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SYNTHESIS AND THERMAL DECOMPOSITION OF $(h^1\text{-}C_6H_5CH_2)(h^5\text{-}C_5H_5)Fe(CO)_2$, $(h^1\text{-}C_6H_5CH_2)(h^5\text{-}C_5H_5)M(CO)_3$ (M = Mo AND W), AND THEIR POLYMER-BOUND ANALOGS*

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Summary

$(h^1$-Benzyl) $(h^5$-cyclopentadienyl)dicarbonyliron, I, $(h^1$-benzyl) $(h^5$-cyclopentadienyl)tricarbonylmolybdenum, II, and its tungsten analog, III, have been prepared, along with linear and crosslinked polystyrenes with I, II, and III as pendant moieties, by the reaction of the corresponding metal carbonyl anions with benzyl chloride. The thermal decomposition of I neat, in decane, or in benzene at 140° gave first order carbon—iron bond homolysis and h^5-cyclopentadienyldicarbonyl dimer, XI, its monobenzylated analog $(C_6H_5CH_2C_5H_4)(C_5H_5)$-$Fe_2(CO)_4$, XII, dibenzyl, and tar. The mole ratio of XI/XII varied between 8—12. Neat decomposition of polymers containing bound I was slow at 140°, but in solution decomposition proceeded to give XI, and polymer-bound dimer XIV at 160° was detected. Similarly, thermal decomposition of II gave $(C_5H_5)_2$-$Mo_2(CO)_6$, XV, and its benzylated analogs $(C_6H_5CH_2C_5H_4)(C_5H_5)Mo_2(CO)_6$, XVI, and $(C_6H_5CH_2C_5H_4)_2Mo_2(CO)_6$, XVII, while decomposition of III gave $(C_5H_5)_2W_2(CO)_6$, XVIII, $(C_6H_5CH_2C_5H_4)(C_5H_5)W_2(CO)_6$, XIX, and $(C_6H_5CH_2C_5H_4)_2W_2(CO)_6$, XX. In these cases benzyl migration to Cp rings predominates even in solution. Solution decompositions also generated dibenzyl except in cumene where toluene was formed. For the decompositions of II and III the results suggest the migrating benzyl groups never become separated from the developing dimer and might "ride up" to attack the *endo* side of the Cp rings. Both linear and crosslinked polymers with pendant units of II and III composed very slowly neat in the solid phase, faster in solution, and in both modes dimers XV and XVIII formed in addition to polymer-bound benzylated analogs of XVI and XIX. Crosslinked polymers were prepared with dimers XI, XV, and XVIII dispersed throughout.

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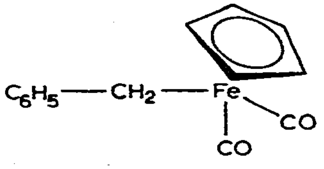
Introduction

During the past several years we have synthesized a variety of transition metal-containing organic polymers in order to uncover unusual properties [1—5]. Conductivity was exhibited by mixed-valence organometallic polymers [6,7]. Polymer-bound organometallic catalysts which function homogeneously while bound to swellable, but insoluble resins [8,9] were made. Polymer-bound organometallic groups have been subjected to thermal [10], or photochemical [11], and oxidative [12] degration to free metal, metal oxides, or metal carbonyl compounds finely divided throughout the matrix.

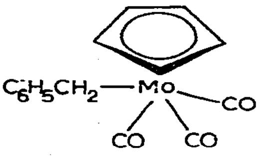
Collman [12] prepared a styrene-divinylbenzene resin with rhodium metal clusters inside the matrix. Upon treatment with carbon monoxide and extraction from the polymer, $Rh_6(CO)_{16}$ was recovered. Pittman et al. [10] demonstrated that thermal decomposition of bound h^4-dienetricarbonyliron groups gave polymers with finely dispersed Fe_2O_3 and that tricarbonylchromium-complexed polystyrene films, on exposure to sunlight, released Cr_2O_3 in the films [11].

Advances in metal carbonyl anion chemistry [13] provided facile routes to polymers where the organometallic group is affixed to the polymer via pendant σ carbon—metal bonds. Treating chloromethylated polystyrene resins with $NaMn(CO)_5$, introduced pendant *Pol*—$C_6H_4CH_2Mn(CO)_5$ functions in polymers [14]. Thermal decomposition at 140° released $Mn_2(CO)_{10}$ within the matrix [14]. In this paper we report the synthesis and thermal decomposition of h^1-benzyl-h^5-cyclopentadienyldicarbonyliron, I, h^1-benzyl-h^5-cyclopentadienyltricarbonylmolybdenum, II (and tungsten, III), and their linear and crosslinked polymers *Pol*—$C_6H_4CH_2M(CO)_x(C_5H_5)$ to which I, II, and III have been affixed.

Thermal decomposition of I had not been studied, although I was known to decompose at 140—150° in air [15]. This task was undertaken to serve as a prototype for the corresponding polymer thermolysis. Irradiation of I (70 h, 25°) in hexane and under argon, gave a 70% yield of the dimer $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ [16]. Thermolysis and photolysis of II, $PhCH_2Mo(CO)_3(h^5\text{-}C_5H_5)$, gave small amounts of the π-complex, IVa and $[h^5\text{-}C_5H_5Mo(CO)_3]_2$ [17]. Benzyl migration to the Cp rings was not mentioned [17]. Similarly, Cotton and Marks [20] found that vacuum pyrolysis of $p\text{-}CH_3C_6H_4CH_2Mo(CO)_3C_5H_5$ and its tungsten analog gave an 11% yield of IVb and a 26% yield of IVc respectively. Wilkinson [18] and Nesmeyanov [19] demonstrated that homolytic carbon—metal bond cleavage (with predominant migration of ethyl and phenyl to the Cp rings) was the major path involved in the decomposition of the related complexes V and VII respectively (eqns. 1 and 2).



