Journal of Organometallic Chemistry, 205 (1981) 353—364
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE FORMATION AND ADDITION POLYMERIZATION OF TWO ORGANOTUNGSTEN MONOMERS: (η^5-VINYLCYCLOPENTADIENYL) TRICARBONYLMETHYLTUNGSTEN AND (η^5-CYCLOPENTADIENYLMETHYL ACRYLATE)TRICARBONYLMETHYLTUNGSTEN

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(Received July 11th, 1980)

Summary

The first report on the preparation, polymerization and copolymerization of two organotungsten vinyl monomers, (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten (IV) and (η^5-cyclopentadienylmethyl acrylate)tricarbonylmethyltungsten (IX) is described. Monomer IV was prepared from a reaction between formylcyclopentadienylsodium and hexacarbonyltungsten in DMF, followed by methylation with methyl iodide to produce (η^5-formylcyclopentadienyl)tricarbonylmethyltungsten (III), and subsequent conversion of the latter into IV under phase transfer conditions employing triphenylmethylphosphonium iodide, 5 *N* sodium hydroxide and benzene. Moreover IX was obtained by sodium borohydride reduction of III, followed by treatment of the resulting carbinol with sodium hydride and subsequent reaction with acryloyl chloride. Monomer IV homopolymerized sluggishly, and copolymerized slowly with styrene under radical initiation in benzene solution. Copolymerizations of IV with methyl methacrylate, acrylonitrile, and *N*-vinyl-2-pyrrolidone were also successful. Monomer IX homopolymerized and copolymerized with styrene and with methyl acrylate. A styrene copolymer of IV when treated with i-$BuAlCl_2$ and oxygen was active as a metathesis catalyst with 3-heptene.

Introduction

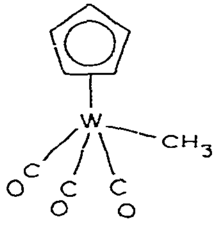
The synthesis and polymerization of organometallic monomers have greatly accelerated in scope in recent years [1]. Interest in this field stems in part from the potential use of such metal-containing polymers for catalysts, semiconductors, UV absorbers, lithographic resists and other uses. The radical-initiated vinyl addition homopolymerization and copolymerization of a variety of vinyl monomers containing transition metals have been investigated, including vinylferrocene [2,3], vinylcymantrene [4,5], (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium [6,7], η^6-styrenetricarbonylchromium [8], ferrocenylmethyl acrylate [9,10] and methacrylate [9,10], η^6-(2-phenylethyl acrylate)tricarbonylchromium [11], 2-ferrocenylethyl acrylate [12] and methacrylate [12], and η^6-(benzyl acrylate)tricarbonylchromium [13]. The topic of vinyl polymerization of organic monomers containing transition metals has recently been reviewed [14].

This paper presents the results of preliminary studies concerning the formation, homopolymerization and copolymerization of two new organotungsten monomers, (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten (IV) and (η^5-cyclopentadienylmethyl acrylate)tricarbonylmethyltungsten (IX). These are the first organotungsten vinyl monomers to be synthesized and studied under polymerization conditions, and are unique in that they each contain a metal—carbon σ-bond. Furthermore, the radical initiated addition polymerization of a transition metal-containing monomer, which has hydrogens α to the metal atom, raises the possiblity that hydrogen abstraction may terminate polymerization or result in chain transfer.

Results and discussion

Monomer syntheses

The parent compound (η^5-cyclopentadienyl)tricarbonylmethyltungsten (I) was first synthesized in 1955 and was found to exhibit unusual stability for a product containing a metal—carbon σ-bond [15,16]. Although photochemically-induced reactions of I have been the subject of recent investigations in our laboratory [17] and elsewhere [18], polymers containing this organotungsten linkage have been obtained only by indirect methods [19,20], due mainly to the lack of synthetic routes to vinyl-containing derivatives of I.



