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# Polystyrene-Bearing Cyclopentadienyl Metal Catalysts: Copolymerization of a Styrene Monomer Containing Cyclopentadiene Synthons

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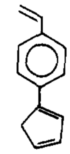
**Abstract:** The reaction of *p*-styrylmagnesium bromide with norbornenone gave *syn*- and *anti*-7-hydroxy-7-(*p*-styryl)norborn-2-ene (**6**) which could be converted to either the *syn*- and *anti*-7-methoxy derivative (**8**) or *anti*-7-chloro-7-(*p*-styryl)norborn-2-ene (**7**). Both styryl monomers **7** and **8** were copolymerized with styrene and divinyl benzene to give polymers (**9**) containing 10 mol % of 7-substituted norbornyl derivatives. Treatment of the 7-chloro polymer (**9c,d**) with butyllithium or reaction of uncross-linked 7-methoxy polymer (**9a**) with sodium–potassium alloy generated the polymer-attached cyclopentadienyl anion that could be converted to a polymer bound $\eta^5$-cyclopentadienyldicarbonylrhodium catalyst (**12**). Quenching the polymer containing cyclopentadienyl anion gave a polymer containing cyclopentadiene units (**11**). This polymer could be converted to the polymer-bound $\eta^5$-cyclopentadienyldicarbonylcobalt analogue (**13**). Although **13** was not a Fischer–Tropsch catalyst, **12** would effect the hydroformylation of 1-hexene and the reduction of aromatic substrates.

The impetus for the use of polymer-attached catalysts for effecting organic reactions has come from a recognition that they most often possesss the advantage of both homogeneous and heterogeneous systems. Knowledge in this area has progressed to a point such that the capabilities of the method and the limitations—at least with the present catalytic systems and supports—have been recognized.[1] Cyclopentadienyl groups attached to cross-linked polystyrene have been used as ligands in hydrogenation,[2-5] isomerization,[5] disproportionation,[5] cyclotrimerization of acetylenes,[5] hydroformylation,[5,6] and Fischer–Tropsch reactions.[7] Catalysts containing transition metals such as titanium,[2-4] zirconium,[4] hafnium,[4] iron,[8] rhodium,[5,6] and cobalt[5-8] have been prepared by exchange onto polystyrene bearing cyclopentadiene or cyclopentadiene anion ligands.

These cross-linked polystyrene catalyst supports containing cyclopentadienyl ligands have all been prepared by modification of commercial resin, either by the reaction of cyclopentadiene anion with chloromethylated polystyrene or by the reaction of cyclopent-2-enone with lithiated polystyrene. There is some evidence that polystyrene containing cyclopentadiene attached directly to the phenyl ring, prepared by lithiation of polystyrene followed by the reaction with cyclopent-2-enone, does not have the integrity of structure expected and behaves anonomously when used as a support for transition metals in catalytic reactions. For example, $\eta^5$-cyclopentadienyldicarbonylcobalt(I) on a polystyrene support would not trimerize acetylenes but surprisingly did serve as a Fischer–Tropsch catalyst.[7] Further, it has been reported[9] that the reaction of cyclopent-2-enone with phenyllithium gives a low yield of phenylcyclopentadiene, and the reaction product also contains carbonyl absorption in the infrared, suggesting 1,4 addition.

Our approach to the synthesis of polymer-attached catalysts has been to synthesize a ligand-bearing monomer, copolymerize it with suitable comonomers and cross-linking monomers, and then exchange the transition metal onto the resulting support. This approach has several advantages, namely that the structure (and purity) of the ligand on the monomer can be assured, the concentration of the ligand in the polymer can be regulated, isolation of the ligand-bearing monomer can be controlled (provided the reactivity ratios are known and the monomer feed is regulated), the nature of the polymer backbone, polar or nonpolar, for example, can be varied (depending on the selection of the comonomer), and finally varying degrees of cross-linking can be introduced.