(I)



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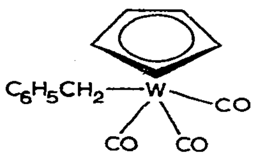

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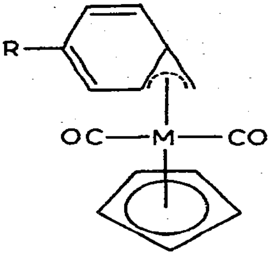
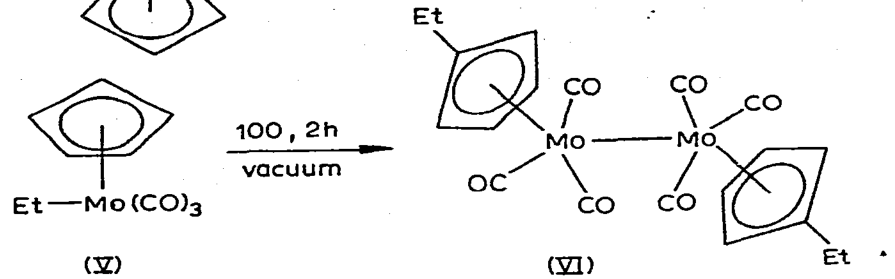
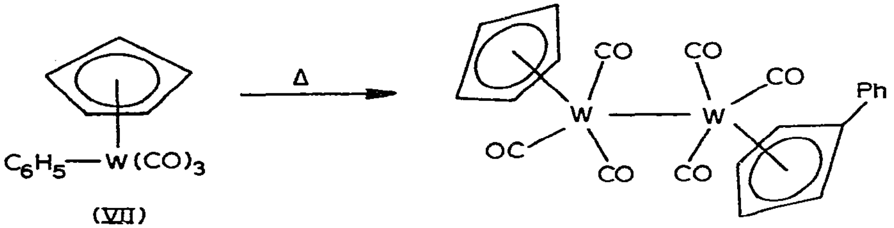


(IVa) M = Mo, R = H
(IVb) M = Mo, R = CH_3
(IVc) M = W , R = CH_3



(V) (VI) (1)



(VII) (2)

Results and discussion

(h^1-Benzyl) (h^5-cyclopentadienyl)dicarbonyliron, I [15], and both its linear and crosslinked polymeric analogs, *Pol*—$C_6H_4CH_2Fe(CO)_2(h^5\text{-}C_5H_5)$ were prepared by the reaction of the h^5-cyclopentadienyldicarbonyliron anion [21] with benzyl chloride or chloromethylated polystyrene in THF (eqn. 3). Linear polymer, VIIIa was obtained in about 65% yield due to difficulties in purification, but replacement of chloride was complete. Reaction of $[h^5\text{-}C_5H_5Fe(CO)_2]^-$ with crosslinked, chloromethylated, styrene—divinylbenzene resins (Bio Rad Labs SX-1, 200—400 mesh, mol. wt. 14000 exclusion limit), previously swollen in THF, gave complete displacement of chlorine in 3 h at 25°. This contrasts with

$$Na^+[h^5\text{-}C_5H_5Fe(CO)_2]^- \xrightarrow[\text{THF}]{PhCH_2Cl,} PhCH_2Fe(CO)_2(h^5\text{-}C_5H_5) + NaCl$$

(I) 51%

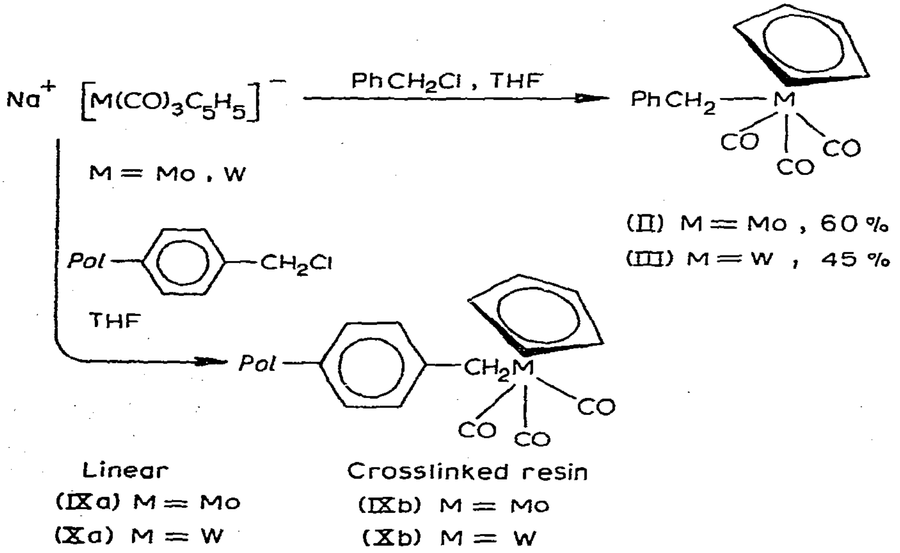
$$\xrightarrow[\text{THF}]{Pol\text{—}C_6H_4CH_2Cl} Pol\text{—}C_6H_4CH_2Fe(CO)_2(h^5\text{-}C_5H_5) \qquad (3)$$

(VIIIa) = linear polystyrene
(VIIIb) = styrene-divinylbenzene resin

the same reactions of this chloromethylated resin with less nucleophilic [22] $[Mn(CO)_5]^-$, where about 80% of the chloride was displaced in 6 h at 60° [23].

The linear polymers VIIIa (where the Fe to phenyl ring ratio varied from 0.15 to 0.30) were soluble in common organic solvents (benzene, THF, CH_2Cl_2). Films were readily cast from CS_2 and CCl_4. The linear chloromethylated polystyrene used in the synthesis of VIIIa was prepared from a narrow mol. wt. distribution (via GPC* $\overline{M}_w/\overline{M}_n = 1.17$, $\overline{M}_n = 12100$) sample. After chloromethylating 25% of the rings and reaction with $[h^5\text{-}C_5H_5Fe(CO)_2]^-$, the distribution increased only slightly to $\overline{M}_w/\overline{M}_n = 1.32$ [23]. No crosslinking was evidenced by GPC. Polymers VIIIa and VIIIb exhibited carbonyl stretching frequencies. ν(CO) (film) 2010 vs and 1945 vs cm^{-1} for VIIIa and (KBr) 2000 vs and 1950 vs cm^{-1} for VIIIb, matching those published [24] for I ($HCCl_3$) ν(CO) 2009 vs and 1951 vs.