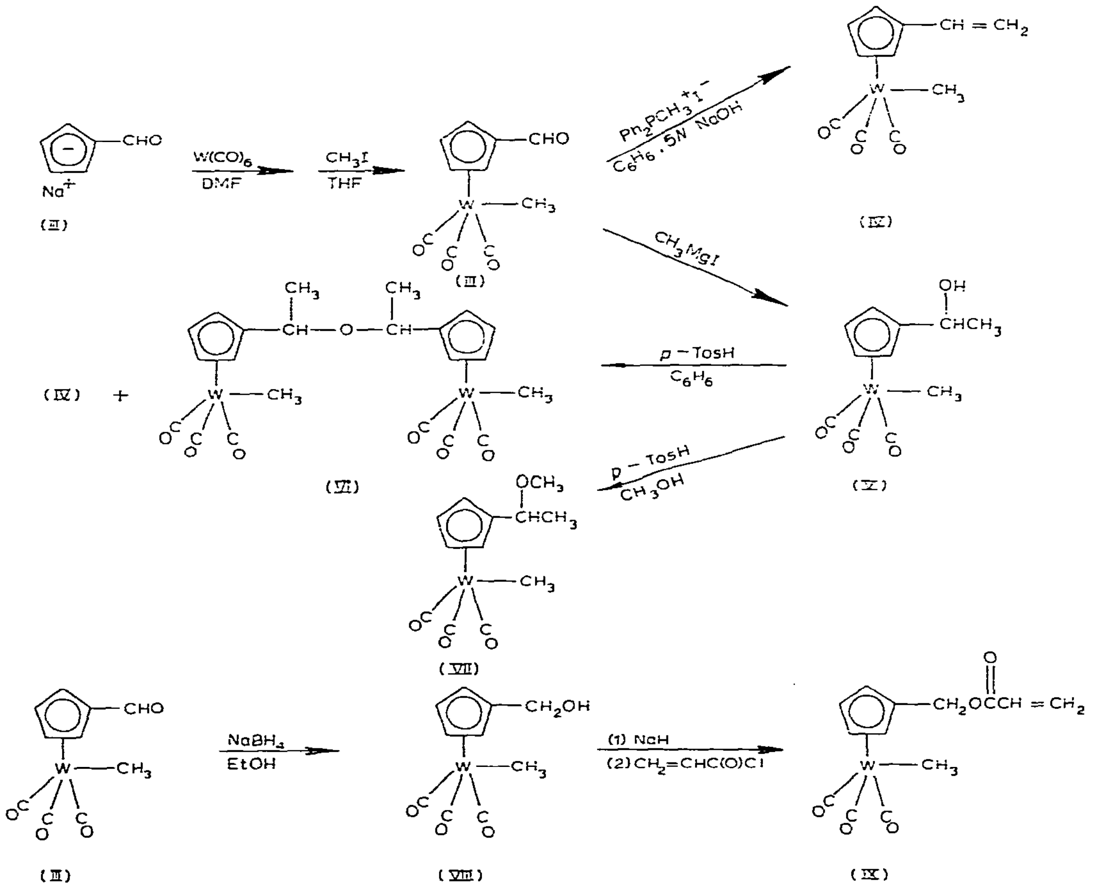
(I)

We have recently developed useful synthetic routes to many new η^5-cyclopentadienyl derivatives of the transition metals which contain functional substituents on the η^5-cyclopentadienyl ring [21]. Adaptation of this method to organotungsten chemistry has allowed us to prepare a valuable precursor to IV and IX, namely, (η^5-formylcyclopentadienyl)tricarbonylmethyltungsten (III). Aldehyde III was obtained in 82% yield from a reaction between formylcyclopentadienylsodium (II) [21,22] and hexacarbonyltungsten in refluxing DMF, followed by removal of the solvent, addition of THF, treatment with methyl iodide, and subsequent purification by chromatography and vacuum sublimation (Scheme 1).

The most satisfactory synthetic route to vinyl monomer IV was found to involve a reaction between aldehyde III in benzene solution with triphenylmethylphosphonium iodide in the presence of 5 *N* sodium hydroxide under phase transfer conditions [23]. Attempted formation of IV under normal Wittig conditions (e.g., $Ph_3P = CH_2$ generated in ethyl ether solution from triphenylmethylphosphonium iodide and n-butyllithium) also produced IV, although in appreciably lower yield.

Formyl derivative III was found to undergo a Grignard reaction with methylmagnesium iodide to give the secondary alcohol [η^5-(1-hydroxyethyl)cyclopentadienyl]tricarbonylmethyltungsten (V) in nearly quantitative yield. Unfortunately, however, repeated attempts to effect dehydration of V to form IV under conditions used for the dehydration of [η^5-(1-hydroxyethyl)cyclopentadienyl]dicarbonylnitrosylchromium to produce (η^5-vinylcyclopentadienyl)dicarbonylnitrosylchromium (benzene, *p*-toluenesulfonic acid) [6,7]

SCHEME 1



were only marginally succesful. Vinyl monomer IV was always obtained in low yield (10—25%), however, the dimeric ether (VI) resulting from partial dehydration of V was consistently the major product (50—65%). The unexpected formation of ether VI under these conditions suggested that other ethers could be similarly obtained under analogous conditions. Accordingly, reaction of V in refluxing methanol with a small amount of *p*-toluenesulfonic acid produced the methyl ether (VII) in 80% yield. The facile formation of VI and VII suggests the intermediacy of a relatively stable carbocation as in the case of the analogous ferrocenyl system [24,25]. Further studies along these lines are in progress.