The problem of synthesis of a cyclopentadiene-bearing styrene monomer centers on the reactivity of the monomer (**1**), that not only could undergo radical polymerization through the cyclopentadiene unit, but also would be expected to undergo self-Diels–Alder polymerization.[10] In this paper, we report the synthesis of a styrene monomer containing a cyclopentadiene synthon, its copolymerization, a method of releasing the protected cyclopentadiene moiety, the conversion of the resulting polymer to catalysts, and certain of the catalytic properties thereof.



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## Results and Discussion

The reaction temperature is critical to the synthesis of phenylcyclopentadienes from phenyllithium and cyclopent-2-enone. Low yields (18.5%) of impure product and appreciable 1,4 addition are obtained at 0 °C in ether,[9] although higher yields have been reported under these conditions.[10] When the reaction is carried out at −78 °C, however, good yields of phenylcyclopentenol, and ultimately phenylcyclopentadiene, can be obtained. Thus, it would not be expected that the same reaction of lithiated polystyrene at higher temperatures would be reliable.[3,7,11] Although the reaction of cyclopent-2-enone with lithiated polystyrene at 0 °C has given a product for which the analyses were satisfactory, the method of analysis would not distinguish cyclopentadiene from either the 1,4-addition product or the alcohol.[11]

In our hands, the reaction of cyclopent-2-enone with phenyllithium in THF or hexane, at 25 °C, gave polycyclopentenone (25–75%) as the predominate product, some 1,4-addition product, the desired phenylcyclopentadiene, and 1-phenylcyclopent-2-en-1-ol. In addition, generation of phenyllithium by the reaction of

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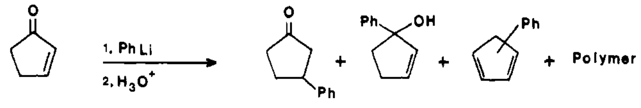
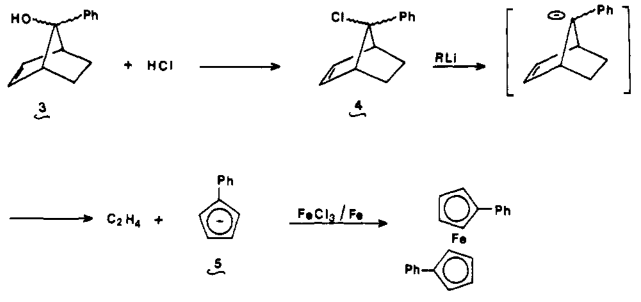
bromobenzene with butyllithium in hexane or THF produced some butylbenzene. The use of *tert*-butyllithium or lithium metal avoided this problem. The reaction of phenyllithium with cyclopent-2-enone either in THF or in hexane gave only 10–20% of the desired product, in agreement with earlier reports.[9] Using conditions analogous to those described[32] for the synthesis of polymer-attached cyclopentadiene by running the lithiation reaction of bromobenzene in hexane at 25 °C, isolating the phenyllithium, and then carrying out its reaction with cyclopentenone in THF at 0 °C gave polycyclopentenone (35%) and four other products (GLC) one of which contained carbonyl absorption. Although it is possible that the reaction of cyclopent-2-enone with lithiated, site-isolated polystyrene may not give such complex reaction products (most of which appear to be condensation/polymerization products), this mode of attachment of cyclopentadiene to polystyrene appears to be less than ideal.



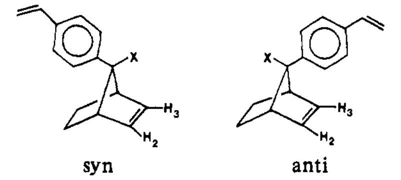
**Phenylcyclopentadiene from the 7-Norbornyl Anion.** The reaction of a mixture of *syn*- and *anti*-7-methoxy-7-phenylnorbornene (**2**) with excess sodium–potassium alloy in dimethoxyethane generates the 7-phenylnorbornyl anion that rapidly undergoes a retro-Diels–Alder reaction at room temperature, yielding the phenylcyclopentadiene anion and ethylene.[12] Although this cyclopentadiene synthon could be utilized to generate polystyrene-attached cyclopentadiene if soluble, uncross-linked polystyrenes were the support, the reaction could not be expected to take place efficiently between the heterogenous, insoluble, cross-linked polystyrene and the alloy. Consequently, we synthesized 7-chloro-7-phenyl norbornene and studied its reaction with butyllithium at 25 °C.