Syntheses of II and III were carried out by the method of King and Fronzaglia [17] where the metal carbonyl anions were each treated with benzyl chloride (eqn. 4). As with VIIIa, narrow mol. wt. distribution ($\overline{M}_w/\overline{M}_n = 1.25$) chloromethylated polystyrene or chloromethylated styrene—divinylbenzene swellable resin (Bio Rad SX-2, 3.0 g, 3.14 mmole Cl) were treated with either excess $Na^+[Mo(CO)_3C_5H_5]^-$ or $Na^+[W(CO)_3C_5H_5]^-$ to generate the corresponding polymers IXa, IXb, Xa, and Xb.



(4)

GPC studies of linear polymers IXa, M = Mo, and Xa, M = W, showed small amounts of branching occurred during reaction with the metal carbonyl anions. Polymers IXa, IXb, Xa, and Xb initially analyzed for more than the theoretical amounts of Mo or W, and their IR spectra exhibited, strong carbonyl bands characteristic of $PhCH_2M(CO)_3C_5H_5$ groups (2020 and 1940 cm^{-1}, M = Mo and 2010 and 1930 cm^{-1}, M = W [17, 20]), an extra band at 3600—3200 (hydrogen bonded OH) and spectral distorsions at 990 and 740 cm^{-1}. The impurity was characterized as hydrated molybdenum (or tungsten) oxides produced from traces of moisture [25] despite use of dry solvents and glassware. Thus, the linear polymers were

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* GPC = gel permeation chromatography.

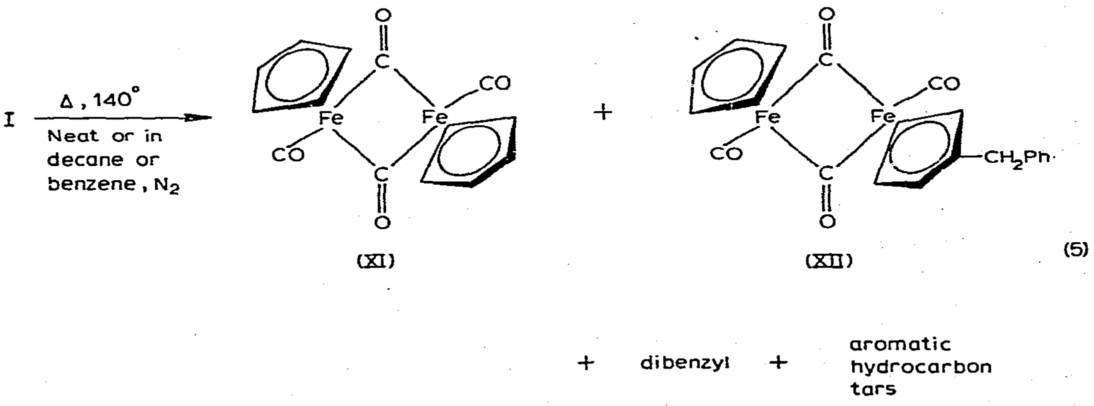
repeatedly reprecipitated from THF into hexane until no further change in analysis occurred. The crosslinked resins were exhaustively extracted with THF and benzene. Despite this, some impurity remained in both linear and crosslinked polymers.

Thermal decompositions

Decomposition of I at 140° neat, in decane, or in benzene gave h^5-cyclopentadienyldicarbonyliron dimer, XI, in high yields, small amounts of the monobenzylated dimer XII, dibenzyl, XIII, and a tar (eqn. 5). Apparently the tar results from reactions of benzyl radicals (no iron was present). Between eight to twelve moles of dimer XI were produced per mole of monobenzylated dimer XII. The products were each characterized by NMR, IR and mass spectrometry; melting points and yields are summarized in Table 1. Dibenzylated dimer $[(PhCH_2C_5H_4)Fe(CO)_2]_2$, analogous to the dimer VI produced during the vacuum thermolysis of V [18], was observed only in trace amounts.

GLC analysis of the reaction product, from decompositions in decane, did not detect toluene. Thus, if homolytic cleavage of the carbon—iron bond in I produces benzyl radicals, these radicals do not abstract hydrogen from solvent in competition with dimerization, attack at the cyclopentadienyl rings, or tar formation. NMR examination of the tar indicated complex phenyl and benzylic proton multiplets. Formation of bibenzyl and XI suggests a free radical mechanism. The ratio of XI/XII is similar whether decompositions are carried out neat or in solution. It should be noted that no XII was reported by Nesmeyanov [16] in his photolytic decompositions of I.

In contrast to neat decompositions of I, linear and crosslinked polymers VIIIa and VIIIb showed no sign of decomposition at 140° after 8 h. IR spectra and GPC chromatograms were unchanged. However, the polymers were solids at this temperature whereas I had melted. Thus, initial homolysis could produce *Pol*—$C_6H_4CH_2\cdot$ and h^5-$C_5H_5Fe(CO)_2\cdot$ which recombine more efficiently within the solid matrix reducing the decomposition rate. When VIIIa was dissolved or VIIIb swollen in benzene, the thermolyses proceeded slowly at 140°. About 10% of the bound units of I decomposed in 8 h. Polymer VIIIa crosslinked and dimer XI was extracted and isolated in each case (eqn. 6).