The reduction of aldehyde III by sodium borohydride in ethanol proceeded smoothly, producing (η^5-hydroxymethylcyclopentadienyl)tricarbonylmethyltungsten (VIII) in nearly quantitative yield. A subsequent reaction between VIII and acryloyl chloride in the presence of pyridine gave the desired acrylate IX, however, in only 32% yield. A better route to IX was developed in which the alcohol VIII was first converted into its sodium salt by means of sodium hydride and then allowed to react with acryloyl chloride. Acrylate IX could be obtained in 60—65% yield by this procedure.

Vinyl monomer IV and acrylate monomer IX were obtained as low melting yellow solids which could most conveniently be purified by means of vacuum sublimation and low temperature crystallization, respectively. The two organotungsten monomers were characterized by means of elemental analysis, mass spectrometry, ^{1}H NMR and IR spectrometry (see Experimental).

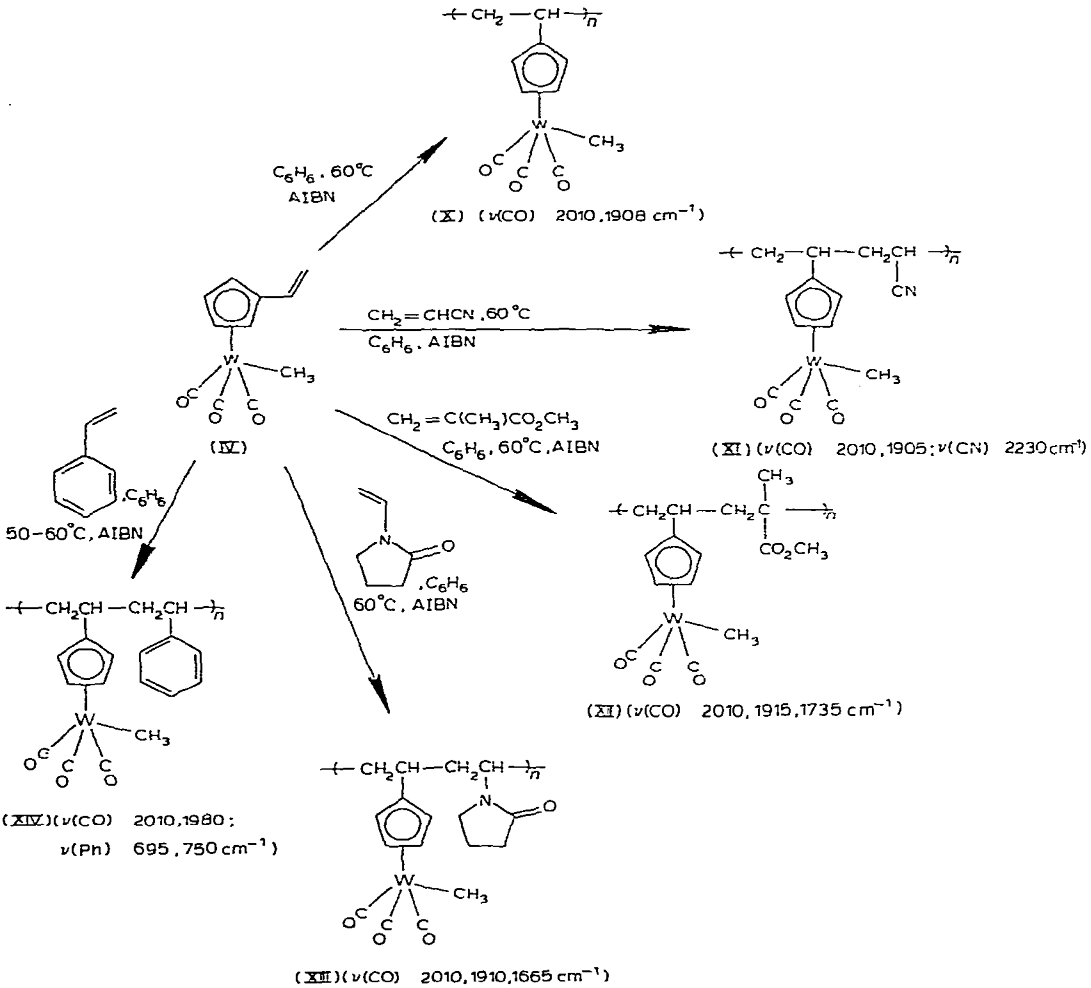
Polymerization studies

Vinyl monomer IV homopolymerized sluggishly under radical initiation (Scheme 2). For example, solution homopolymerizations in benzene using AIBN as initiator at [IV]/[AIBN] ratios of ca. 33 gave only 10—15% yields in 150—160 h. A typical example is summarized in Table 1. However, good yields of copolymers were obtained in copolymerizations with acrylonitrile, methyl methacrylate, and *N*-vinyl-2-pyrrolidone at IV/comonomer ratios of 30/70. This range of comonomers spans a wide range of electronic properties from electron-poor to electron-rich vinyl groups. The rather low intrinsic viscosities of these copolymers suggest extensive chain-transfer may have occurred. Chain-transfer studies are now in progress and will be reported later [26].