The reaction of *syn*- and *anti*-7-phenylnorbornen-7-ol (**3**)[13] with aqueous hydrochloric acid gave the corresponding syn–anti mixture of 7-chloro-7-phenylnorbornene (**4**) in 90% yield. When the chloronorbornene (**4**) was allowed to react with *n*-butylithium in THF or dimethoxyethane, phenylcyclopentadiene anion (**5**) was generated in >70% yield, as indicated by absorptions at δ 5.5 and 5.8 in the $^1H$ NMR spectrum.[12] This spectrum also showed dissolved ethylene (δ 5.0). The reaction in hexane proceeded very slowly. Although some side reaction products were observed in dimethoxyethane, in THF the anion was generated cleanly. The reaction could be carried out at 0–25 °C with either *n*-butyl- or *tert*-butyllithium, but little reaction took place below −30 °C. A solution of this anion could be converted to the corresponding ferrocene derivative.[14]



**Monomer and Polymer Synthesis.** The reaction of styrylmagnesium bromide with 2-norbornen-7-one at 0–10 °C gave, after quenching, a 68% yield of *syn*- and *anti*-7-(*p*-styryl)norborn-2-en-7-ol (**6**). The remaining product was polymer obtained during the distillation of the product. The styryl alcohol (**6**) could be chlorinated either with aqueous hydrochloric acid or acetyl chloride to give *anti*-7-chloro-7-(*p*-styryl)norborn-2-ene (**7**) in 88 and 50% yields, respectively. The chloride also could be obtained directly from the crude alcohol in a 65% overall yield from 2-norbornen-7-one.

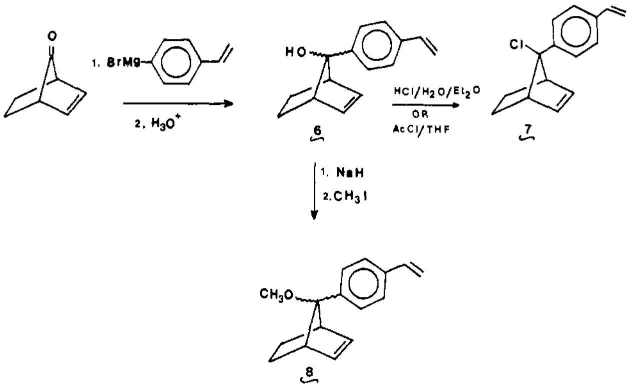
Table I. $^1H$ NMR Chemical Shifts of Norbornene Vinyl Protons, $H_2$ and $H_3$



syn anti

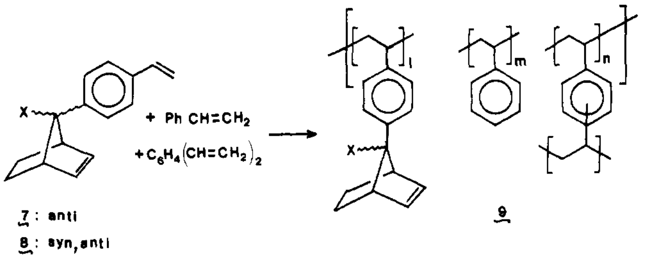
| X | syn | anti |
|---|---|---|
| (4) Cl (7-phenyl) | 6.05 | 5.70 |
| (6) OH | 6.10 | 5.75 |
| (7) Cl | 6.15 | 5.95 |
| (8) $OCH_3$ | 6.10 | 5.80 |

In order to compare the reaction of the 7-methoxy analogue on polystyrene, the syn and anti mixture of 7-methoxy-7-(*p*-styryl)norborn-2-ene (**8**) was prepared from **6** by the reaction of the alkoxide with methyl iodide.



