

Synthesis and addition polymerization of vinylbenzyl transition metal compounds

By: Shreyas S. Kher and [Terence A. Nile](#)

S.S. Kher and T.A. Nile (1991) "Synthesis and Addition Polymerization of Vinylbenzyl Transition Metal Compounds," *Transition Metal Chemistry*, 16, 28.

Made available courtesy of Springer Verlag: The original publication is available at <http://www.springerlink.com>

*****Reprinted with permission. No further reproduction is authorized without written permission from Springer Verlag. This version of the document is not the version of record. Figures and/or pictures may be missing from this format of the document.*****

Summary:

The synthesis of three vinylbenzyl complexes ($\eta^5\text{-C}_5\text{H}_5\text{-M}(\text{CO})_n(\text{CH}_2\text{C}_6\text{H}_4\text{CH}=\text{CH}_2)$, [(1), M = Mo, n = 3; (2), M = W, n = 3; (3), M = Fe, n = 2] is reported. Complexes (1) and (2) have been copolymerized with monomers, such as styrene, methyl methacrylate, and N-vinyl-2-pyrrolidone, in benzene using azoisobutyronitrile as initiator. The rates of incorporation of (2) into copolymers with styrene and methyl methacrylate were the same as the rate of incorporation of the organic monomer. The homopolymerization of (2) was also carried out. Polymerizations occurred satisfactorily except for the copolymerization of (1) with styrene, where little incorporation of the organometallic monomer occurred.

Article:

Introduction

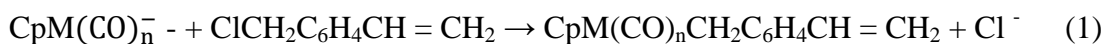
Organometallic polymers containing transition metals are of current interest⁽¹⁻³⁾. These organometallic polymers are expected to show novel properties and to be useful for processes such as the controlled release of iron in the treatment of anemia or as hydrogenation catalysts⁽²⁾. Two possible routes to organometallic polymers have been explored: the synthesis of organometallic monomers and their subsequent polymerization⁽⁴⁾, or the attachment of a transition metal complex to a preformed organic polymer⁽⁵⁾.

This paper deals with the synthesis of transition metal vinylbenzyls, (1)-(3), and their homopolymerization and copolymerization. The synthesis of (2) has recently been reported, as has its copolymerization with octadecyl methacrylate⁽⁶⁾.

Results and discussion

Monomer synthesis

The transition metal vinylbenzyls were prepared by reacting the appropriate metal anion with a mixture of *meta*- and *para*-isomers of vinylbenzyl chloride, Equation (1), presumably resulting in a similar mixture of



(1) M = Mo, n = 3; 64% yield, $\nu(\text{CO})$ 2010, 1920 cm^{-1} ; (2) M = W, n = 3; 42% yield, $\nu(\text{CO})$ 2005, 1920 cm^{-1} ; (3) M = Fe, n = 2; 8% yield, $\nu(\text{CO})$ 2000, 1950 cm^{-1} isomeric transition metal complexes. The spectral properties of (1)-(3) were similar to those reported for the corresponding benzyl compounds⁽⁷⁻⁹⁾. Complex (3) was isolated in low yield because of its instability in solution, making purification difficult. The synthesis of the chromium analog of (1) and (2) was attempted, but pure products could not be isolated.

Synthesis and characterization of the copolymers

A variety of copolymerizations were carried out in order to investigate the utility of the organometallic monomers that had been synthesized. ($\eta^5\text{-Cyclopentadienyl}$)vinyl-benzyltricyarbonyltungsten, (2), and ($\eta^5\text{-$

cyclopentadienyl)-vinylbenzyltricarbonylmolybdenum, (1), were used as they were readily available in reasonable quantity and were quite stable. Styrene, methyl methacrylate, *N*-vinylpyrrolidone and acrylonitrile were chosen as Rausch and others have successfully copolymerized similar organometallic compounds with these organic monomers⁽¹⁰⁾.