Copolymerizations with styrene gave very low yields unless they were subjected to subsequent reinitiations performed by several readditions of initiator. For example, when 3 mol percent of IV was used, only a 9% copolymer yield was obtained at 50°C using 0.01% initiator. Using styrene alone at these conditions, a high polystyrene yield would be expected. Thus, IV retards the rate of polymerization, but high yields (>50%) can be achieved by reinitiation.

Monomer IX homopolymerized more readily than IV, but still sluggishly compared to other acrylates. It also copolymerized with styrene (M_1) and with methyl acrylate (M_2). The copolymers were identified by elemental analyses and by their IR spectra (see Schemes 2 and 3). Gel permeation chromatography of each copolymer showed one peak, indicating that mixtures of homopolymers were not obtained.

SCHEME 2



Polymers containing IV have been used successfully as metathesis catalysts. For example, a copolymer of IV with styrene (XIV) (31 mol percent IV, entree 7, Table 1) was treated with isobutylaluminum chloride and oxygen in hexane and *trans*-3-heptene. This gave an active metathesis system at 20° C which produced *trans*-4-octene, *trans*-3-hexene, and other products (one identified as 4-ethyl-2-octene). Thus, this polymer species appears to behave similar to polystyrene-bound (η^5-cyclopentadienyl)tricarbonylbenzyltungsten as a metathesis catalyst when treated with i-BuAlCl$_2$ [27]. The major difference chemically between XIV and the benzyltungsten polymer is that the former has a