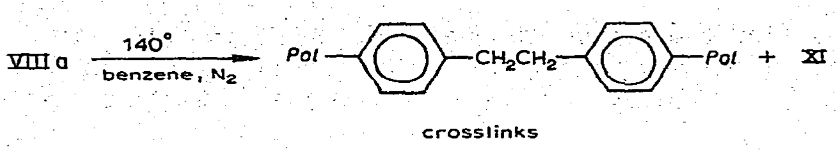
No 1795—1770 cm^{-1} bands (indicative of bound monobenzylated XIV)

TABLE 1

THERMAL DECOMPOSITION OF (h^1-BENZYL) (h^5-CYCLOPENTADIENYL)DICARBONYLIRON, I, AT ABOUT 140° UNDER NITROGEN

Solvent	Temp. (°C)	Time (h)	I (charged moles X 10^3)	Products I (recovered moles X 10^3)	XI (moles X 10^3)	XII (moles X 10^3)	XIII (moles X 10^3)	Tar (g)
Neat	140	6.5	4.33	0.31	1.78	0.16	0.47	0.14
Neat[a]	140	6.5	4.33	0.39	1.80	0.16	0.42	0.05
Neat	140	6.5	5.58	0.42	2.32	0.21	0.65	0.20
Decane	142	6.5	5.61	0.82	2.07	0.27	0.53	0.11
Decane	142	6.5	5.82	0.81	2.02	0.24	0.61	0.08
Benzene	140	8.0	4.3	1.16	1.27	0.21	0.12	0.17

[a] This reaction was carried out at 150 μ pressure.



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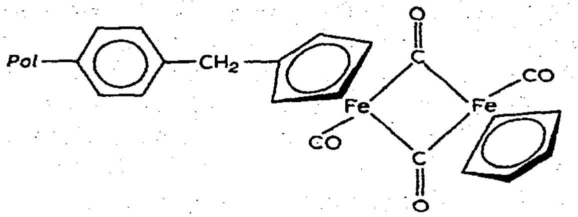


observed
after
thermolysis
at 160°

(XIV)

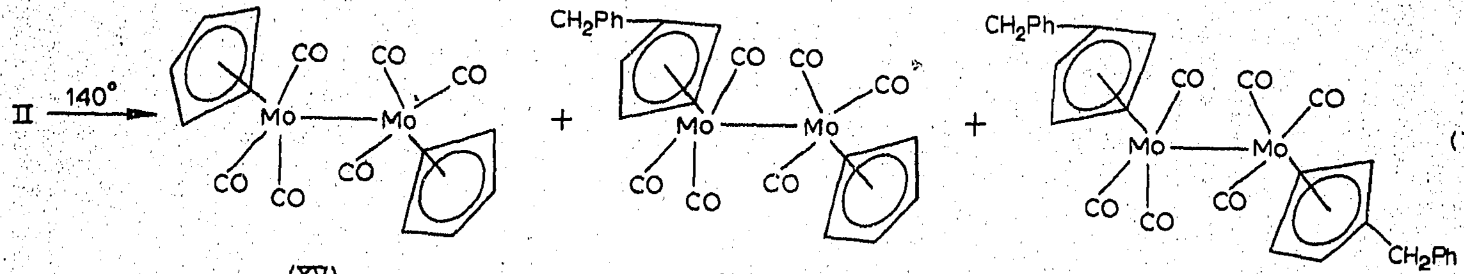
were detected in the polymer after thermolysis at 140°. Bridging carbonyls in dimers XI and XII absorb strongly in this region. However, after heating VIIIa 8 h at 160°, more than 85% of the organometallic sites decomposed and a band at 1790 cm^{-1} appeared. Reactions of VIIIb were similar to VIIIa. More cross-linking in resin VIIIb was indicated by a decreased ability to swell. Heating dry, degassed VIIIb to 160° caused the decomposition of XI giving units of XIV within the matrix. Similarly, some XI was trapped in the resin by first swelling with benzene, then greatly reducing the swelling with methanol, and heating. The "polymer-enclosed" XI, so generated, could be recovered by subsequent extraction with THF or toluene.

Crude rate studies in benzene indicated thermal decomposition of I was first order at concentrations from 0.03 to 0.92 molar. These initial rates were approximated by following the decrease in intensity of the 2009 cm^{-1} band of I and the increase in the 1790 cm^{-1} band of XI.

Thermal decompositions of II and III were also carried out neat, in decane, and in benzene. Carbon—metal bond cleavage was followed by collapse to dimer. Significantly, large amounts of benzyl migration to the Cp rings occurred versus decompositions of $PhCH_2Fe(CO)_2C_5H_5$ (eqns. 7 and 8). Product yields were determined by high pressure liquid chromatography (see Table 2) and isolation achieved by column chromatography.

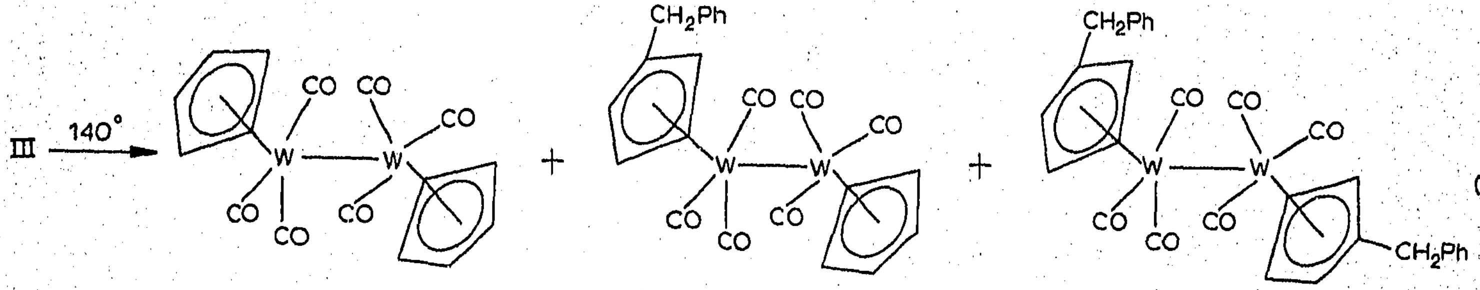
Compounds I, II and III cannot undergo metal hydride elimination. Thus, homolytic cleavage would occur. Furthermore, the greater stability of $PhCH_2\cdot$ versus $CH_3\cdot$ or $CH_3CH_2\cdot$ should facilitate homolytic cleavage. Since $PhCH_2\cdot$ is much less reactive than $CH_3\cdot$ or $CH_3CH_2\cdot$ and since $PhCH_2\cdot$ does not substitute benzene [26] or ferrocene [27, 28], substitution of the C_5H_5 rings of dimers XV and XVIII seems improbable. This suggested that benzyl migration from Mo and W to the ring in the decompositions of II and III was occurring by a "concerted homolysis" where the $PhCH_2\cdot$ radical simultaneously attacks the Cp ring during generation or never really becomes free of the rest of the molecules.

