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SYNTHESIS AND THERMAL DECOMPOSITION OF POLYMER-BOUND (h^1-BENZYL)PENTACARBONYLMANGANESE*

C.U. PITTMAN, Jr.** and R.F. FELIS***

Department of Chemistry, The University of Alabama, University, Alabama 35486 (U.S.A.)

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Summary

Both linear and cross-linked chloromethylated polystyrenes were treated with pentacarbonylmanganese anion in THF to generate pendant (h^1-benzyl)-pentacarbonylmanganese functions throughout the polymers. The thermal decomposition of $PhCH_2Mn(CO)_5$ at 140° generated $Mn_2(CO)_{10}$ and bibenzyl in high yields in benzene and decane solutions. No hydrogen or toluene was found. Thermal decomposition of both the linear, (II) and cross-linked (III) polymers containing pendant *Pol*—Ph—$CH_2Mn(CO)_5$ groups proceeded similarily, both neat and in solution, resulting in $Mn_2(CO)_{10}$ and *Pol*—Ph—CH_2CH_2—Ph—*Pol*. Polymers containing $Mn(CO)_{10}$ trapped throughout the matrix were prepared. Polymers II and III as well as $PhCH_2Mn(CO)_5$ were studied as hydroformylation catalysts but were not found to be effective.

Introduction

Many organo—transition metal-containing organic polymers have now been prepared. Example classes include polymers where the metal is π-bonded [1—4], chelated as coordination complexes [5], or bound by phosphine or nitrogen ligands [6—9]. These latter polymers are increasingly important because of their use in fixed-bed catalysts for organic synthesis [10—12]. However, polymers where the transition metal is attached to the matrix by a carbon-to-metal σ-bond are virtually unknown. We have found the use of metal carbonyl anions [13] provides particularly convenient routes to incorporate transition metal carbonyl moieties into polymers [10].

One may envision that thermal decomposition of metal carbonyl moieties within a polymer matrix could free metals [14], metal oxides [15, 16], or

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[**] To whom inquiries should be sent.

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organometal carbonyl groups. For example, polyacrylates containing pendant h^4-dieneiron tricarbonyl groups decompose to free Fe_2O_3 in tiny particle sizes within the resin [15]. The thermal or photolytic decomposition of linear polystyrene films, where $—Cr(CO)_3$ units were π-complexed to phenyl rings, resulted in Cr_2O_3 deposition [16].

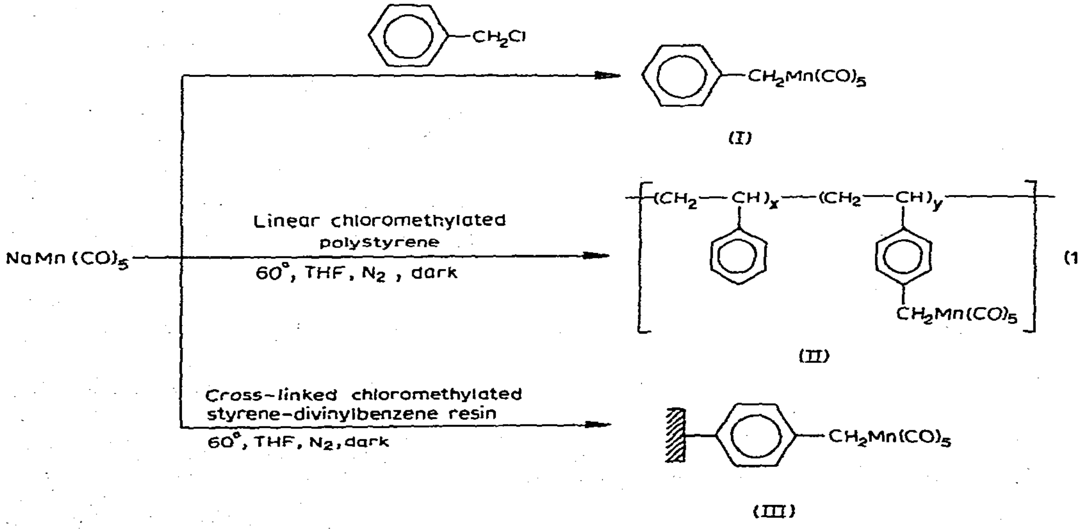
The thermal stability of metal—carbon σ-bonds varies widely. At −35° $CH_3Co(CO)_4$ decomposes [17] while $CH_3W(CO)_3C_5H_5$ is stable to above 145° [18]. Stability of metal—carbon bonds usually increases as the electron withdrawing ability of R does [18]. Benzyl complexes usually decompose rapidly in chlorinated solvents [19]. The thermal decompositions of $EtMo(CO)_3(C_5H_5)$ [20], $PhW(CO)_3(C_5H_5)$ [21], and the photolytic decomposition of $PhCH_2Fe(CO)_3(C_2H_5)$ [22] all give carbon—metal bond cleavage followed by collapse to their corresponding cyclopentadienylmetal carbonyl dimers. Thermal decomposition studies of ^{14}C labeled acetylpentacarbonylmanganese were conducted in connection with its decarbonylation reaction [23, 24], but little work on thermolysis of alkyl- or arylpentacarbonylmanganese derivatives is available.