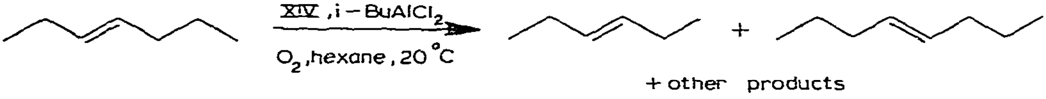


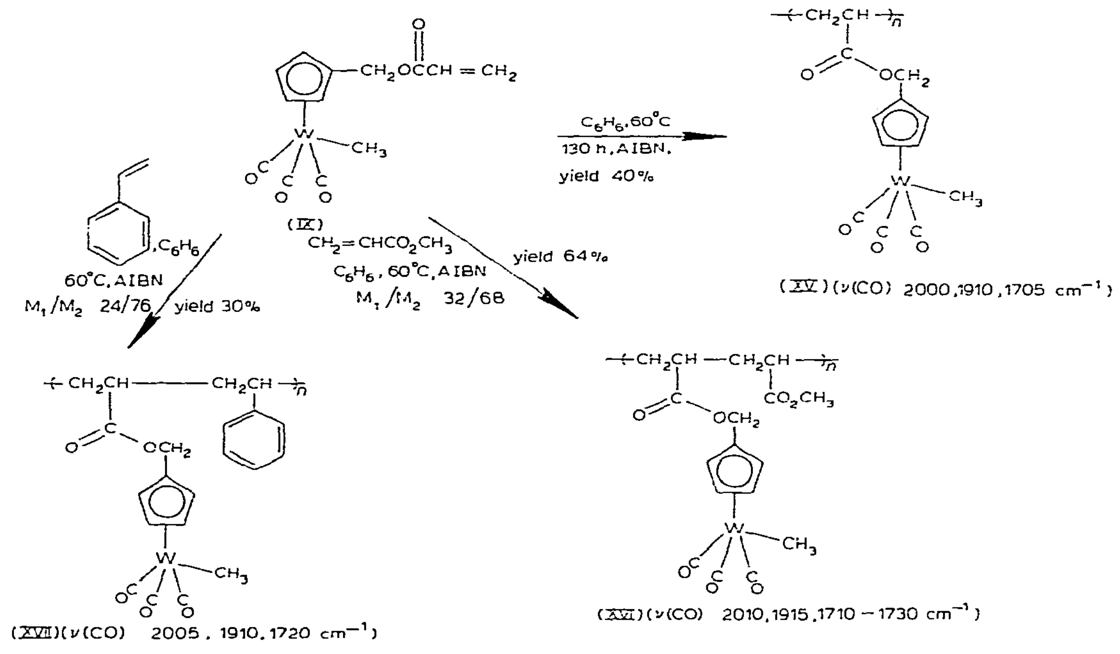
TABLE 1

HOMO- AND CO-POLYMERIZATION OF IV (M_1) IN BENZENE AT 60°C

Sample no.	Copolymer designation [a]	M_1 in feed		AIBN (mol)	C_6H_6 (ml)	Time (h)	Copolymer yield (%)	Copolymer		M_1 in copolymer (mol%)	[η] THF 30°C
		mol	mol%					%C	%W		
1	P(VCT)	1.3×10^{-3}	100	4.1×10^{-5}	3	158	12	—	—	—	—
2	P(VCT-AN)	1.3×10^{-3}	30	1.4×10^{-4}	3	158	65	39.8	37.9	32	0.28
3	P(VCT-MMA)	1.4×10^{-3}	30	1.4×10^{-4}	3	158	77	45.6	26.0	23	0.30
4	P(VCT-NVP)	1.3×10^{-3}	30	1.5×10^{-4}	3	158	52	40.0	36.9	47	0.32
5	P(VCT-ST) [b]	5.4×10^{-4}	3.2	3.9×10^{-6}	2	60	9	86.9	4.0	2.4	—
6	P(VCT-ST) [c]	1.6×10^{-3}	30	1.2×10^{-4}	4	30	32	44.7	31.6	34	—
7	P(VCT-ST) [c]	2.0×10^{-3}	47	1.3×10^{-4}	4	37	58	53.1	30.3	31	—

[a] VCT = IV, ST = styrene, AN = acrylonitrile, MMA = methyl methacrylate, NVP = *N*-vinyl-2-pyrrolidone, AIBN = azobis(isobutyronitrile). [b] Run at 50°C. [c] Polymerization followed by GC; reinitiated 3 times; final yields are given.

SCHEME 3



σ-bonded methyl group while the latter has a σ-bonded benzyl group (to tungsten). The latter was a more active metathesis catalyst, giving a 23% conversion of 3-heptene in one hour compared to 3% for XIV under identical conditions.

Experimental

All operations were carried out under nitrogen using Schlenk tube techniques. Hexane, pentane, benzene, and dimethylformamide were purified by distillation from calcium hydride under nitrogen. Ethyl ether was predried over sodium and distilled under nitrogen from sodium/benzophenone. Tetrahydrofuran was predried with potassium hydroxide and then with sodium and finally distilled under nitrogen from sodium/benzophenone. Column chromatography was carried out with Ventron-Alfa neutral grade alumina. The alumina was heated with a heat gun while mixing on a rotary evaporator attached to a vacuum pump for 2 h. The alumina was then deactivated with 5% (by weight) argon-saturated water. Tungsten hexacarbonyl was obtained from Pressure Chemical Co. NMR and IR spectra were recorded on Varian A-60 and Beckman IR-10 spectrometers, respectively. Mass spectra were obtained using a Perkin—Elmer—Hitachi RMU 6L mass spectrometer. Microanalyses were performed by the Microanalytical Laboratory, Office of Research Services, University of Massachusetts, Amherst.

The vinyl monomers styrene, methyl acrylate, methyl methacrylate, acrylonitrile, and *N*-vinyl-2-pyrrolidone were given both aqueous alkaline (10%

NaOH) and acid (10% H_2SO_4) washings to remove inhibitors, followed by distilled water washes, drying (anhydrous Na_2SO_4), and distillation (from CaH_2) under vacuum. Azobis(isobutyronitrile) was recrystallized three times from dry methanol and dried in vacuo. Benzene was washed (conc. H_2SO_4, $NaHCO_3$, distilled water), dried ($CaCl_2$), and distilled from sodium/benzophenone before use in polymerization experiments.

(η^5-Formylcyclopentadienyl)tricarbonylmethyltungsten (III)

Formylcyclopentadienylsodium [21,22] (5.40 g, 46.5 mmol) and tungsten hexacarbonyl (16.02 g, 45.5 mmol) were added to a 250-ml three-neck round-bottom flask equipped with a condenser and gas inlet and outlet valves. To this was added 150 ml of DMF, and the mixture refluxed for 3 h. The DMF was removed under vacuum (0.01 mmHg) to give a black oil. The oil was dissolved in 150 ml of THF, and excess methyl iodide added. The mixture was allowed to stir at room temperature for 20 h. The THF was removed under vacuum to give an oily solid. The residue was extracted with five 100-ml portions of ethyl ether, and the extracts were filtered through a short plug of alumina. The ether was removed under vacuum to give a brown solid. This solid was sublimed at 80°C/0.01 mmHg to give 14.1 g (82%) of (η^5-formylcyclopentadienyl)tricarbonylmethyltungsten as yellow crystals, m.p. 135°C (dec). IR (Et_2O): ν(CO) 2030, 1945, 1705 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.47, s, $W-CH_3$; 5.62, t, H(3,4); 5.74, t, H(2,5); 9.57, s, CHO. Found: C, 32.07; H, 2.34. $C_{10}H_8O_4W$ calcd.: C, 31.94; H, 2.14%. Mass Spectrum: M^+ *m/e* 376 (^{184}W).

