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Preliminary communication

ORGANOMETALLIC POLYMERS CONTAINING TRICARBONYL(η^4-DIENE)-RUTHENIUM(0) AND -IRON(0) AS PENDANT GROUPS

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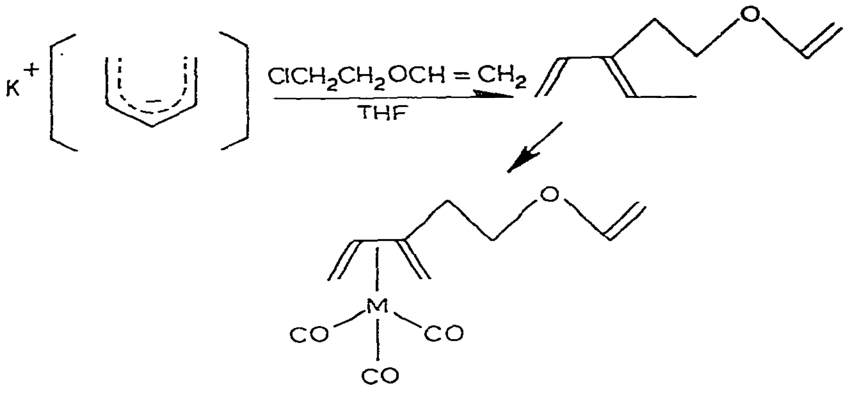
Summary

Vinyl ethers containing tricarbonyl(1—4-η^4-1,3-pentadiene)-ruthenium(0) and -iron(0) species were prepared utilizing selective dienylation with pentadienylpotassium and were polymerized with cationic initiators to give high molecular weight polymers. The diene-metal moieties were converted into tricarbonyl(1—3-η^3-allyl)metal species by protonation with dry HCl. Tricarbonyl-(3-allyl-1—4-η^4-1,3-pentadiene)iron(0) also undergoes cationic polymerization but the presence of its isomer, tricarbonyl(3-propenyl-1—4-η^4-1,3-pentadiene)-iron(0) inhibits the polymerization.

Preparation of novel organometallic polymers containing functional organoruthenium(0) or -iron(0) moiety has been severely hampered by the inhibition of conventional vinyl polymerization due to the preferential attack of catalysts on such reactive moieties as ruthenium(0) or iron(0) species. For example, attempted polymerization of vinyl organometallics such as tricarbonyl(1—4-η^4-1,3,5-hexatriene)iron has been totally unsuccessful, although some chemically stable vinylmetallocenes are known to undergo radical polymerization under rather mild conditions [2]. Recently, the utility of anionic catalysts was demonstrated for the polymerization of organometal-containing acrylic monomer systems [3]. This paper describes the advantages of the use of cationic initiators for the polymerization of monomers containing functional organometal moieties.

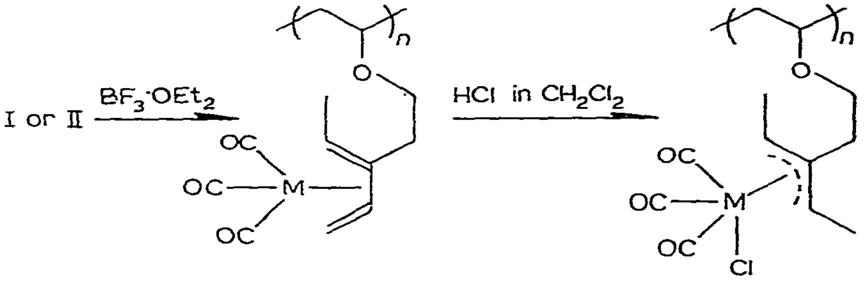
In view of recent interest in organometallic ruthenium(0) complexes as catalysts and in the specific physical properties of organometallic polymers, we have examined the cationic polymerization of specially designed tricarbonyl(3-vinyloxyethyl-1—4-η^4-1,3-pentadiene)metal (where metal is ruthenium(0) or iron(0)) and have successfully prepared high molecular weight polymers.

Thus, taking advantage of the selective dienylation with pentadienylpotassium [4], the following conjugated diene was prepared in THF (base-catalyzed isomerization of 3-vinyl-4-pentenyl vinyl ether to 3-vinyl-3-pentenyl vinyl ether occurred quantitatively during the reaction [5]) and was converte



(I, M = Ru ;
II, M = Fe)

to η^4-diene-metal complexes. The thermal reaction of terminal 1,3-dienes with $Ru_3(CO)_{12}$ generally results in formation of a mixture of diene oligomers and ill-defined Ru clusters [6a,b]*. The presence of two alkyl substituents on the 1,3-diene system seems to prevent such undesirable reactions and results in good yields (85% for I, 72% for II) of (tricarbonyl)metal complexes. These monomers are readily polymerized by cationic initiators such as $BF_3 \cdot OEt_2$ (1 mol%, based on monomer) or $TiCl_4$ in CH_2Cl_2 at −20°C to give air-stable yellow elastomers of the desired structure, III and IV, in 75 and 62% yield, respectively. The ^1H NMR spectra of I and III (Fig. 1) clearly indicate that they assume (*E*)-configuration. The ^1H NMR spectra of II and IV are essentially the same as those of I and III, respectively. The molecular weights of the polymers obtained by precipitation in methanol were measured by GPC (using a HSG 40-15 column and THF as an eluent) as 15000 for III and 21000 for



(III, M = Ru : IV, M = Fe)

(V)

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*Tricarbonyl(1—4-η^4-butadiene)ruthenium was recently prepared by a ligand exchange reaction [6b].