We report the synthesis of linear and cross-linked polystyrenes containing the $C_6H_5CH_2Mn(CO)_5$ group and the thermal decomposition of these polymers. For comparison we studied the decomposition of $C_6H_5CH_2Mn(CO)_5$ itself. Furthermore, the use of these polymers as hydroformylation [25] catalysts was examined.

Results

Synthesis and characterization

Benzylpentacarbonylmanganese was prepared in 70% yield from the reaction of benzyl chloride with the pentacarbonylmanganese anion [23]. Both linear and cross-linked chloromethylated polystyrene samples were treated with pentacarbonylmanganese anion at 60° in THF (1). The linear chloromethylated polystyrene was prepared from a narrow distribution polystyrene ($\overline{Mw}/\overline{Mn}$ 1.17, Mn 12,100) by the method of Pepper, Paisley and Young [26], except chloromethyl ethyl ether was used in place of chloromethyl methyl ether. Chloromethylation only



slightly broadened the distribution ($\overline{M}w/\overline{M}n$ 1.25). The cross-linked chloromethylated resin used was purchased (Bio-Rad Labs, 14,000 mol. wt, exclusion limit, 1.5 g, 1.6 mmol of Cl). It was pre-swollen for 24 h in THF under nitrogen.

In all cases high yields of metal carbonyl-containing polymer were recovered. Most chlorine was displaced by $Mn(CO)_5$ units despite the low nucleophilicity [27] of $NaMn(CO)_5$. Under similar conditions, the linear chloromethylated polymer reacted more rapidly than the cross-linked resin. For example, after 1 h at 60° in THF, 77% of the chlorine had been displaced from the linear polymer by $Mn(CO)_5^-$ vs. 74% replacement after 6 h for the resin. Many chloromethyl groups lie deep within the pores or channels of the resin and they may be inaccesible, or only reached with difficulty, by the ionic $Na^+Mn(CO)_5^-$ which must diffuse into the hydrophobic resin.

The polymeric metal carbonyls were identified by their IR spectra. The reported CO stretching frequencies of $C_6H_5CH_2Mn(CO)_5$ in cyclohexane [28] are 2106, 2012, and 1992 cm^{-1}. Those observed in the soluble polymer were (in nujol) 2102 and 1992 cm^{-1} while those of the resin-bound species were (KBr) 2100 and 2000. In both polymers the 2100 band was broad and unresolved. Polymer II was also characterized by NMR, intrinsic viscosity, and gel permeation chromotagraphy (GPC). No cross-linking occurred during the reaction of the soluble chloromethylated polymer with $Mn(CO)_5^-$ and the molecular weight distribution broadened only slightly from $\overline{M}w/\overline{M}n$ 1.25 to 1.45.

Thermal decomposition studies

The thermal decomposition of $C_6H_5CH_2Mn(CO)_5$ served as a model for the corresponding polymer decompositions. At 140° $C_6H_5CH_2Mn(CO)_5$ decomposed to give high yields of 1,2-diphenylethane and $Mn_2(CO)_{10}$, neat, in benzene, or in decane (eqn. 2). No other products were detected except small amounts of tar. Representative decomposition yields are summarized in Table 1. Thermolyses in decane or benzene did not produce detectable amounts of toluene, thus ruling out hydrogen abstraction from solvent by benzyl radicals.

