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ORIGINAL PAPER

Ring-opening polymerization of $(CH_3)_2Si[CpMo(CO)_3]_2$, a molecule with an $–Si(CH_3)_2–$ bridge between two cyclopentadienyl ligands

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Abstract The $(CH_3)_2Si[CpMo(CO)_3]_2$ complex (**1**) was synthesized and used to explore ring-opening polymerization (ROP) as a method to prepare high molecular weight polymers containing Mo–Mo bonds along their backbones. Attempts to initiate ROP of **1** using *n*-BuLi or $PtCl_2$ did not yield any polymers. The X-ray crystal structure of **1** shows that the Si center is not strained, and it is suggested that no ROP occurred because **1** is less strained than other organometallic ROP monomers, such as the silicon-bridged ferrocenophanes. Thermal ROP (TROP) of **1** was successful and yielded a polymer ($M_w = 210{,}000$ g mol^{-1}) containing both Mo–Mo single bonds and Mo≡Mo triple bonds. When $CO_{(g)}$ is passed over the polymer in the solid state, the Mo≡Mo triple bonds are converted to Mo–Mo single bonds. Attempts to increase the yield of the TROP polymer by increasing the reaction times led to polymer decomposition. The decomposition is likely caused by the weakness of the Mo–Mo bond, cleavage of which causes the polymer to degrade.

Keywords Ring-opening polymerization · Thermal ring-opening polymerization · Metal–metal bonds · Photochemically degradable

Introduction

A long-term goal of our research is to design photochemically degradable polymers that have tunable lifetimes [1, 2]. To prepare such polymers it is necessary to understand the effects of various environmental and molecular parameters on the onset and rate of degradation. The photochemical degradation reactions of polymers are mechanistically intricate, which can make the interpretation of these effects

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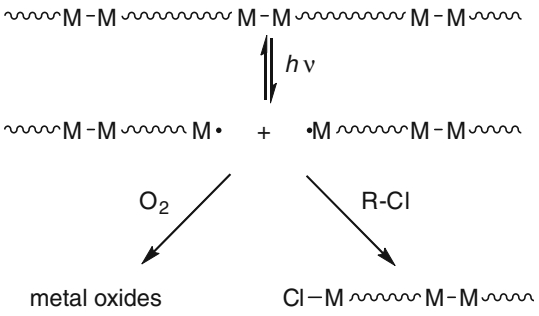


Scheme 1 Photochemical reaction of a polymer with metal–metal bonds along its backbone

difficult [3]. For that reason, we study model polymers with degradation pathways that are less mechanistically complex. In particular, the photochemical degradation of polymers is conveniently studied using polymers that have organometallic molecules containing metal–metal bonds along their backbone [1, 2]. Such polymers are photodegradable because the metal–metal bonds can be cleaved with visible light and the resulting metal radicals captured with an appropriate radical trap, typically O_2 or a molecule with a carbon–halogen bond (Scheme 1) [4]. By studying the photodegradation of these polymers, we have been able to extract information without the mechanistic complications inherent in degradation reactions that involve organic radicals. For example, metal radicals do not lead to cross-linking so we can avoid this complicating feature found with organic radicals. In addition, the metal–metal bond is a chromophore, and its distinctive absorption bands in the visible region can be used to monitor the photodegradation reactions by electronic absorption spectroscopy [5–7]. The use of UV–Vis methods to quantify and compare the various degradation rates is a time-saving technique because polymer degradation reactions have typically been monitored by stress testing, molecular weight measurements, or attenuated total reflection (ATR) spectroscopy, all of which can be laborious and time consuming. The utility of the metal–metal bond-containing polymers in photodegradation studies was demonstrated in previous investigations into the effects of mechanical stress [8], polymer morphology [9], and temperature [10] on polymer photodegradation rates.

Synthetic methods for the preparation of metal-containing polymers are relatively underdeveloped and the incorporation of metal–metal bonds into the backbone of a polymer, in particular, presents a synthetic challenge [2]. The metal–metal bond in organometallic dimers is relatively weak [11, 12] (e.g., $D_{\mathrm{Mo–Mo}} \approx 32$ kcal mol^{-1}) and will not stand up to many of the reaction conditions typically used for the synthesis, isolation, and purification of organic polymers [1]. For example, the metal–metal bond is subjected to disproportionation by the nucleophiles and coordinating solvents that are commonly used in polymerization reactions [1]. Polymerization strategies must therefore be carefully designed to avoid cleavage of the metal–metal bond during polymerization.