(η^5-Vinylcyclopentadienyl)tricarbonylmethyltungsten (IV)

(η^5-Formylcyclopentadienyl)tricarbonylmethyltungsten (1.13 g, 3.0 mmol) was dissolved in 9 ml of benzene. To this solution was added triphenylmethylphosphonium iodide (2.43 g, 6.0 mmol), followed by 18 ml of 5 *N* sodium hydroxide solution. The mixture was stirred at room temperature for 46 h. The layers were then separated, and the aqueous layer was extracted once with 30 ml of ethyl ether. The combined organic layers were washed with dilute ammonium chloride solution, water, and dried over anhydrous magnesium sulfate. The solution was filtered and the organic solvent evaporated on alumina under reduced pressure. The resulting residue was added to a column of alumina (1.5 × 18 cm) and the column was eluted with hexane. A yellow band came down the column and was collected under nitrogen. Removal of the solvent under vacuum gave 0.90 g (80%) of (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten as bright yellow crystals. Further purification was accomplished by sublimation at 50°C/0.01 mmHg, m.p. 39—40.5°C. IR (melt): ν(CO) 2000, 1915 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.04, s, $W-CH_3$; 5.1—5.5, m, Cp + vinyl; 6.0—6.5, m, vinyl. Found: C, 35.42; H, 2.80. $C_{11}H_{10}O_3W$ calcd. C, 35.32; H, 2.69%.

(η^5-Hydroxymethylcyclopentadienyl)tricarbonylmethyltungsten (VIII)

(η^5-Formylcyclopentadienyl)tricarbonylmethyltungsten (2.50 g, 6.65 mmol) was dissolved in 30 ml of 95% ethanol, and sodium borohydride (0.13 g, 3.33 mmol) was added. The reaction mixture was allowed to stir at room temperature for 3 h. The mixture was hydrolyzed with dilute HCl, and extracted with ethyl ether. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed under vacuum to give 2.41 g (96%) of (η^5-hydroxymethylcyclopentadienyl)tricarbonylmethyltungsten as a yellow solid. An analytical sample was obtained by sublimation at 50°C/0.01 mmHg, m.p. 71—73°C. IR ($CHCl_3$): ν(CO)2015, 1935 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 0.43, s, W—CH_3; 1.98, s, OH; 4.45, s, methine; 5.44, m, Cp. Found: C, 31.92; H, 2.72. $C_{10}H_{10}O_4W$ calcd.: C, 31,77; H, 2.67.

(η^5-1-Hydroxyethylcyclopentadienyl)tricarbonylmethyltungsten (V)

A solution of methylmagnesium iodide was prepared from magnesium (0.58 g, 24.0 mmol) and excess methyl iodide in ethyl ether. To this solution was added (η^5-formylcyclopentadienyl)tricarbonylmethyltungsten (6.0 g, 16.0 mmol) dissolved in ethyl ether, and the solution was refluxed for 4 h. The reaction mixture was hydrolyzed with ammonium chloride solution, the aqueous and organic layers were separated, and the aqueous layer extracted once with ether. The combined organic layers were washed with water and then dried over anhydrous magnesium sulfate. The solution was filtered and the solvent removed under vacuum to give 5.65 g (90%) of (η^5-1-hydroxyethylcyclopentadienyl)tricarbonylmethyltungsten as a yellow liquid. An analytical sample was obtained by molecular distillation. IR (neat): ν(CO) 2005, 1920 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 0.45, s, W—CH_3, 1.47, d, methyl; 2.22, s, OH; 4.65, q, methine; 5.39, m, Cp. Found: C, 33.66; H, 3.11. $C_{11}H_{12}O_4W$ calcd.: C, 33.70; H, 3.09%.