$$C_6H_5CH_2Mn(CO)_5 \xrightarrow[\text{Benzene, decane or neat}]{140^\circ,\ N_2} C_6H_5CH_2CH_2Ph + Mn_2(CO)_5 \qquad (2)$$

Benzyl radicals do not readily substitute or abstract hydrogen from benzene or linear hydrocarbons [29, 30], so it was of interest to attempt to trap benzyl radicals produced in these decompositions. Decompositions conducted in dilute (0.001 *M*) cumene solution at 140° gave toluene, not 1,2-diphenylethane, as the major product, in addition to $Mn_2(CO)_{10}$. This strongly implies the intervention of benzyl radical intermediates. Furthermore, hydrogen was not detected in any of these decompositions, carried out in sealed tubes, when the gas phase was examined by mass spectroscopy. This showed that $HMn(CO)_5$, which might later eliminate hydrogen on dimerization, was not formed as an intermediate in significant amounts.

The reaction was followed by IR spectroscopy through the first 15% of the reaction. In benzene, both the disappearance of $C_6H_5CH_2Mn(CO)_5$ and formation of $Mn_2(CO)_{10}$ appeared to follow first order kinetics in this region over the concentration range of 0.4 to 0.02 mol l^{-1}. Thus, it appears that rate determining carbon—manganese bond homolysis occurs followed by self-dimerization of $PhCH_2^{\cdot}$ and $Mn(CO)_5^{\cdot}$.

Decompositions of soluble and cross-linked resins II and III proceeded similarly under nitrogen giving $Mn_2(CO)_{10}$. Soluble polymer II became highly cross-linked during thermolysis. The decomposition of pendant benzylpentacarbonylmanganese groups was faster in solution than when conducted neat. For example, after 8 h, the 2100 cm^{-1} CO stretch exhibited an intensity suggesting about 20% of the benzylpentacarbonylmanganese groups had disappeared. A 16% yield of $Mn_2(CO)_{10}$ was recovered by extraction. The greater decomposition rate in solution might be attributed to the greater mobility of radicals in solution. In the neat solid, initial carbon—manganese homolysis could reverse readily due to matrix immobilization.

$$Pol\text{—}PhCH_2Mn(CO)_5 \overset{140^\circ}{\rightleftharpoons} Pol\text{—}PhCH_2^{\bullet} + {}^{\bullet}Mn(CO)_5 \rightarrow Pol\text{—}PhCH_2CH_2Ph\text{—}Pol + Mn_2(CO)_{10} \qquad (4)$$

The $Mn_2(CO)_{10}$, from polymer thermolyses, was recovered by swelling followed by benzene or THF extraction. However, $Mn_2(CO)_{10}$ was deposited within the matrix of the cross-linked resin beads when they were decomposed in a poor so vent for the polymer such as decane. IR spectroscopy confirms that $Mn_2(CO)_{10}$ is posited in the polymer. The bands at 2100 and 2000 cm^{-1} were replaced by the three band pattern characteristic of $Mn_2(CO)_{10}$. Here, the polymer structure was not swollen but was "collapsed" and $Mn_2(CO)_{10}$ molecules had limited mobility as they formed. Hence they were trapped in a very fine dispersion throughout the body of the bead. When more highly cross-linked (i.e. 2.5% divinylbenzene) resins were used, the mobility decreased. Some $Mn_2(CO)_{10}$ can be thought of as "dissolved" in the plastic matrix. It was possible to recover a portion of this $Mn_2(CO)_{10}$ formed by swelling and extracting with THF and benzene.

Attempts to catalyze hydroformylation

Alkyl- [31], benzyl- [31, 32] and acyl- [31] pentacarbonylmanganese were

TABLE 1

THERMAL DECOMPOSITIONS OF (h^1-BENZYL)PENTACARBONYLMANGANESE AND ITS POLYMER-BOUND ANALOGS AT 140° FOR 8 h UNDER NITROGEN

Species decomposed	Solvent [a]	Products isolated		
		$Mn_2(CO)_{10}$	$PhCH_2CH_2Ph$	Tar [b]
I	Neat	77	65	8
I	Decane	84	78	3
I	Benzene	86	77	3
I	Cumene	85	[e]	2
II	Neat	16 [c]	[f]	
II	Benzene	54	[f]	
III	Neat	8 [c]	[f]	
III	Decane	12 [d]	[f]	
III	Benzene	48	[f]	