In prior articles, we reported methods for synthesizing polymers with metal–metal bonds using step- [13–17], chain-, ADMET- [18, 19], click- [20], and ROMP-methods [1, 2]. To increase the repertoire of methods for synthesizing polymers

with metal–metal bonds along their backbone, we recently began an investigation of ring-opening polymerization (ROP) methods. Anionic ROP has been successfully employed to polymerize a variety of silicon-bridged ferrocenophanes [21, 22]. In this article, we report on ROP methods for the preparation of polymers containing Mo–Mo bonds along their main chain.

Experimental

Materials

All reactions were carried out using Schlenk techniques or in a glove box with a nitrogen atmosphere. The $(CH_3)_2Si(C_5H_5)_2$ ligand and the $Mo(CO)_3(CH_3CN)_3$ complex were prepared according to literature procedures [23, 24]. All HPLC grade solvents were deoxygenated by passing them through columns of alumina and copper oxide under an argon atmosphere. *n*-Butyllithium, platinum (II) chloride, and dichlorodimethylsilane were obtained from commercially available vendors and were used as received.

Instrumentation

^{1}H NMR spectra were recorded on a Varian Unity/Inova spectrometer operating at 299.9 MHz and were referenced to residual $CDCl_3$. Infrared spectra were recorded in a CH_2Cl_2 or $CDCl_3$ solution using a CaF_2 cell with a Nicolet Magna IR spectrometer. Samples for NMR and IR were prepared in a nitrogen glovebox in the dark. Gel permeation chromatography (GPC) was used to determine the molecular weights of the polymer samples with respect to polystyrene standards. GPC was performed using a Waters 515 HPLC pump with HR3 and HR4 Styragel columns and a Waters 4110 Differential Refractometer. DSC analyses were performed at a heating/cooling rate of 10 °C min^{-1} under N_2 using a TA instruments DSC 2920 Modulated differential scanning calorimeter. Samples for DSC analysis were prepared and sealed in aluminum pans under an N_2 atmosphere in a glovebox and maintained under N_2 until analysis.

Synthesis of $(CH_3)_2Si[(C_5H_4)Mo(CO)_3]_2$ (**1**)

The synthesis of **1** was adapted from a literature report [25]. In a 250-mL Schlenk flask, $Me_2Si(C_5H_5)_2$ (0.56 g, 2.97 mmol) was dissolved in THF (100 mL), cooled to −40 °C, and deprotonated by the addition of *n*-butyllithium (4.1 mL, 1.6 M in hexanes). After few minutes, the solution was slowly warmed to 25 °C. $Mo(CO)_3(CH_3CN)_3$ (1.91 g, 6.27 mmol) was added in a dry box and the mixture was stirred at 25 °C. After 24 h, $Fe(III)(NO_3)_3{\cdot}9H_2O$ (3.86 g, 9.55 mmol), dissolved in 20 mL deionized (DI) water with 1 mL acetic acid, was added to the solution. The red THF/H_2O solution was added to a separatory funnel and Et_2O (50 mL) was added, which resulted in separation of the organic and water layers. The organic layer was collected and washed three times with DI water and dried

Table 1 Reaction conditions used for the BuLi-initiated ROP reaction of **1**

Reaction time (min)	[Monomer]:[initiator]	Monomer (mg)	Initiator (μL)
160	10:1	49.1	50
160	50:1	52.1	10
489	100:1	48.3	5

over Na_2SO_4. The solvent was removed under vacuum to yield a red solid. Single crystals were obtained by cooling a solution of the complex in CH_2Cl_3/hexanes. ^{1}H NMR: δ 5.58, 5.29 (C_5H_4, 8H, m); 0.07 (CH_3, 6H, s). IR: ν(C≡O) 2015s, 1959b, 1915b cm^{-1}.

ROP of **1** initiated by *n*-BuLi [21]

The reaction was carried out by the addition of *n*-BuLi (0.18 M in hexanes) to a solution of **1** in THF (2 mL); see Table 1 for the reaction times. The reaction was terminated by the addition of a few drops of DI water. Hexanes were added to precipitate any product, which was then dried under vacuum for 18 h.

Transition metal-catalyzed ROP of **1** [26]

$PtCl_2$ (2.25 mg; 5.5×10^{-4} mmol) was added to a solution of **1** (35 mg; 0.055 mmol) in toluene (5 mL) while under N_2 in a dry box. The solution was stirred at 25 °C for 20 h. The precipitated solid was separated by vacuum filtration and washed with cold THF (3 × 3 mL) and then dried under vacuum for 18 h.