To test this possibility, II was decomposed at 140° in cumene. Benzyl radicals, separated from $C_5H_5Mo(CO)_3$, would efficiently abstract hydrogen from cumene [29], thus precluding substitution of the Cp rings of dimer XV. However, if a "concerted homolysis" occurred, substitution of the Cp rings would proceed despite the presence of cumene. When II was decomposed in cumene, the product distribution resembled that obtained in benzene except no



(XV) (XVI) (XVII)

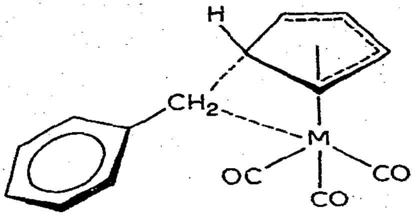
(7)



(XVIII) (XIX) (XX)

(8)

dibenzyl was formed. We tentatively suggest that the benzyl radical rides directly from the metal to the *endo* side of the Cp ring (see XXI), although cage recombination cannot be excluded at this time.



(XXI)

Polymers IXa, IXb, Xa, and Xb decomposed more rapidly in solution than neat. Furthermore, larger amounts of XV and XVIII were recovered in solution decompositions. In the absence of solvent, carbon—metal recombination would be more efficient since the polymers were solid and radicals would be expected to have lower mobility. In solution, $[C_5H_5M(CO)_3]^{\cdot}$ would have sufficient mobility to allow dimer formation. This effect is illustrated in Table 3. In solution, however, dimer (XV, XVIII) formation occurred in competition with benzyl migration. This resulted in polymer-bound dimer analogs of XVI and XVII from IXa and IXb and XIX and XX from Xa and Xb. The tungsten polymers Xa and Xb decomposed more slowly than their molybdenum analogs IXa and IXb. In accord with the well known increase in metal—carbon bond strengths going from Cr to Mo to W [30].

Linear polymers IXa and Xa extensively crosslinked during decomposition, presumably due to formation of dibenzyl units (i.e. *Pol*—$C_6H_4CH_2CH_2C_6H_4$—*Pol)*, and to dibenzylated dimer formation (i.e. *Pol*—$C_6H_4CH_2C_5H_4M(CO)_3M(CO)_3C_5H_4CH_2$-$C_6H_4$—*Pol)*. The progress of the decompositions was monitored by watching the decrease of the carbonyl bands of *Pol*—$C_6H_4CH_2M(C_5H_5)(CO)_3$ units (2020 vs and 1940 vs M = Mo; and 2010 vs and 1915 vs M = W) and the growth of dimer carbonyl bands (1950—1960 vs and 1890—1950 vs M = Mo; and 1950 vs 1900 vs M = W).

TABLE 2

PRODUCT DISTRIBUTION FROM THE THERMAL DECOMPOSITION OF BOTH (h^1-BENZYL) (h^5-CYCLOPENTADIENYL) TRICARBONYLMOLYBDENUM, II, AND TUNGSTEN, III, AFTER 8 h AT 140°

Compound	Solvent	Products yield (%)							
		dibenzyl[a]	XV[b]	XVI[b]	XVII[b]	XVIII[b]	XIX[b]	XX[b]	unidentified[c] tar
II	neat	0	8	12	64				8
II	decane	12	15	9	55				18
II	benzene	13	13	17	49				15
II	cumene	0	7	15	56				6
III	neat	0				36	11	41	4
III	decane	9				29	17	37	7
III	benzene	11				24	19	38	12

[a] Based on 100% if all benzyl groups in II or III went to dibenzyl. [b] Based on the total moles of metal in II or III charged to the reaction. [c] Based on weight of II or III charged. This material could involve molecules of solvent.

TABLE 3

AMOUNT OF DIMER XV AND XVIII FORMED DURING DECOMPOSITION OF POLYMERS IXa, IXb, Xa, AND Xb[a]

Polymer	Decomposition solvent	Dimer[b] yield (%)
IXa	neat	0.5
IXa	benzene	13
IXb	neat	0
IXb	benzene	6
Xa	neat	0.2
Xa	benzene	12
Xb	neat	0
Xb	benzene	7

[a] Heated for 8 h at 140° after N_2 degassing. [b] Based on total metal present on polymer.

Experimental

GPC and LC studies were done on a Waters ALC/GPC-301 instrument with (for GPC) 16 ft. of styragel columns. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Gas chromatography was performed with a Varian Aerograph 90P3 using 20% Se-30 on 60/80 Chromosorb W, 1/4" by 4' stainless steel columns. Synthesis of the narrow distribution chloromethylated polystyrene has been described [14, 23].

(h^1-Benzyl)(h^5-cyclopentadienyl)dicarbonyliron, I

Compound I was prepared as described previously [20, 24]. Its mass spectrum, NMR and IR spectra agreed with those expected [24, 31], m.p. 51.5°, lit. [15] 54°.