Complex (2) and styrene were dissolved in benzene and the mixture was boiled under reflux for 24 h in presence of the radical initiator, azo-isobutyronitrile, AIBN. The resulting solution was precipitated in hexane and the copolymer was recovered by filtration and drying (64%, yield). The i.r. spectrum showed the presence of carbonyl groups, $\nu(2110)$ and $\nu(1920)$ cm^{-1} , and which compares with the carbonyl stretching frequencies of 2005 and 1920 cm^{-1} for the monomer. The similarity in the carbonyl stretching frequency pattern suggests that the environment of the tungsten atom has changed somewhat, but that its overall environment is similar to that in the monomer. This conclusion is consistent with the formulation of the product as a styrene (η^5 -cyclopentadienyl)vinylbenzyltricarbonyltungsten co-polymer. The elemental analysis gave a tungsten content of 20% which means there are *ca.* four units of styrene for every unit of (2). The molar feed ratio of styrene to (2) was also *ca.* 4:1, suggesting that the rate of incorporation of both the monomers is the same.

Other copolymerizations were carried out using (1) and (2); the results are summarized in Table 1. For the combination (2)-methyl methacrylate, elemental analysis indicates that the ratio of incorporation of organic monomer is similar to the feed ratio, suggesting that again the rate of incorporation of both monomers is the same. However, the rate of incorporation of (2) into the (2)-*N*-vinylpyrrolidone copolymer appears to be higher. On the other hand, the rate of incorporation of (1) is less than the organic monomer for both styrene and methyl methacrylate copolymerizations. All copolymers were a pale yellow. Complex (2) was also homopolymerized in benzene using AIBN as catalyst in 20% yield. The pale yellow polymer had carbonyl stretches at 2008 and 1915 cm^{-1} (Nujol).

The chemistry of these organometallic polymers is currently under investigation in our laboratories.

Table 1. Copolymerizations of vinylbenzyl organometallic monomers with organic monomers^a.

Organometallic monomer	Organic monomer	Feed ratio ^b	Metal content ^c of copolymer (%)	Incorporation ratio ^d	Yield (%)	I.r. [$\nu(\text{CO}) \text{cm}^{-1}$] ^e
(1)	Styrene	4:1	0.2	Very small	30	2010, 1920
(1)	Methyl methacrylate	4:1	9.37	7:1	41	2005, 1962, 1920, 1730
(2)	Styrene	4:1	20.00	4:1	64	2008, 1920
(2)	Methyl methacrylate	5:1	18.77	5:1	37	2008, 1917, 1735
(2)	<i>N</i> -Vinylpyrrolidone	4:1	33.18	1:1	42	2005, 1960, 1415, 1678

^aInitiated by AIBN in C_6H_6 solution; ^bRatio of organic monomer to organometallic monomer; ^cDetermined by elemental analysis of polymer for Mo or W; ^dBased on elemental analysis; ratio of incorporation of organic monomer: organometallic monomer; ^eNujol mull.

Molecular weight

The copolymer obtained from styrene and (η^5 -cyclopentadienyl)vinylbenzyltricarbonyltungsten gave molecular weights of the order of 11,000 as determined by viscosity measurements. Although the molybdenum content of the copolymer obtained from styrene and (η^5 -cyclopentadienyl)vinylbenzyltricarbonylmolybdenum was low, the molecular weight obtained (7000) still emphasizes the fact that the organometallic monomer can undergo copolymerization and withstand it. Pittman and others have copolymerized (η^5 -cyclopentadienyl)vinylbenzyltricarbonylmanganese with styrene and obtained copolymers with molecular weight in the 40,000-80,000⁽¹¹⁾ range. The lower molecular weights with the vinylbenzyls may be due to the instability of the metal-benzyl bond.

Experimental

Experiments were carried out in all-glass apparatus under a N_2 atmosphere. THF, Et_2O , PhH and hexane were distilled from Na/K alloy or sodium benzophenone radical anion under a N_2 atmosphere. Styrene was purified by washing with aqueous NaOH followed by distilled H_2O , drying and distillation under reduced pressure. *N*-

vinylpyrrolidone was purified by distillation *in vacuo* of a commercial sample. Methyl methacrylate and acrylonitrile were washed with 10% aqueous NaOH, 10% H₂SO₄, distilled H₂O; the organic layers were separated, dried over anhydrous Na₂SO₄ and distilled. Vinylbenzyl chloride, consisting of a mixture of *meta*- and *para*-isomers, was purchased from Eastman Kodak and was used without further purification. ¹H n.m.r. spectra were recorded either on Varian T 60 or Varian EM 360 instruments, using TMS as an internal standard.

I.r. spectra were recorded on a Perkin Elmer 1320 spectrophotometer using NaCl cells. The purity of the organic monomers was determined by g.l.c. on a Varian 3300 gas chromatograph. C and H microanalyses were carried out by MIC ANAL, Tucson, Arizona and all other microanalyses were performed by Galbraith laboratories, Knoxville Tennessee.