TROP of **1** using DSC

Before bulk-scale reactions, the TROP reactions were performed by differential scanning calorimetry (DSC) to determine optimal thermal reaction conditions. The procedure was adapted from the literature [27]. The sample was heated from 25 to 250 °C at a rate of 10 °C/min. The DSC thermograms showed a melting point of the monomer at ≈120 °C, the possible onset of TROP at 150 °C, and an exotherm, suggesting polymerization occurred.

TROP of **1**

A sample of **1** (50 mg; 0.092 mmol) was placed in an NMR tube while under N_2 in a dry box and sealed with parafilm. The neat sample was heated at 150 °C in an oil bath for 3 h. The reaction was monitored using IR and GPC. The polymer product (**2**) contains both Mo–Mo single bonds as well as Mo–Mo triple bonds. IR after 1 h: ν(C≡O) 2011m, 1955s, 1913m cm^{-1}; IR after 3 h: ν(C≡O) 2011w, 1955s, 1913m, 1892s, 1851s cm^{-1}. GPC: M_n = 140,000 g mol^{-1}, M_w = 210,000 g mol^{-1}.

Reaction of polymer **2** with CO

Polymer **2** (50 mg, 2.38×10^{-7} mmol) was put in a 100-mL Schlenk flask under N_2 and then $CO_{(g)}$ was purged through the flask for 20 min. The product was dissolved in THF for characterization by IR spectroscopy. $\nu(C \equiv O)$: 2011w, 1955s, and 1913m cm^{-1}.

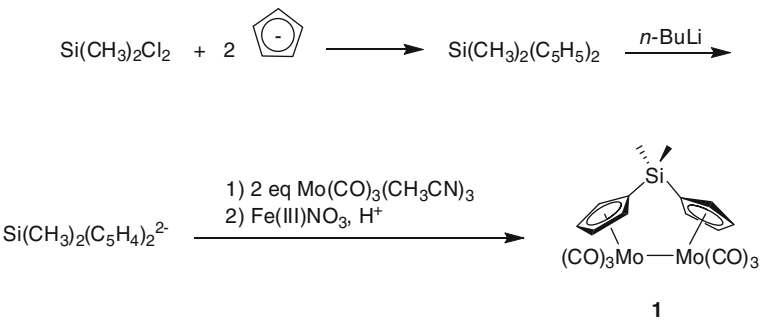
Discussion

Synthesis of $(CH_3)_2Si[(C_5H_4)Mo(CO)_3]_2$ (**1**)

Complex **1** was synthesized by a modification of a literature procedure [25]. The synthesis route is shown in Scheme 2. The product was characterized by ^1H NMR and IR spectroscopy, and the data are consistent with the spectra reported in the literature. Single crystals of **1** suitable for X-ray cystallographic analysis were grown by dissolving the complex in CH_2Cl_2, adding hexanes, and then cooling the solution in a refrigerator at 3 °C. The crystal structure is shown in Fig. 1. Note the complex has a gauche conformation, as expected because of the $Si(CH_3)_2$ unit bridging the two C_5H_4 rings. The C4–Si–C4A angle is 111°, which is essentially unstrained for a tetrahedral Si center. The Mo–Mo bond distance [3.1925(5) Å] is slightly shorter than that of the unbridged $Cp_2Mo_2(CO)_6$ complex (3.222 Å) [28].

ROP of **1**

n-BuLi is generally an efficient initiator for ROP, and therefore the anionic ROP of **1** using *n*-BuLi as an initiator was attempted using conditions described in the literature for successful ROP reactions [21]. A THF solution of complex **1** and *n*-BuLi was stirred for 3 h at 23 °C. After this time, several drops of DI water were



Scheme 2 Synthesis of $(CH_3)_2Si[(C_5H_4)Mo(CO)_3]_2$ (**1**)