[a] Reactions in solution. [b] Yield based on weight of the starting material. The tar contained benzyl and manganese carbonyl moieties. It was not further purified. [c] Recovered by THF and benzene extraction of thermolyzed polymer. After 40 h at 140° a 30% yield of $Mn_2(CO)_{10}$ was obtained from II. [d] $Mn_2(CO)_{10}$ was recovered by THF and benzene extraction. Heating in decane for 70 h gave an appreciable build up of $Mn_2(CO)_{10}$ within the polymer matrix. A 32% yield of $Mn_2(CO)_{10}$ was isolated on extraction and more $Mn_2(CO)_{10}$ was trapped in the resin (IR). [e] Toluene formed. Only traces of 1,2-diphenylethane were detected. [f] Any 1,2-diphenylethane units formed would be part of the polymer matrix.

claimed to be potent hydroforylation catalysts. Although high yields of products were reported in the examples cited, the fate of the catalyst was not discussed. As part of a program to anchor homogeneous catalysts to polymers [6, 10], we investigated hydroformylation of cyclohexene and 1-pentene over $C_6H_5CH_2$-$Mn(CO)_5$ and polymeric catalysts II and III. The only difference between the patent reports and those reported here was the use of the olefin as a solvent in the previous studies. Benzene was employed in order to keep the polymer networks swollen and temperatures were varied between 115—150°.

In all cases only 1,2-diphenylethane, $Mn_2(CO)_{10}$, unreacted olefin, and traces of aldehyde were recovered from the reaction. When linear polymer II or cross-linked resin III was used, large amounts of $Mn_2(CO)_{10}$ were recovered, and analysis showed a drastic drop in the percent metal in the recovered polymer. In one example, polymer II analyzed for 3.67% Mn before the reaction vs. 0.42% afterwards. Only very small amounts of aldehyde were obtained (< 1%) when pressures to 2000 psi were employed, and different ratios of carbon monoxide and hydrogen had no effect. Clearly, thermolysis of the catalyst took place at a faster rate than hydroformylation in the temperature range from 115—150°. The aldehyde formed was not due to catalysis by $Mn_2(CO)_{10}$, since attempts to catalyze the reaction with $Mn_2(CO)_{10}$ (1500 psi, 1/1 H_2 and CO in benzene, 120—140°, 12 h) failed. Hydroformylation might compete with decomposition at greater H_2/CO pressures. One experiment with 1-pentene at 4500 psi and 1/1 H_2/CO gave a 5% yield of hexanal (branched/normal ratio = 0.23) at 135°. It is apparent that $C_6H_5CH_2Mn(CO)_5$ derivatives are not good hydroformylation catalysts for the conditions used here as had been intimated before [31, 32].

Experimental

IR spectra were recorded on a Beckman IR-33 or on a Perkin Elmer 337 and NMR spectra on a 60 MHz Hitachi—Perkin Elmer R-20B spectrometer. GPC was performed using a Waters model 301 instrument and mass spectra on a CEC Model 21-104. Melting points were uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. and by Meade Microanalytical Laboratories, Amherst, Mass. Gas chromatography studies used a Varian Aerograph 90P3 Type GC. Percent yields are reported as percents of the isolated product after final purification unless stated otherwise.

Synthesis of chloromethylated polystyrene

Polystyrene ($\bar{M}w/\bar{M}n$ 1.17, $\bar{M}n$ 12,100; 50g, 0.48 mol of phenyl rings) was dissolved in chloromethyl ethyl ether (300 ml) under nitrogen and heated to 45° with vigorous stirring. To this, 62 ml of the ether (making 3.95 total moles) containing anhydrous stannic chloride (6.75 ml, 0.0572 mol) was introduced. The color of the solution changed immediately to light green from pale yellow. The reaction proceeded exactly 3 min and 10 sec and was quenched by adding wet 1,4-dioxane (35 ml) which caused a return to its original color. The solution was precipitated in methanol (6 l) after cooling. The polymer was reprecipitated twice from THF into a 2/1; MeOH/H_2O solution (4 l), and dried in vacuo (60°, 1 mm, 24 h) to give quantitative yields of the polymer: IR (film) exhibited characteristic polystyrene and chloromethylated polymer bands with two major absorptions at