Linear polystyrene-bound (h^1-benzyl) (h^5-cyclopentadienyl)dicarbonyliron, VIIIa

The dimer $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ (3.8 g, 11 mmol) in THF (60 ml) was converted to $Na^+[h^5\text{-}C_5H_5Fe(CO)_2]^-$ as described before [21]. After removal of amalgam and cooling to −70°, chloromethylated polystyrene (1.25 g, 2.98 mmol Cl) in dry THF (30 ml) was added. After warming to 23° for 3 h, the polymer was precipitated in hexane (large excess). Precipitation was repeated twice followed by drying at 25° in vacuo. However, the purity was not sufficient. Thus, CS_2 solutions of polymer were repeatedly filtered through alumina under nitrogen to give a clear orange solution. Removal of solvent gave the polymer as a brown flakey powder: NMR (CS_2) δ 6.94 (broad s, *m*- and *p*-phenyl-H), 6.43 (broad s, *o*-phenyl-H), 4.30 (s, C_5H_5), 2.48 (s, CH_2), 2.1—1.0 (m, chain protons); IR(film) 3070 w, 3030 m-s, 2930 s, 2860 w; (CO_{str}) 2010 vs, 1945 vs; 1601 s, 1490 s, 1355 s, 835 s, 755 s, 698 s, Anal. Found: Cl, 0.00 Fe, 10.31; Calcd. polymer where all chloromethyl groups have reacted: Cl 0.00; Fe, 10.00%.

Polystyrene—divinylbenzene-bound (h^1-benzyl) (h^5-cyclopentadienyl)dicarbonyliron, VIIIb

A 1.5 g (1.57 mmol Cl) sample of Bio-Beads (Bio Rad Labs SX-2, 200—400 mesh, mol. wt. 14000 exclusion limit) swollen in THF under nitrogen for 24 h was reacted with $Na^+[h^5\text{-}C_5H_5Fe(CO)_2]^-$ which was prepared as described [21] from $[h^5\text{-}C_5H_5Fe(CO)_2]_2$ (0.8 g, 2.27 mmol). After stirring 24 h, the beads were washed times (stirring for 24 h) in dry deoxygenated THF and dried in vacuo to give VIIIb: IR(KBr) 3020 s, 2950 s; ν(CO) 2000 vs and 1950 vs, 1601 s, 1495 s, 1455 s, 1030 m, 830 s, 750 s, 698 s cm^{-1}. Anal. Found: Cl, 0.00; Fe, 4.97. Calcd. for VIIIb where all chlorine displaced: Cl, 0.00; Fe, 5.1%.

Thermolysis of (h^1-benzyl) (h^5-cyclopentadienyl)dicarbonyliron, I

Neat. Compound I (1.5 g, 5.58 mmol) was degassed, repressurized with nitrogen in a tube, and heated at 140° for 6.5 h. TLC analysis (pentane and silica gel) found dibenzyl, I and XI (dimer XII was in the spot for XI). Attempts to separate XI and XII on a 15 cm F-20 alumina column (pentane and benzene gradients) failed, but a 3 ft. dry packed silica column succeeded. Thus, I (112 mg, 0.42 mmol), XI (820 mg, 2.32 mmol), XII (93 mg, 0.21 mmol), dibenzyl (118 mg, 0.65 mmol), and tar (201 mg) were obtained and characterized: I, IR, NMR and mass spectra were identical with those of an authentic sample; XI m.p. 192° [35]; NMR (CS_2)δ 4.67 (s, C_5H_5), mass spectrum (70 eV) *m/e* (rel. intensity 186 (0.107) $(C_5H_5)_2Fe^+$, 177 (0.158) $C_5H_5Fe(CO)_2^+$, 121 (1.00) $C_5H_5Fe^+$, 56 (0.564) Fe^+; IR (CS_2), 3070 w, 2925 m, 2051 w, 2000 vs, 1950 vs, 1784 vs, 830 s cm^{-1}. Dimer XII was obtained as blue-black crystals, m.p. 162°, mass spectrum (70 eV) *m/e* (rel. intensity) 211 (0.16) $PhCH_2Fe(C_5H_5)^+$, 121(1.00)-$C_5H_5Fe^+$, 91 (0.51) $PhCH_2^+$, NMR (CS_2) δ (broad band 4.6, 9H, Cp protons), 7.10 (s, 5H, phenyl-H), 5.54 (s, 2H, CH_2); IR, complex patterns in the carbonyl region, at least 4 bands from 2060 to 1930 cm^{-1} and a broad intense band at 1780 cm^{-1}. Dibenzyl had IR and NMR spectra identical with those of an authentic sample. In decompositions at 160°, small amounts of dibenzylated $[PhCH_2C_5H_5Fe(CO)_2]_2$ were obtained as purple crystals (from acetone—ligroin) m.p. 152°, lit. [32] 151°.

In decane. Compound I (1.5 g, 5.6 mmol) in freshly distilled n-decane (17 ml), was degassed, repressurized with nitrogen and heated 6.5 h at 142°. Cooling, concentrating the solution, and dry column chromatography gave products as described above in yields given in Table 1.

In benzene. Compound I (1.19 g, 4.3 mmol) in dry benzene (15 ml) under nitrogen was heated for 8 h at 140°. The products were separated and characterized as described above.

Thermolysis of linear polymer VIIIa both neat and in benzene at 140° and 160°

Polymer VIIIa (0.423 g) was degassed, repressurized with nitrogen and heated to 140° for 8 h. Then it was cooled, dissolved into benzene, precipitated into 30—60° petr. ether. No XI was found. Recovered polymer was identical (IR, GPC) to VIIIa.

Then VIIIa (0.476 g) in dry deoxygenated benzene (15 ml) was heated to 140° for 8 h without formation of a precipitate. The solution changed from yellow to red. Precipitation into 30—60° petr. ether recovered the polymer. Dimer XI (10 mg) was recovered from the filtrate (m.p. 192°, lit [32] 192°). The recovered polymer's IR spectrum was almost unchanged since only 10% of the organometallic units decomposed. No bands in the 1770—1800 cm^{-1} region were observed. Recovered polymer was only partially soluble in benzene, and the THF soluble portion exhibited a very broad mol. wt. distribution indicative of extensive branching. Similar decompositions of VIIIa (0.503 g), at 160° for 8 h, gave a more highly crosslinked polymer with an absorption at 1790 cm^{-1} indicative of polymer-attached benzylated dimer (i.e. XIV). Also, 0.131 g of XI was isolated.