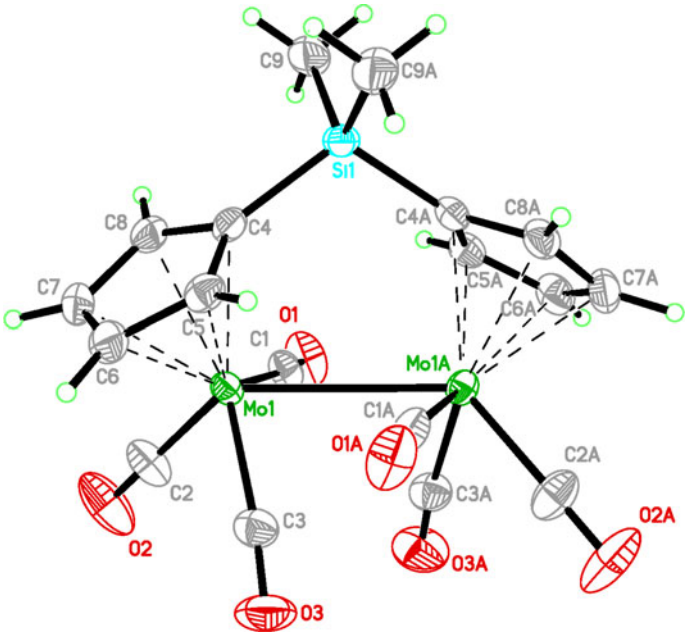


Fig. 1 Thermal ellipsoid plot of complex **1**. Selected bond lengths (Å) and angles (°): Mo(1)–Mo(1), 3.1925(5); Si(1)–C(9), 1.858(2); Si(1)–C(4), 1.872(2); C(2)–Mo(1)–C(1), 75.75(9); C(9)#1–Si(1)–C(9), 112.82(6); C(9)#1–Si(1)–C(4), 109.19

added to terminate the initiation of any further reaction and then hexanes were added to precipitate any product. IR analysis of the precipitate showed that the $\nu(C\equiv O)$ region of the spectrum was unchanged compared to starting material (2011s, 1955s, 1913m cm^{-1}), indicating the dimer unit is still in the gauche conformation. A polymer product would likely yield a *trans* conformation of the Cp rings (which has a different IR spectrum, see "Discussion"). In addition, GPC analysis of the precipitate showed no increase in molecular weight above that of the starting material, and it is concluded that polymerization did not occur. Three different monomer:initiator ratios were used in the reaction (Table 1), but in all cases no reaction occurred. One explanation for the lack of reactivity is that there is insufficient ring strain in **1** to drive the ROP reaction, compared to other molecules (e.g., silicon-bridged ferrocenophanes [21, 27, 29, 30]) that are typically polymerized by this method. As shown in the crystal structure of **1**, the C4–Si–C4A bond angle (111°) is not significantly different from the unstrained tetrahedral value of 109.7°. In comparison, the Cp–Si–Cp bond angle for $Fe(\eta^5\text{-}C_5H_4)_2Si(CH_3)_2$ is only 96° [27].

Additional attempts to do ROP on complex **1** were carried out using $PtCl_2$ as a catalyst [22]. For these experiments, complex **1** was dissolved in toluene and 1 mol% $PtCl_2$ was added. The reaction was stirred at 25 °C for 20 h, during which time a precipitate formed. Infrared spectroscopy of the precipitate dissolved in THF

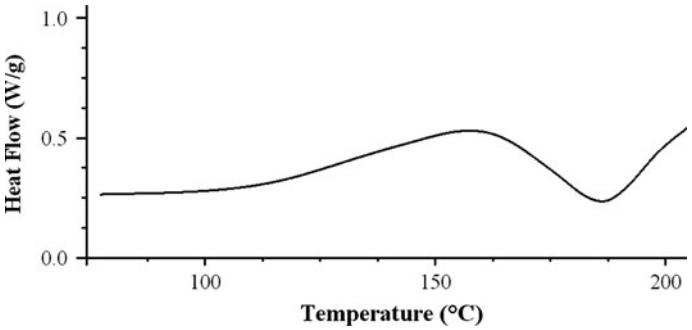


Fig. 2 DSC thermogram of the TROP reaction of complex **1**. The onset of melting is ≈120 °C, and the onset of TROP is ≈155 °C

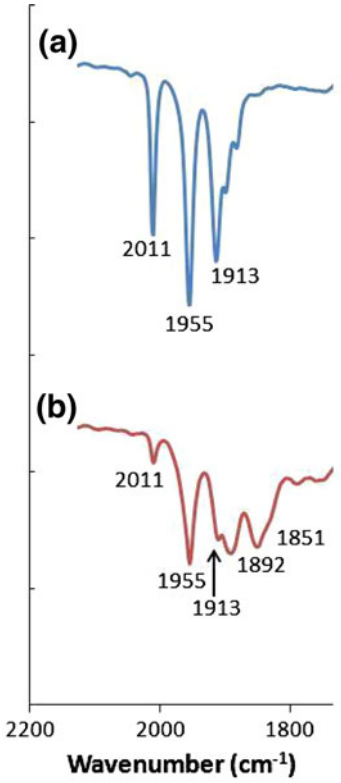


Fig. 3 IR spectra of the TROP reaction of **1** after *a* 1 h and *b* 3 h. The *y*-axis is percentage transmittance

showed no change in the spectrum compared to starting material. In addition, GPC analysis of the precipitate showed no change in the molecular weight compared to starting material. As with the anionic ROP attempt, it is speculated that there is insufficient ring strain to drive the ROP reaction.