1268 cm^{-1} (X—CH$_2$ wagging) and 828 cm^{-1} (*p*-disub. benzene C—H bending); (CS$_2$): δ 6.97 (broad s, *m*- and *p*-phenyl C—H), 6.43 (broad s, *o*-phenyl C—H), 4.38 (s, CH$_2$—Cl), 2.1—1.0, ppm (very broad m, chain protons); integration indicated 0.18 Cl per phenyl group. Found: C, 84.89; H, 7.28; Cl, 7.49; O, 0.0% (i.e. 0.25 Cl per phenyl ring). The GPC showed no cross-linking and only slight broadening of the molecular weight distribution. Using conditions described above, reaction for 1 h 25 minutes gave 0.36 Cl per phenyl group. Reacting 3 h resulted in 0.54 Cl per phenyl group.

Synthesis of (h^1-benzyl)pentacarbonylmanganese

A 1% (by wt.) sodium amalgam was used to reduce Mn$_2$(CO)$_{10}$ (2.5 g, 5.0 mmol) in dry deoxygenated THF (100 ml). After 3 h the dark gray anion solution was decanted under nitrogen through glass wool; benzyl chloride (1.15 ml, 10 mmol) was added slowly by syringe, and the mixture was heated to 60° for 30 min in the dark. Now the solution was bright yellow and NaCl was observed. Centrifugation removed NaCl and solvent was removed in vacuo at 25°. Trituration with 30—60° pet. ether gave a sandy colored solid whose sublimation (70°, 1 mm) produced 2.1 g of pale-yellow powder, (70% yield): IR(CS$_2$) 3080m, 3068m, 3030s, 2965m, 2945m; ν(CO) 2100s, 2010vs, 1990vs, 1220m, 1100m, 763vs, 704vs, 652vs cm^{-1}; NMR(CS$_2$): δ 7.07 (s, 5H, phenyl-H), 2.38 (s, 2H, CH$_2$): mass spectrum (70 eV) *m/e* (rel intensity): 286 parent peak; 230 (0.02) $C_6H_5CH_2Mn(CO)_3^+$, 202 (0.034) $C_6H_5CH_2Mn(CO)_2^+$, 174 (0.031) $C_6H_5CH_2MnCO^+$, 146 (0.115) $C_6H_5CH_2Mn^+$, 91 (1.00) $C_6H_5CH_2^+$, 65 (0.203) $C_5H_5^+$, 55 (0.520) Mn$^+$; m.p. 35—36°, lit. 37.5—38.5°.

Synthesis of polystyrene-bound (h^1-benzyl)pentacarbonylmanganese

A pentacarbonylmanganese anion solution, produced from Mn$_2$(CO)$_{10}$ (2.5 g, 5 mmol) in the same manner described above, was decanted under nitrogen into a dry deoxygenated THF solution containing chloromethylated polystyrene (5 g, 10 mmol of Cl). The reaction mixture was heated in the dark for 1 h at 60°, with stirring. Following centrifugation and filtration, THF solutions of the polymer were precipitated three times in methanol (2000 ml). The resulting powder then was dried in vacuo for 24 h at room temperature to give 4.8 g of the title polymer. IR (nujol): ν(CO) 2100s, 2000vs; remaining bands (KBr): 3070w, 3060m, 3020s, 2920s, 2925m, 1601s, 1495s, 1460s, 1260w, 1080m, 1030m, 750vs, 700vs cm^{-1}. NMR (CS$_2$): δ 6.98 (s, *p*- and *m*-phenyl, H), 6.45 (s, *o*-phenyl-H), 4.40 (very small s, —CH$_2$Cl), 2.30 (s, —CH$_2$—), 2.1—1.0 (very broad, chain protons); $|\eta|$ (THF, 30°) 0.132 d l g^{-1}; GPC (THF, 30°) $\overline{Mw}/\overline{Mn}$ 1.45. GPC indicated no crosslinking. Found: Mn, 6.64; Cl, 1.59. Calcd. for polymer where all chlorine is displaced: Mn, 8.65; Cl, 0.0%.