Dehydration of (η^5-1-hydroxyethylcyclopentadienyl)tricarbonylmethyltungsten (V)

(η^5-1-Hydroxyethylcyclopentadienyl)tricarbonylmethyltungsten (3.15 g, 8.03 mmol) and *p*-toluenesulfonic acid (0.16 g, 0.84 mmol) were dissolved in 75 ml of benzene. The reaction mixture was then refluxed for 45 min. The black solution was cooled to room temperature and the solvent removed under vacuum on alumina. The resulting residue was added to a column of alumina (1.5 × 15 cm). Elution of the column with hexane gave a yellow band which was collected under nitrogen. Removal of the solvent under vacuum gave 0.57 g (19%) of (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten. Further elution with hexane/ether gave another yellow band which was collected under nitrogen. The solvent was removed under vacuum to give 2.0 g (65%) of bis-[1-(η^5-cyclopentadienyltricarbonylmethyltungsten)ethyl] ether (VI) as a yellow powder. An analytical sample was obtained by repeated recrystallization from hexane/ether to give pale yellow crystals, m.p. 103—105°C. IR ($CHCl_3$): ν(CO) 2005, 1915 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 0.44, s, W—CH_3; 1.42, d, methyl; 4.45, q, methine; 5.40, m, Cp. Found: C, 34,46; H, 2.85. $C_{22}H_{22}O_7W_2$ calcd.: C, 34,49, H, 2.90%. Mass Spectrum: M^+ *m/e* 766 ($2^{184}W$).

(η^5-1-Methoxyethylcyclopentadienyl)tricarbonylmethyltungsten (VII)

(η^5-1-Hydroxyethylcyclopentadienyl)tricarbonylmethyltungsten (1.50 g, 3.83 mmol) and *p*-toluenesulfonic acid (0.15 g, 0.79 mmol) were dissolved in 75 ml of methanol. The reaction mixture was refluxed for 2 h. The solution was cooled to room temperature and the solvent removed under vacuum on alumina. The resulting residue was added to a column of alumina (1.5 × 15 cm). Elution of the column with pentane/ether brought down a yellow band which was collected under nitrogen. The solvent was removed under vacuum to give 1.26 g (80%) of (η^5-1-methoxyethylcyclopentadienyl)tricarbonylmethyltungsten as a yellow liquid. An analytical sample was obtained by molecular distillation. IR (neat): ν(CO) 2005, 1910 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ (ppm) 0.43, s, W—CH_3; 1,43, d, methyl; 3,46, s, methoxy; 4.11, q, methine; 5.38, s, Cp. Found: C, 35.33; H, 3.48. $C_{12}H_{14}O_4W$ calcd.: C, 35,49; H, 3.47%.

(η^5-Cyclopentadienylmethyl acrylate)tricarbonylmethyltungsten (IX)

Method A: In a single-neck flask was placed (η^5-hydroxymethylcyclopentadienyl)tricarbonylmethyltungsten (1.0 g, 2.7 mmol) followed by 50 ml of benzene and 0.44 ml of pyridine. To this solution was added acryloyl chloride (0.43 ml, 5.3 mmol), which gave immediate precipitation of a white solid. The solution was allowed to stir at room temperature for 3 h, and then 10 g of alumina was added. The solvent was removed under vacuum, and the resulting residue was added to a column of alumina (1.5 × 15 cm). Elution of the column with pentane/ether gave a yellow band which was collected under nitrogen. The solvent was removed under vacuum to give 0.37 g (32%) of (η^5-cyclopentadienylmethyl acrylate)tricarbonylmethyltungsten as a yellow crystalline solid. The compound could be further purified by recrystallization from hexane/ether, m.p. 35—37°C. IR (neat): ν(CO) 2000, 1910, 1730 cm^{-1}. ^{1}H NMR ($CDCl_3$): 0.45, s, W—CH_3; 4.92, s, methine; 5.42, m, Cp; 5.92—6.46, m, vinyl. Found: C, 36.20; H, 2.87. $C_{13}H_{12}O_5W$ calcd.: C, 36.13, H, 2.80%.

Method B: Sodium hydride (3.2 mmol as a 50% dispersion) was added to a 100-ml three-neck round-bottom flask equipped with a condenser and gas inlet and outlet valves. The sodium hydride was washed with pentane, and 50 ml of THF was added. Then (η^5-hydroxymethylcyclopentadienyl)tricarbonylmethyltungsten (1.0 g, 2.7 mmol) was added and the reaction was refluxed for 20 min. The resulting brown solution was cooled in ice and acryloyl chloride (0.26 ml, 3.2 mmol) was added. The reaction was stirred at 0°C for 30 min. and then refluxed for 30 min. The solvent was evaporated on alumina under reduced pressure, and the resulting residue added to a column of alumina (1.5 × 15 cm). The column was eluted with pentane/ether to give a yellow band which was collected under nitrogen. The solvent was removed under vacuum to give 0.75 g (65%) of (η^5-cyclopentadienylmethyl acrylate)tricarbonylmethyltungsten.