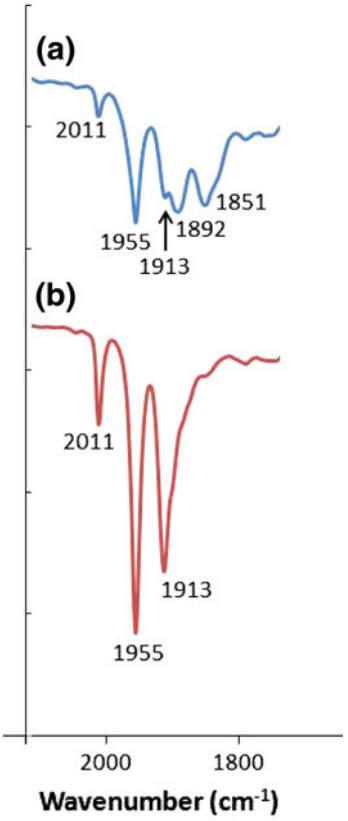
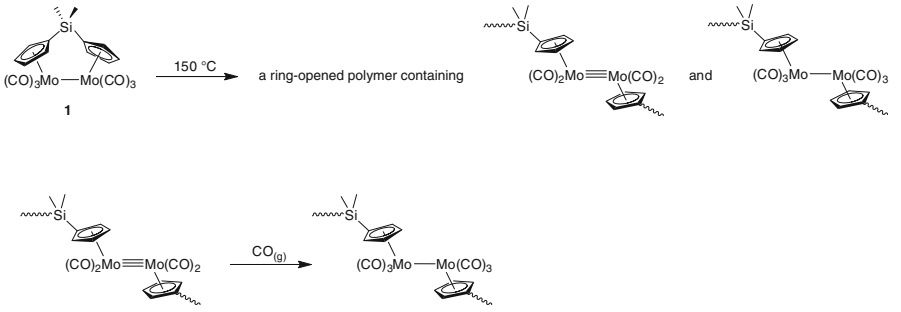


Fig. 4 IR spectra of the TROP reaction of **1** after *a* 3 h and *b* after $CO_{(g)}$ was passed over the sample. The *y*-axis is percentage transmittance



Scheme 3 TROP reaction of complex **1**

Thermal ROP (TROP) of $(CH_3)_2Si[(C_5H_4)Mo(CO)_3]_2$ (**1**)

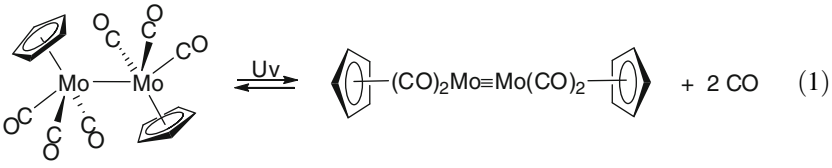
Literature precedents show that ROP can also occur by heating ferrocenylsilanes [27, 31]. In unsymmetrical silicon-bridged ferrocenophanes, the reaction mechanism involves the non-selective cleavage of a Si–C(Cp) bond. The product that

forms is an amorphous regio-irregular polymer, which is not desirable. Consequently, anionic-initiated ROP and transition metal-catalyzed ROP are the preferred synthetic methods for these monomers. However, complex **1** is symmetrical and there will be no problem with non-selective Si–C bond cleavage. The optimum temperature [32] for the TROP polymerization reaction was determined using DSC. The DSC thermogram (Fig. 2) shows that complex **1** melts at $\approx$120 °C and has an exotherm at $\approx$150 °C. The TROP reactions were therefore carried out at 150 °C in a silicone oil bath, and the reaction progress was monitored by IR and GPC. After 3 h, GPC analysis showed a partial conversion of complex **1** to a polymer (M_n = 140,000 g mol^{-1}, $\sim$250 repeat units) with a PDI = 1.5 (M_w = 210,000 g mol^{-1}). In addition to polymer, the GPC analysis showed that a significant amount of starting material remained, as well as a small amount of low molecular weight oligomers. The IR spectrum after 3 h also confirmed that polymerization had occurred. In particular, the carbonyl stretching band at 2,011 cm^{-1} had significantly decreased in intensity compared to the spectrum of the starting material (Fig. 3). In the IR spectrum of a $Cp_2Mo_2(CO)_6$ unit, the intensity of the band at 2,011 cm^{-1} is indicative of the conformation of the Cp ligands [33, 34]. In a molecule with a *trans* conformation, the band is weak but the band is intense for a *gauche* conformation. All of our previous polymers containing the $Cp_2Mo_2(CO)_6$ unit exhibit a weak (or absent) band at 2,011 cm^{-1} [1, 2], indicative of a *trans* conformation, as is expected for steric reasons in molecules without bridges between the Cp rings.