Thermolysis of styrene—divinylbenzene-bound (h^1-benzyl) (h^5-cyclopentadienyl)dicarbonyliron, VIIIb, both neat and in benzene

Polymer VIIIb (430 mg, 3.92 mmol of Fe), was heated 8 h at 140° under nitrogen followed by 24 h of benzene extraction (Soxhlet). Decomposition products were not formed. The IR spectra of the resin was unchanged. Heating to 160° gave XI which could be extracted. Some XI (and presumably XII) were trapped in the increasing crosslinked matrix (shown by absorption in the 1780—1795 cm^{-1} region [33]). Resin VIIIb (457 mg, 4.04 mmol of Fe), swollen under nitrogen for 24 h in dry benzene (20 ml), was heated at 140° for 8 h giving a red solution. Extraction (as described above) gave XI as a black powder (18 mg). Further heating at 160° gave more XI while some XI and XII was trapped in the matrix (IR). Dimer trapping was enhanced in neat decompositions or using benzene—methanol mixtures.

(h^1-Benzyl) (h^5-cyclopentadienyl)tricarbonylmolybdenum, II

Benzyl chloride was treated with $Na^+[Mo(CO)_3C_5H_5]^-$ [21] according to King and Fronzaglia [17] to give yellow crystals of I (from Et_2O at —78°) in 60% yield: m.p. 86—88°, lit. [17] 87—88°; IR ν(CO) 2020 vs, 1940 vs, also 820 vs 760 vs, 700 vs cm^{-1}; NMR (CS_2), δ 7.09 (s, 5H, phenyl-H), 5.13 (s, 5H, Cp-H), 2.87 (s, 2H, CH_2).

(h^1-Benzyl) (h^5-cyclopentadienyl)tricarbonyltungsten, III

The method described above, using $W(CO)_6$ (9.34 g, 28.6 mmol), NaC_5H_5 (3.38 g, 38.5 mmol) and benzyl chloride (3.96 g, 31.2 mmol) gave III (45%, recrystallized from 30—60° petr. ether) as yellow crystals: m.p. 98—100°; NMR ($DCCl_3$) δ 7.20 (s, 5H, phenyl-H), 5.32 (s, 5H, Cp-H), 3.02 (s, 2H, CH_2); IR (nujol) ν(CO) 2010 vs, 1930 vs [20], other bands (KBr), 3090 w, 3005 w, 2935 w, 1601 m, 1490 m, 1205 m, 1010 m, 835 s, 760 s, 737 m, 704 s cm^{-1}.

Linear polymers IXa and Xa

Linear chloromethylated polystyrene ($\overline{M}_w/\overline{M}_n$ = 1.25, $\overline{M}_n$ = 12000, 1.2 g, 2.4 mmol Cl) was added to a THF (60 ml) solution of $Na^+[Mo(CO)_3C_5H_5]^-$ [21] (3.5 mmol). After stirring 36 h in the dark and precipitation into hexane under nitrogen, the yellow polymer analyzed for 16.1% Mo vs. 13.9% if all chlorine had been displaced. A broad OH stretch indicated an impurity. Five additional reprecipitations gave an orange polymer, IXa with 14.4% Mo and exhibited: IR, ν(CO) (nujol) 2020 vs and 1940 vs cm^{-1}; NMR (CS_2) δ 6.95 (broad s, *p*- and *m*-phenyl-H), 6.45 (*o*-phenyl-H), 4.94 (s, Cp-H), 4.37 (s, Cl—CH_2), 2.1—1.0 (broad, m, chain protons). Polymer Xa was prepared similarly. At 23° chloromethylated polystyrene (1.2 g, 2.4 mmol Cl) in THF was added to $Na^+[W(CO)_3C_5H_5]^-$ [21] under nitrogen. After 36 h in the dark, Xa was worked-up as described above. Not all of the chlorine was displaced, but all chlorine could be replaced using more of the anion and longer reaction times. Hydrated metal oxide impurity was present. Six reprecipitation steps gave Xa: IR ν(CO) 2010 vs and 1930 vs cm^{-1}; NMR (CS_2)δ 6.98 (broad s, *m*- and *p*-phenyl-H), 6.45 (s, *o*-phenyl-H), 4.98 (s, Cp-H), 4.39 (s, Cl-CH_2), 2.89 (s, W-CH_2), 2.1—1.0 (broad m, chain protons). Anal. Found: C, 69.87; H, 6.05; Cl, 2.29; W, 19.62. Calcd. where all Cl was displaced: W, 24.8%.

Crosslinked Resins IXb and Xb.

Chloromethylated styrene—divinylbenzene beads (Bio Rad Labs, SX-1, 200—400 mesh, mol. wt. 14000 exclusion limit) were swollen (3.0 g, 3.14 mmol Cl) in sodium-dried THF (60 ml) for 24 h and $Na^+[Mo(CO)_3C_5H_5]^-$ [21] (3.75 mmol) in THF (75 ml) was added under nitrogen. After refluxing 48 h in the dark, decanting the THF, and extracting the beads with THF (68h) a yellow resin IXb was obtained: IR (KBr) ν(CO) 2020 vs and 1930 vs. Analysis showed all chlorine was not displaced: Found Cl, 2.98; Mo, 4.39. Calcd.: Cl, 0.0; Mo, 8.25%. Using 3 equivalents of $Na^+[Mo(CO)_3C_5H_5]^-$ (over Cl) greater displacement of Cl was achieved (Mo, 8.11, Cl, 0.63%). Similarly, Xb was prepared by swelling 3.0 g of chloromethylated resin THF (60 ml) for 24 h and treating it for 48 h at 65° with $Na^+[W(CO)_3C_5H_5]^-$ [21] (3.75 mmol). THF extraction gave yellow polymer beads: IR (KBr) ν(CO) 2010 vs and 1920 vs cm^{-1}. Anal. Found: Cl, 3.50; W, 6.45 vs. W, 14.8% if all chlorine were replaced. Using five equivalents of $Na^+[W(CO)_3C_5H_5]^-$ in the above reaction displaced most of the chlorine Cl, 0.43, W, 13.10%).