Polymerizations

All polymerizations and copolymerizations were performed in sealed tubes in vacuo. The monomers, AIBN, and benzene were introduced into dried polymerization tubes and subjected to three freeze-pump-thaw cycles. The tubes were then sealed and placed in constant temperature baths at 60°C (±0.5°). After the appropriate reaction time the contents of the tubes were poured into excess dry hexane/pentane. The polymers were then reprecipitated three times from tetrahydrofuran into pentane/hexane followed by drying in vacuo (15—20 torr) at 25°C for 15 h.

Homopolymerization of IV

Monomer IV (0.5 g, 1.34 mmol) and AIBN (6.7 mg, 4.1 × 10^{-2} mmol) were weighed into a dry polymerization tube and dissolved in 3.0 ml of dry benzene. The solution was subjected to three freeze-pump-thaw cycles and finally sealed under vacuum. The tube was kept in an oil bath at 60°C (±0.5°) for 158 h. The tube was opened and the solution was added dropwise into agitated dry hexane (200 ml). The polymer was filtered and washed three times with dry hexane. When dry on the filter, the polymer was dissolved in 10 ml of dry THF and precipitated by dropwise addition into rapidly stirred dry hexane (200 ml). The precipitation was done three times and finally the polymer was collected on a tared filter paper, washed with dry hexane and dried in vacuo at 25°C for 15 h. The polymer weighed 0.06 g (12%). The ν(C=C) stretching frequency characteristic for IV was no longer observed in the polymer.

Copolymerization of IV with methyl methacrylate

Monomer IV (0.5 g, 1.34 mmol) and 0.3116 g (3.16 mmol) of methyl methacrylate together with AIBN (22.4 mg, 0.137 mmol) were weighed into a dry polymerization tube and dry benzene (3 ml) was introduced. After three freeze-pump-thaw cycles, the tube was sealed under vacuum and kept in an oil bath at 60°C (±0.5°) for 138 h. When the reaction was over, the tube was opened and the solution was added to rapidly stirring dry hexane (200 ml). The polymer was filtered and washed with dry hexane three times. When dry on the filter, the copolymer was reprecipitated three times by dissolving it into dry THF (10 ml) and dropping the solution into dry hexane (200 ml) with rapid stirring. The polymer was finally collected, washed with dry hexane three times, and dried in vacuo at 25°C for 15 h. The yield of polymer was 0.64 g (77%). Other copolymerizations were conducted in a similar manner.

Copolymerization of IX with methyl acrylate

Monomer IX (0.25 g, 0.59 mmol), methyl acrylate (0.11 g, 1.26 mmol), AIBN (8 mg, 4.9×10^{-2} mmol) and benzene (3.0 ml) were introduced into a polymerization tube and subjected to three freeze-pump-thaw cycles. The tube was sealed under vacuum and kept at 60°C (±0.5°) for 130 h. The tube was opened and the solution was added dropwise to rapidly stirring dry hexane (200 ml). The copolymer was filtered, washed three times with hexane and redissolved in THF (10 ml). Reprecipitation was done three times by adding the solution of the polymer to dry hexane (200 ml) each time, followed by three washings with hexane. Finally the polymer was collected, washed three times with hexane, and dried in vacuo at 25°C for 15 h. The yield of polymer was 0.23 g (64%). Other copolymerizations were conducted in a similar manner.

Metathesis of trans-3-heptene

Polymer XIV (20 mg, 30.3% W, 32 mol percent M_1, 0.03 mmol W) and *trans*-3-heptene (1.78 ml, 12.7 mmol) were placed in a dry 5-ml capacity Schlenk tube. The mixture was degassed via five freeze-pump-thaw cycles. Isobutylaluminium dichloride (0.06 ml of a 1.179 *M* solution in hexane, 0.07 mmol) and O_2 (0.84 ml, 0.036 mmol) were added via a syringe. The contents were mixed with a magnetic stirrer. After 60 min the reaction mixture was neutralized with a small amount of methanol and analyzed using a Hewlett—Packard

5985 GC/MS system and a 6′ X 1/8″, 15% SE-30 on Anakrom AS, copper column. The following program was used: 40° C (2 min), temperature programmed 10° C/min to 200° C. The following products were indentified via computer-assisted mass spectral correlation: *trans*-3-heptene (97% recovered, 12.3 mmol), *trans*-4-octene (0.10%, 0.013 mmol), *trans*-3-hexene (1.71%, 0.22 mmol), 4-ethyl-2-octene (0.30%, 0.038 mmol), and other unidentified components.

Acknowledgement

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to a National Science Foundation grant to the Materials Research Laboratory, University of Massachusetts, for support of this research program (M.D.R.). The support of the Office of Naval Research (Inorganic Polymers Program) and the Army Research Office Grant DAAG 29-76-6-0182 (to C.U.P.) is gratefully acknowledged. We also wish to thank Mr. W. Craig Spink for assistance in the synthesis of monomer IV during the early stages of the program.

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