GPC analysis showed that reaction times longer than 3 h resulted in decomposition of the polymer product. For example, after 6 h of reaction, the high molecular weight polymer had completely disappeared and only the starting material and low molecular weight oligomers were present.

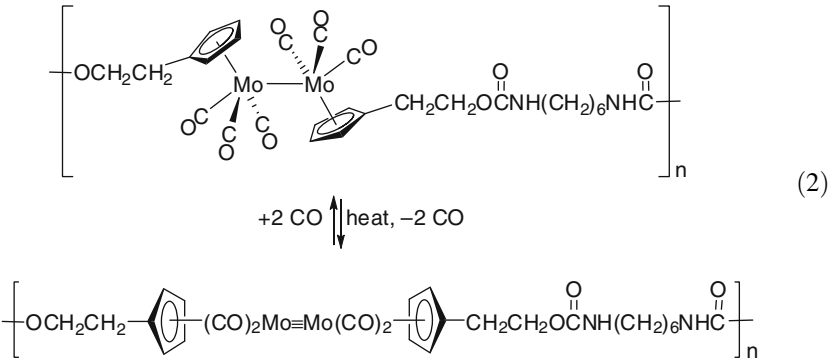
The reversible loss of CO

An interesting reaction of the $Cp_2Mo_2(CO)_6$ molecule is that heating it results in the loss of two CO ligands to form the $Cp_2Mo_2(CO)_4$ complex, which has a Mo$\equiv$Mo triple bond (Eq. 1) [35]



(1)

This reactivity is also found in selected polymers that contain the $Cp_2Mo_2(CO)_6$ unit. For example, careful heating of the polyurethane in Eq. 2 results in a product polymer with a Mo$\equiv$Mo triple bond [14].



(2)

Formation of a Mo≡Mo triple bond also occurred when complex **1** was heated, as evidenced by the growth of two new bands in the IR spectrum at 1,892 and 1,851 cm^{-1} and the decrease in intensity of bands at 1,955 and 1,913 cm^{-1} (Fig. 4) [14, 35]. The former bands are characteristic of the $Cp_2Mo_2(CO)_4$ unit (with a Mo≡Mo triple bond) and the latter two bands are characteristic for those of the $Cp_2Mo_2(CO)_6$ unit. Because both $Cp_2Mo_2(CO)_6$ and $Cp_2Mo_2(CO)_4$ are present, it is suggested that the polymer formed in the TROP reaction contains a mixture of Mo–Mo and Mo≡Mo units.

The $Cp_2Mo_2(CO)_4$ unit reacts readily with CO. Thus, when $CO_{(g)}$ was passed over the $Cp_2Mo_2(CO)_4$-containing polymer for 20 min, the Mo≡Mo triple bond units disappeared and more of the Mo–Mo single bond units appeared, as indicated by the respective decrease and increase in the IR band intensities for these units, Fig. 4 [14]. The TROP reaction and the reaction with CO are summarized in Scheme 3.

Conclusions

The absence of ring strain at the Si center in molecule **1** prevents this molecule from reacting in ROP reactions initiated by anionic initiators or by metal catalysts such as $PtCl_2$. The ROP reaction, however, can be thermally driven, and the result is a high molecular weight polymer with $M_n \approx 140{,}000$ g mol^{-1}. It is tempting to conclude therefore that ROP is a viable method for synthesizing high molecular polymers with metal–metal bonds. However, attempts to increase the yield of polymer by increasing the reaction times led to polymer decomposition. The decomposition is likely caused by the weakness of the Mo–Mo bond, cleavage of which causes the polymer to degrade. Any statement about the usefulness of TROP must be tempered by the usual caution one has when dealing with metal–metal bonded polymers, namely that they are not robust at temperatures above ≈70 °C.

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