Representative thermolysis of II and III

Neat decompositions. Samples (1.0 g) of II (or III) were degassed, repressurized with nitrogen, and heated at 140° for 8 h. TLC of the product mixture from II (alumina or on silica) showed two partially resolved bands, but no dibenzyl or II was detected. The IR spectrum (KBr or Nujol) exhibited broad intense carbonyl bands at 1960 and 1905 cm^{-1} characteristic of the dimers (i.e. a mixture XV, XVI and XVII) [33]. TLC analysis of the residue from II exhibited a broad band which benzene—chloroform development partially split into two. No dibenzyl or II was detected. The IR (KBr or Nujol) of the crude product indicated dimers ν(CO) 1960 (br) vs and 1907 (br) vs cm^{-1} [33]. Dry column chromatography (silica gel, benzene, benzene—$CHCl_3$, benzene—ethanol, and benzonitrile solvent combinations) of the residue from II gave 5—8% yields of dimer XV; IR ($CHCl_3$) identical to that reported [33], m.p. 214—216° (dec.), lit. [33] 215—217° and a 70—75% yield of a mixture of XVI and XVII which proved difficult to further separate on a column. Thus, these mixtures were analyzed by high pressure liquid chromatography (3 ft. × 2.3 mm column, Corasil II support, chlorobenzene or $CHCl_3$). Small amounts of XV, XVI, and XVII were separated and yields (see Table 2) were determined by this method on aliquots from each reaction. Both XVI and XVII exhibited ν(CO) (KBr) at 1950—1965 vs and 1895—1910 vs cm^{-1} in addition to 690 and 760 cm^{-1} monosubstituted phenyl ring bands. The NMR spectra ($DCCl_3$) of XVI showed a 5/9 ratio of phenyl (δ 7.3) to Cp (δ 5.3—5.4) protons, while XVII exhibited a 10/8 ratio of phenyl (δ 7.4) to Cp (δ 5.4—5.5) protons. In both XVI and XVII, the benzylic protons appear at (δ 3.8) with areas of 2 and 4 respectively. Anal. XVI found: C, 48.10; H, 2.63; Mo, 32.64;

calcd.: C, 47.60; H, 2.78; Mo, 33.07%; for XVII found: C, 53.20, H, 3.54; Mo, 28.22; calcd.: C, 53.75; H, 3.31, Mo, 28.62%. Both XVI and XVII underwent decomposition between 180—190°.

Similarly, XVIII, XIX and XX were separated from the decomposition residues of III. Dimer XVIII was isolated as reddish-purple crystals, m.p. 238—240° (dec.), lit. [34] 240—242°, and the IR spectrum was as reported [33]. The IR spectrum of XIX ($HCCl_3$) ν(CO) 1960 (br) vs, 1905 (br) vs, shoulders observed, monosubstituted phenyl deformation at 700 and 750, and Cp-H deformation at 840 s cm^{-1} and that of XX were similar except the 700 and 750 cm^{-1} bands of XX were more intense, relative to the 840 cm^{-1} band. Poor NMR spectra (due to solubility limitations and paramagnetic impurities in XIX and XX) exhibited phenyl-H at δ 7.3, Cp-H at δ 5.4, and Ph-CH_2 at δ 3.4 in about the expected area ratios. Anal. XIX found: C, 36.95; H, 2.31; W, 47.89; Calcd: C, 36.53; H, 2.13; W, 48.64%; for XX found C, 43.01; H, 2.50; W, 42.74; calcd: C, 42.58; H, 2.62, W, 43.45%.

Decomposition in decane, benzene and cumene. Either II or III, dissolved in deoxygenated solvent (roughly 1 g to 15—20 ml of solvent), was degassed, repressurized with nitrogen, and heated to 140° for 8 h. The solutions turned purple and part of the decomposition product (mainly the unbenzylated dimer, either XV or XVIII) precipitated due to lower solubility. The entire product was dissolved in $CHCl_3$, and analyzed by liquid chromatography (results in Table 2). Solution decompositions of II and III, in decane and benzene, produced the three dimers and dibenzyl (isolated by chromatography over alumina; mass and IR spectra identical with those of an authentic sample) which were analyzed by liquid chromatography. No toluene was detected by GLC in decompositions carried out in decane or benzene, but when cumene was used, GLC demonstrated toluene was formed.

Thermolysis of linear polymers IXa and Xa, neat and in benzene.

Neat decompositions were carried out under nitrogen for 8 h at 140°. Polymer (0.5 g of IXa or Xa) was dissolved in benzene (15 ml) in solution decompositions and heated 8 h at 140°. Soluble IXa and Xa became partially insoluble during heating due to crosslinking. IR bands characteristic of *Pol*—$C_6H_4CH_2M(CO)_3C_5H_5$ were replaced by those of *Pol*—$C_6H_4CH_2C_5H_4M(CO)_3M(CO)_3C_5H_5$ and/or *Pol*—$C_6H_4CH_2C_5H_4M(CO)_3M(CO)_3C_5H_4CH_2C_6H_4$—*Pol* appearing at 1950—1960 vs and 1890—1905 vs for M = Mo and 1950 vs and 1900 vs when M = W. Continuous IR monitoring showed neat decompositions proceeded much slower than in solution. Dimers XV (from IXa) and XVIII (from Xa) were isolated by decanting, extracting the residual crosslinked polymer (benzene, THF, and chloroform), concentrating combined solutions, and recrystallization from benzene—$CHCl_3$ or by chromatography (yields in Table 3).

Thermolyses of resins IXb and Xb neat and in benzene. The resins were heated to 140° for 8 h under nitrogen both neat and swollen in benzene solutions. On neat thermolysis, IXb darkened from yellow color to a rust color and Xb became brownish-purple. The polymers were swollen and extracted (benzene and THF) but only traces of XV and XVIII were formed in neat decompositions of IXb and Xb. However, carbonyl bands appeared indicating polymer -bound dimer species were generated. Dimers XV and XVIII were, however, isolated from the benzene solution decompositions of IXb and Xb, in amounts similar to those obtained in solution decompositions of II and III. The dimers were recovered from the reaction solutions and the combined benzene and THF extractions and recrystallized from benzene—$CHCl_3$.

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