(n⁵-Cyclopentadienyl)vinylbenzyltricarbonyl-molybdenum

Mo(CO)₆ (9.50 g, 36 mmol) was dissolved in 25 ml MeCN and the solution was boiled under reflux in a N₂ atmosphere for 24 h. The solvent was removed *in vacuo* and dry THF (25 cm³) was added to the flask, followed by 1.0M NaCp solution (36 cm³, 36 mmol) in THF. The reaction mixture was heated to reflux for 1 h and then cooled in an ice-bath. Vinylbenzyl chloride (4.94 g, 32 mmol), dissolved in dry THF (15 cm³), was then added and the mixture was stirred for 8 h. The solvent was removed *in vacuo* and the residue was extracted with CH₂Cl₂ (100 cm³) in three equal portions, filtered and collected. The filtrate was concentrated and passed through a silica gel column (50/50 hexane/CH₂Cl₂) under N₂. The first fraction was collected and concentrated, the solid residue was dissolved in PhH and ligroin (90°-120°) was added to the flask. The solution was cooled to facilitate recrystallization and filtered to give bright yellow crystals of (n⁵-cyclopentadienyl)vinylbenzyltricarbonylmolybdenum (6.03 g, 64% yield), m.p. 102° C. (Found: C, 63.7; H, 4.59. C₁₇H₁₄MoO₃·C₆H₆ calcd.: C, 62.7; H, 4.59%) ¹H n.m.r. (C₆D₆): δ(ppm): 2.33 (2H) s MoCH₂C₆H₄CH=CH₂; 4.10 (5H) broad s, C₅H₅MoCH₂C₆H₄CH=CH₂; 4.48-5.64 (3H), complex m, MoCH₂C₆H₄CH=CH₂; 6.64 (4H), broad d, MoCH₂C₆H₄CH=CH₂. I.r. (CH₂Cl₂): ν(CO): 2010vs, 1920vs cm⁻¹.

(n⁵-Cyclopentadienyl)vinylbenzyltricarbonyltungsten

W(CO)₆ (6.00 g, 17 mmol) was dissolved in EtCN (52 cm³) and the solution was heated to reflux for 120 h under a N₂ atmosphere. The solvent was removed *in vacuo* and 1.0M CpNa solution (17 cm³, 17 mmol) in THF was added to the flask. The reaction was boiled under reflux for 1.5 h. Vinylbenzyl chloride (2.35 g, 15 mmol) in 25 ml THF was added to the ice-cooled solution of metal anion and the mixture was stirred overnight at room temperature. The solvent was removed *in vacuo* and the yellow-brown residue was extracted with CH₂Cl₂ (100 cm³) in three equal portions, filtered and collected. The solution was concentrated and hexane (25 ml) was added to bring about the crystallization. Fine golden-yellow crystals of (n⁵-cyclopentadienyl)vinylbenzyltricarbonyltungsten were obtained (2.5 g, 42% yield), m.p. 74° C (lit⁽⁶⁾ m.p. 86°). Found: C, 46.1; H, 3.3. C₁₇H₁₄O₃W₁ calcd: C, 45.4; H, 3.1%. ¹H n.m.r. (CDCl₃): δ(ppm): 2.91 (2H) s, WCH₂C₆H₄CH=CH₂; 4.4 (5H) s C₅H₅WCH₂C₆H₄CH=CH₂; 5.50-6.91 (3H) complex m, WCH₂C₆H₄CH=CH₂; 7.12 (4H) broad d, WCH₂C₆H₄CH=CH₂. I.r. (CH₂Cl₂) ν(CO): 2010vs, 1920vs cm⁻¹.

Attempted preparation of (n⁵-cyclopentadienyl)-vinylbenzyltricarbonylchromium

Cr(CO)₆ (7.21 g, 33 mmol) dissolved in EtCN (50 cm³) was boiled under reflux for 24 h under a N₂ atmosphere. EtCN was removed *in vacuo* and the residue was dissolved in THF (25 cm³) and cooled in ice. Cold 1.0M CpNa solution (36 cm³, 36 mmol) in THF was added to the flask and the mixture was stirred overnight at room temperature. The solvent was removed *in vacuo* and the residue was extracted with CH₂Cl₂ (100 cm³) in three equal portions, filtered and collected. The product was extremely unstable in solution as well as in solid state. It was thought to be light-, heat-, and moisture-sensitive. The product decomposed immediately after each purification which made isolation impossible.