Synthesis of styrene—divinylbenzene-bound (h^1-benzyl)pentacarbonylmanganese

Reduction of Mn$_2$(CO)$_{10}$ (0.32 g, 0.794 mmol) for 3 h with a 1% Na amalgam in dry deoxygenated THF (60 ml) gave Na$^+$Mn(CO)$_5^-$. This solution was decanted under nitrogen into chloromethylated Bio-Beads (Bio-Rad Labs, 14,000 mol. wt. exclusion limit, 1.5 g, 1.6 mmol of Cl) that had been preswollen for 24 h in THF (100 ml). After stirring at 60° for 6 h in the dark, the beads were extracted three times (24 h) with deoxygenated THF. IR (KBr): 3060w, 3020m, 2920s, 2850m; ν(CO) 2100s, 2000vs; 1601s, 1490s, 1455s, 1070s, 1030m, 905m, 820m, 760s, 700vs cm^{-1}. Found: Mn, 3.67; Cl, 2.99. Calcd. for beads where all chlorine is displaced: Mn, 4.97; Cl, 0.00%.

Thermolysis of (h^1-benzyl)pentacarbonylmanganese in decane

The title compound (1.00 g, 3.55 mmol), dissolved in nitrogenated decane (50 ml), was heated to 140° for 8 h. TLC (pentane, silica gel) indicated the presence of only 1,2-diphenylethane and $Mn_2(CO)_{10}$. The decane was removed in vacuo at 50°. The mixture was dissolved in 30—60° pet. ether under nitrogen and $Mn_2(CO)_{10}$ crystallized at −78° (0.58 g, 1.49 mmol). IR: ν(CO) (nujol), 2045s, 2020vs, 1980s cm^{-1}. The 1,2-diphenylethane was isolated from 0.08 g of tar by chromatography over silica gel (0.25 g, 1.38 mmol). In decompositions of 10^{-1} *M* solutions of I, toluene was not found by GLC. Blank runs indicated a 2% yield of toluene could easily be detected.

Thermolysis of (h^1-benzyl)pentacarbonylmanganese in benzene

In a pyrex tube $C_6H_5CH_2Mn(CO)_5$ (1.00 g, 3.55 mmol), dissolved in dry benzene (50 ml), was heated for 8 h at 140° under nitrogen. The reaction mixture became turbid. TLC revealed the presence of $Mn_2(CO)_{10}$ and 1,2-diphenylethane plus a little tar. Centrifugation separated the tar (0.03 g) which exhibited: IR: ν(CO) (nujol), 2040s, 2020vs, 1975s, 1920s cm^{-1}. The benzene solution was concentrated, chromatographed (alumina, 30—60° pet. ether) to give $Mn_2(CO)_{10}$ (0.59 g, 1.53 mmol) and 1,2-diphenylethane (0.24 g, 1.36 mmol). 1,2-diphenylethane exhibited: IR (CS_2) identical with an authentic sample; mass spectrum (70 eV) *m/e* (rel intensity) 182 (0.231) parent peak, 91 (1.00) $C_6H_5CH_2^+$, 65 (0.218) $C_5H_5^+$. $Mn_2(CO)_{10}$ IR: ν(CO) (nujol), 2040s, 2020s, 2020vs, 1980s cm^{-1}. Decompositions employing 10^{-1} *M* solutions of I were examined unsuccessfully by GLC for toluene.

Thermolysis of (h^1-benzyl)pentacarbonylmanganese in cumene

In deoxygenated, triply-distilled cumene (1 l) $C_6H_5CH_2Mn(CO)_5$ (1.00 g, 3.55 mmol) was dissolved. Another 1 g sample was dissolved in 50 ml of cumene. Both were decomposed at 140° for 8 h. In both, toluene was detected by GLC (18% dinonyl phthalate on Chromosorb W, 6′, ¼″, 110—150°). By comparison to standard toluene—cumene solutions, it was estimated that, at least, 90% of the benzyl groups in I gave toluene in the more dilute solution and, at least, 75% did so in the more concentrated solution. $Mn_2(CO)_{10}$ was isolated in 85% yield.

