$ (3), and a decarbonylation product of 3, $Mn_2(CO)_7[\mu\text{-}\eta^4\text{-}C_3H_3NEt_2]$ (4), were obtained in yields of 16%, 8%, and 22%, respectively, by heating 1 to reflux in THF solvent. All three compounds were characterized by crystallographic methods. Compound 2 is the first example of a metal complex containing a aminoallene ligand. This ligand bridges the two metal atoms. Compound 3 contains a bridging η^2 metalated aminoallyl ligand. Compound 4 contains a bridging η^4 metalated aminoallyl ligand. Crystal data: for 1, space group $P2_1/c$, a = 13.608 (2) Å, b = 13.874 (8) Å, c = 20.044 (3) Å, β = 92.32 (1)°, Z = 8, 2293 reflections, R = 0.053; for 2, space group $P2_1/n$, a = 10.414 (2) Å, b = 24.02 (1) Å, c = 7.618 (2) Å, β = 107.86 (1)°, Z = 4, 1412 reflections, R = 0.040; for 3, space group $P\bar{1}$, a = 10.999 (2) Å, b = 12.684 (3) Å, c = 7.076 (2) Å, α = 93.08 (2)°, β = 107.90 (2)°, γ = 101.63 (2)°, Z = 2, 1891 reflections, R = 0.022; for 4, space group $P2_1/n$, a = 17.904 (2) Å, b = 7.509 (2) Å, c = 24.555 (4) Å, β = 91.19 (1)°, Z = 8, 2180 reflections, R = 0.031.

Introduction

Since their discovery approximately 30 years ago, ynamines or aminoacetylenes, RC_2NMe_2, have proved to be versatile reagents for a variety of organic syntheses.[1] Studies of their coordination in metal complexes have shown that they generally adopt an unusual asymmetric bridging coordination in which the amine-substituted carbon atom is bonded to only one metal atom,[2-6] as is found in the complexes $Fe_2(CO)_7(\mu\text{-}MeC_2NEt_2)$,[2a] $Re_2(CO)_8(\mu\text{-}MeC_2NMe_2)$,[6] and $Os_3(CO)_9(\mu\text{-}HC_2NEt_2)(\mu\text{-}H)_2$.[3]



$Fe_2(CO)_7(\mu\text{-}MeC_2NEt_2)$



$Os_3(CO)_9(\mu\text{-}HC_2NEt_2)(\mu\text{-}H)_2$

A theoretical analysis of the triosmium complex indicated that the unusual coordination can be attributed in

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† On leave from the Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan.

(1) (a) Ficini, J. *Tetrahedron* **1976**, *32*, 1449. (b) Viehe, H. G. *Angew. Chem., Int. Ed. Engl.* **1967**, *9*, 767.

0276-7333/92/2311-1473$03.00/0