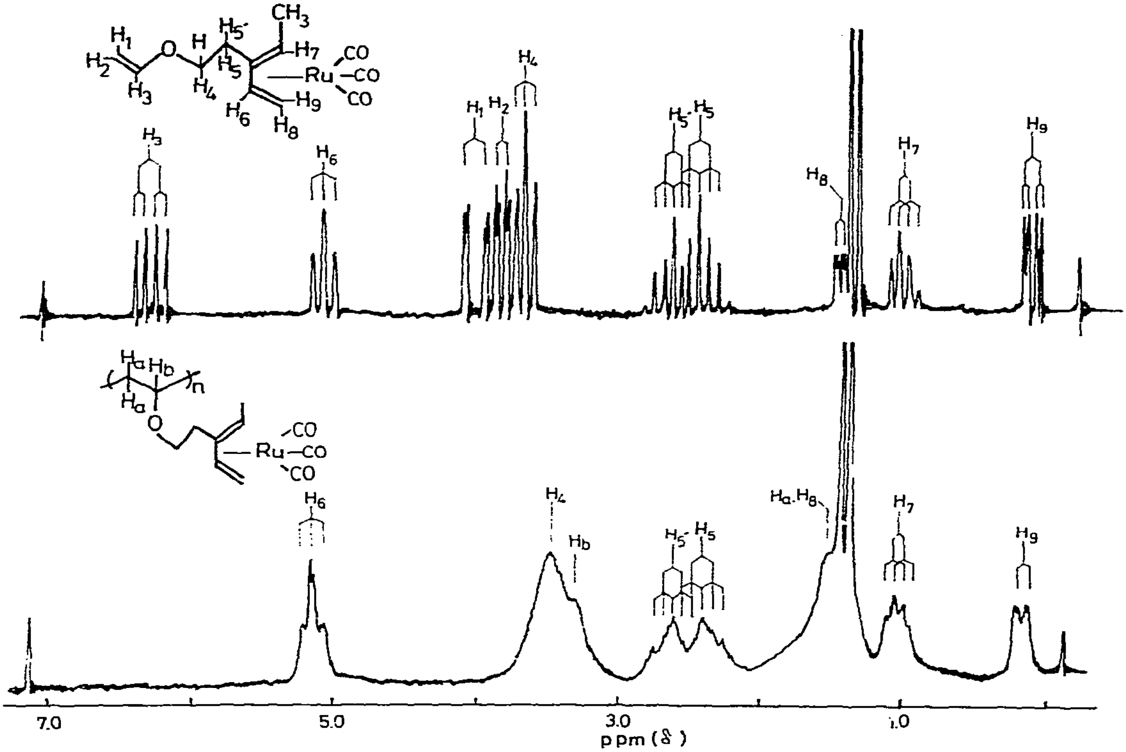
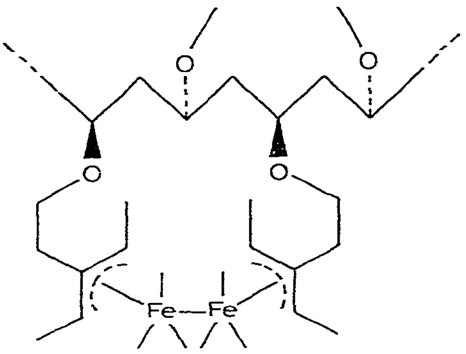


Fig. 1. ^{1}H NMR (100 MHz) spectra of tricarbonyl(3-vinyloxyethyl-1—4-η^4-1,3-pentadiene)ruthenium(0) (I) and its polymer (III) in $CDCl_3$ at 30°C.

IV. The molecular weight distributions (M_w/M_n 2.4 for III and 1.4 for IV) were rather sharp compared to poly(vinylmetallocenes) prepared by radical polymerization. The resulting polymer IV was treated with dry HCl at −70°C in CH_2Cl_2 to give a polymer V containing chloro(tricarbonyl)-η^3-allyliron species, as evidenced by IR and ^{1}H NMR; the CO absorption at 2060, 1987, 1970 cm^{-1} observed for III shifted to 2080, 2035, 2005 cm^{-1} after reaction. The presence of one type of methyl protons at 2.05 ppm shows that the two methyl groups of V are in *syn* position in accord with the result of protonation of tricarbonyl(1,3-pentadiene)iron [7]. Addition of HCl at higher temperatures (>0°C) caused the cleavage of the ether linkage to cleave the metal species from the polymer.