Neat thermolysis of soluble polymer II

Polymer II (0.368 g, 0.44 mmol of Mn) was degassed, nitrogenated, and heated for 8 h at 140°. Extraction (benzene) of the thermolysis product and evaporation gave a yellow powder as the sole product with the same R_f (TLC) value as $Mn_2(CO)_{10}$. IR ν(CO) (nujol): 2055vs, 1980s cm^{-1}. The remaining insoluble resin was dried. IR (KBr): broad OH peak 3600—3200m, 3060w, 3030m, 3000s, 2900s, 2820m, 2100m, 2035—2000s, 1960m, 1800w, 1600s, 1490s, 1450s, 810m, 750m, 695s, 645s cm^{-1}. IR ν(CO) (nujol): 2100s, 2000s cm^{-1}. The intensity of the carbonyl bands at 2100 and 2000 cm^{-1} demonstrated that 80% of the pendant $PhCH_2$—$Mn(CO)_5$ groups remained. Extraction of the cross-linked polymer for 24 h with THF (50 ml) and benzene (50 ml), evaporation, and liquid chromatography of the residue gave $Mn_2(CO)_{10}$ (14 mg, 35 mmol, 16% yield).

Thermolysis of soluble polymer II in benzene

Polymer II (1.00 g, 1.21 mmol of Mn) was dissolved in benzene (40 ml), degassed, and heated for 8 h at 140° giving a yellow gel on the sides of the tube. Filtration and precipitation into 30—60° pet. ether gave traces of polymer (0.03 g) IR (KBr): broad 3600—3200m, 3060w, 3040m, 3010s, 2900s, 2095m, 2000s, 1935m, 1601s, 1490s, 1460s, 820m, 760s, 700s cm^{-1}. TLC (benzene/pentane 30/70) of a yellow powder from the filtrate showed only one spot (R_f value of $Mn_2(CO)_{10}$). IR ν(CO) (nujol): 2040s, 2010vs, 1975s cm^{-1}. The gelled resin was extracted with benzene (24 h, under nitrogen) and dried. IR (KBr): broad 3600—3200s, 3060w, 3040m, 3000s, 2890s, 2825w, 2100m, 2000s, 1940m, 1600s, 1490s, 1450s, 825m, 755s, 695s cm^{-1}. The bands at 2100m and 2000s cm^{-1} indicated some $Mn(CO)_5$ groups were still intact after 9 h. Intensity measurements showed ≈ 10% as many pendant-$Mn(CO)_5$ groups were present as in samples decomposed neat. Extraction of the decomposed polymer with THF (50 ml) and benzene (50 ml), for 24 h gave $Mn_2(CO)_{10}$ (0.13 g, 0.33 mmol).

Thermolysis of insoluble resin III in decane, benzene, and neat

Beads of polymer III (2.00 g, 1.33 mmol of Mn) were placed in a glass tube, degassed, and heated to 140° for 8 h giving a yellow brown product that was extracted (benzene, 24 h) and dried. IR ν(CO) (nujol): 2100w, broad 2000—1900w, 1870w, 1880w, 1600s, remaining bands (KBr) 3060w, 3030m, 3000s, 1480s, 1450s, 1025m, 900m, 750s, 700s cm^{-1}. Approximately 10% of the $Mn(CO)_5$ groups decomposed. An 8% yield of $Mn_2(CO)_{10}$ was obtained. Polymer III (2.00 g, 1.33 mmol of Mn): was also decomposed in decane and benzene. The beads were swollen for 24 h under nitrogen. In decane the beads swell very little. The swollen resin was heated for 8 h at 140° and the solvent became yellow. TLC indicated $Mn_2(CO)_{10}$ was present and evaporation gave $Mn_2(CO)_{10}$: IR ν(CO) (nujol): 2040s, 2020vs, 1980s cm^{-1}. The polymer, decomposed in decane, exhibited IR bands showing $Mn_2(CO)_{10}$ was trapped in the matrix with most of the original *Pol*—$Mn(CO)_5$ groups. These beads were extracted with benzene to give $Mn_2(CO)_{10}$ (16%). The remaining polymer showed: IR: 3060w, 3045m, 3070s, 2900s, 2818m, 2100m, 2000s, 1600s, 1490s, 1455s, 1030m, 910m, 815m, 760s, 700s cm^{-1}. The band intensities at 2100 and 2000 showed that < 5% of the $Mn(CO)_5$ groups remained after decomposition in benzene. Extraction with both benzene and THF recovered a 48% yield of $Mn_2(CO)_{10}$.

Analysis for hydrogen

The gas phase components of the decompositions were analyzed by mass spectroscopy, but hydrogen was not detected. Also, I (5×10^{-2} mol) was decomposed in degassed benzene (100 ml) in a sealed tube with a 30 ml gas volume. Analysis of the gas phase after decomposition vs. standard gas samples demonstrated no hydrogen was generated.

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