(n⁵-Cyclopentadienyl)vinylbenzylidicarbonyliron

Cyclopentadienyliron dicarbonyl dimer (4.84 g, 16 mmol) was dissolved in dry THF (100 cm³) and this solution was added to a 3-neck flask containing 1% Na/Hg amalgam (0.097 g Na, 97.0 g Hg) and stirred overnight, then separated from unreacted Na/Hg and then cooled to -78° C. Vinylbenzyl chloride (5.00 g, 32 mmol) in THF (25

cm³) was added to the cold reaction flask and the contents were stirred overnight. The solvent was removed *in vacuo* and the residue was extracted with hexane and passed through a silica gel column using hexane as the eluent. The first fraction was collected and concentrated to give orange crystals. The solid was recrystallized using CH₂Cl₂ and ligroin (90°-120°). It was extremely unstable both in solution and in the solid state. Finally, orange crystals of (n⁵-cyclopentadienyl)vinylbenzylidicarbonyl-iron were recovered (0.37 g, 8% yield), m.p. 49°-50° C. (Found: C, 65.2; H, 4.5. C₁₆H₁₄O₂Fe calcd: C, 65.3; H, 4.2. ¹H n.m.r. (CDCl₃); δ(ppm); 2.70 (2H) s, FeCH₂C₆H₄CH=CH₂; 4.67 (5H) s, C₅H₅FeCH₂C₆H₄CH=CH₂; 5.00-6.86 (3H) complex m, FeCH₂C₆H₄CH=CH₂; 7.13 (4H) broad d, FeCH₂C₆H₄CH=CH₂. I.r. (CH₂Cl₂) ν(CO): 2000vs, 1950vs cm⁻¹.

Copolymerizations of (2) with styrene

(n⁵-Cyclopentadienyl)vinylbenzyltricarboxyltungsten (0.50 g, 1.1 mmol) and styrene (0.50 g, 4.8 mmol) were dissolved in (PhH 5 cm³) and the solution was heated to reflux under a N₂ atmosphere in the presence of AIBN (10 mg) for 24 h. The resulting solution was precipitated in hexane, filtered, and the precipitate was dried to yield a light brown powdery mass of styrene (n⁵-cyclopentadienyl)-vinylbenzyltricarboxyltungsten copolymer (0.33 g, 66% yield based on the organometallic monomer). Elemental (Found: W, 20.0). I.r. (Nujol) ν(CO): 2010s, 1920vs cm⁻¹. Approximate MW (viscosity measurements): 11,000.

Other copolymerizations

In each case, 0.5 g of monomer was used with PhH (5 cm³) and AIBN (10 mg). All copolymerizations were performed at reflux in PhH for 24 h and then the polymers were precipitated in hexane. Yields and analytical data are included in Table 1.

References

- (1) C. E. Carraher, Jr., J. E. Sheats and C. U. Pittman, Jr.,
- (2) *Organometallic Polymers*, Academic Press, New York, 1978. (2) J. E. Sheats, C. U. Pittman, Jr. and C. E. Carraher, Jr., *Chem. Brit.*, 709 (1984).
- (3) B. M. Culbertson and C. U. Pittman, Jr., *New Monomers and Polymers*, Plenum Press, New York, 1984.
- (4) C. U. Pittman, Jr., *Organometal. React. and Synth.*, 6, 1 (1977).
- (5) R. F. Felis and C. U. Pittman, Jr., *J. Organometal. Chem.*, 72, 389 (1974).
- (6) J. E. Sheats, F. Hessel, L. Tsarouhas, K. G. Podejko, T. Porter, L. R. Kool and R. L. Nolen, in B. M. Culbertson and C. U. Pittman, Jr. (Eds.), *New Monomers and Polymers*, Plenum Press, New York, 1984, p. 269.
- (7) R. B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, 88, 709 (1966).
- (8) C. U. Pittman, Jr. and R. F. Felis, *J. Organometal. Chem.*, 72, 399 (1974).
- (9) J. Biblier and A. Wojcicki, *J. Amer. Chem. Soc.*, 88, 4862 (1966).
- (10) D. W. Macomber, M. D. Rausch, T. V. Jayaraman, R. D. Priester and C. U. Pittman, Jr., *J. Organometal. Chem.*, 205, 353 (1981).
- (11) T. D. Rounsefell, G. V. Marlin, C. U. Pittman, Jr., *Macromolecules*, 6, 1 (1973).