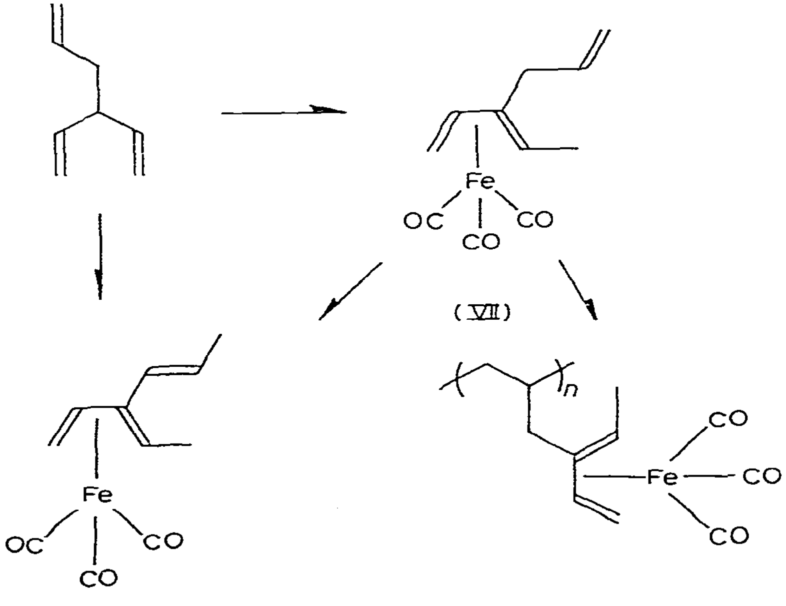
For preparation of the polymers which contain metal—metal bonds between the neighboring two chloro(tricarbonyl)-η^3-allyliron species, reactions of V with $AgPF_6$, $AgBF_4$, Sn—Hg or $Na_2[Fe(CO)]_4$ were examined because these reagents are known to be effective for the elimination of halide anions attached to a metal [8]. Metal—metal bond formation by the elimination with silver salts was unsuccessful and 80% of V was rapidly converted into III by reactions in anhydrous acetone, ethanol or CH_2Cl_2 at 10°C. Tin-amalgam and zinc powder, however, served as good coupling reagents and the polymer VI which was soluble in CH_2Cl_2, was obtained. The IR spectrum of VI obtained by reaction with tin amalgam showed the CO absorptions at 2090, 2040, 2000 cm^{-1},



(VI)

and the visible spectrum in CH_2Cl_2 showed an absorption at 580 nm. Polymer VI was thermally unstable in CH_2Cl_2 or THF and gradually decomposed to give III in 5 h at 20°C but polymer VI obtained as a solid by evaporation of solvent remained green in color for 2 days in air, although it became insoluble in common solvents. Polymer VI obtained by reaction with $Na_2[Fe(CO)_4]$ showed the same IR spectrum as that obtained with tin amalgam but it was insoluble in common solvents, presumably due to the cross-linking between the polymer chains.

Another example of cationic polymerization includes tricarbonyl(3-allyl-1—4-η^4-1,3-pentadiene)iron(0) (VII) as monomer which is prepared by the following reactions. The π-complexation requires some caution because isomerization of VIII generally accompanies the reaction when it was performed at higher temperatures (>80°C). The use of $Fe_3(CO)_{12}$ is not suitable for this



(VII)

(VIII)

(IX)

reason, but VII was obtained in good yield (70%) with $Fe_2(CO)_9$ at 30°C in pentane. Cationic polymerization of VII with $BF_3 \cdot OEt_2$ in CH_2Cl_2 at –30°C gave a 40% yield of a linear oligomer IX which could be further converted to an oligomer containing chloro(tricarbonyl)-η^3-allyliron(0) species in a similar manner as described for IV or could be demetallated by cerium(IV). The molecular weight of the demetallated oligomer was 1900. Radical copolymerization of VII with styrene (1/5 molar ratio) by AIBN at 60°C in benzene provided an air-stable polymer containing the units of VII and styrene in 1/6 ratio. It is surprising that the addition of a small amount of VIII (5%) to VII inhibits completely the cationic homopolymerization of VII or its copolymerization with styrene. This is presumably due to the predominant trapping of the cationic catalytic species or the propagating chain ends by VIII to form a stabilized cationic metal complex as was reported for vinylferrocene [9].

The polymers thus obtained have tricarbonyl(η^4-1,3-diene)metal or (η^3-allyl)-metal species bound in polymer side chains. They may be chemically or photochemically modified for use as catalysts or reagents in organic transformations. To this end, one good example, the synthesis of unsaturated ketones via a π-allyliron tetracarbonyl cation bound to a polymer, has so far been reported [10].

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