The syn and anti isomers of the 7-styrylnorbornene derivatives (**6**–**8**) were distinguished by the $^1H$ NMR chemical shifts of the norbornene vinyl protons (Table I). The 7-phenylnorbornen-7-*anti*-ol and *anti*-acetate have identical chemical shifts (δ 5.83) downfield from the synisomers, δ 6.23 and δ 6.06, respectively.[13] Mixtures of syn and antiisomers of **6** and **8** were isolated from the reactions, the ratio of *anti*-**6** to *syn*-**6** being 9:1 from the Grignard reaction in THF, a higher ratio than that reported for the reaction of norborneneone with phenylmagnesium bromide in ether (3:1). Compound **7** was obtained, however, as the pure antiisomer.

Both the 7-methoxy (**8**) and the 7-chloro (**7**) norbornene monomers were copolymerized with styrene to give soluble random copolymers or with styrene and divinylbenzene in the presence of a free-radical initiator to yield insoluble polymer supports. The polymerization reaction proceeded without any appreciable chain transfer occurring at the 7-chloro position, at least as indicated by a comparison of the $^{13}C$ spectrum of *anti*-7-chloro-7-phenylnorborn-2-ene with that of the copolymer.



7: anti
8: syn,anti

| | X | *l* | *m* | *n* |
|---|---|---|---|---|
| 9a | $OCH_3$ | 0.1 | 0.9 | |
| b | $OCH_3$ | 0.1 | 0.8 | 0.1 |
| c | Cl | 0.1 | 0.9 | |
| d | Cl | 0.1 | 0.8 | 0.1 |

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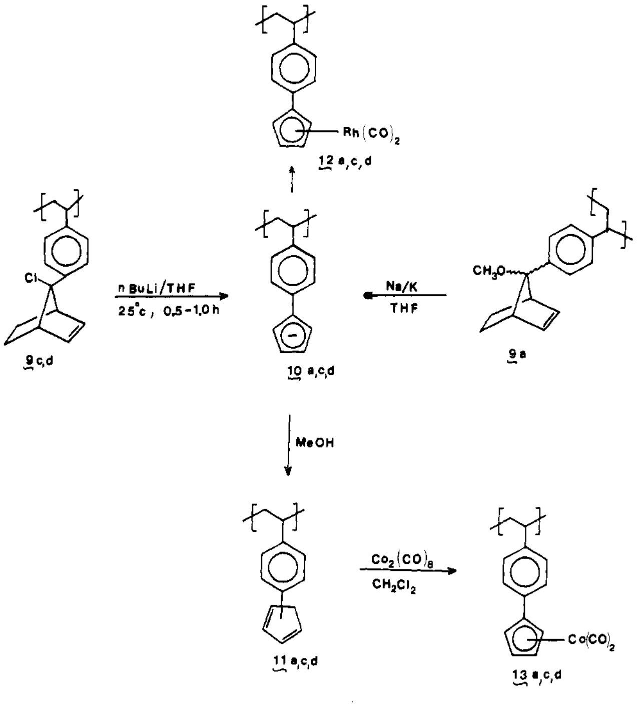
Table II. Hydrogenation with **12d**[a]

| substrate (mmol) | g of **12d** | time, h | product(s) | yield, % | recovered substrate, % |
|---|---|---|---|---|---|
| $C_6H_6$ (56) | 0.20 | 70 | $C_6H_{12}$ | 100 | 0 |
| $C_6H_6$ (42) | 0.15[b] | 9 | $C_6H_{12}$ | 100 | 0 |
| $C_6H_5CH_3$ (56) | 0.20 | 52 | $C_6H_{11}CH_3$ | 100 | 0 |
| $C_6H_5OCH_3$ (56) | 0.20 | 38 | $C_6H_{11}OCH_3$ | 100 | 0 |
| $C_{10}H_8$[c] (33.6) | 0.20 | 65 | $C_{10}H_{18}$ | 42 | 0 |
| | | | $C_{10}H_{12}$ | 58 | |
| $CH_3COCH_3$ (84) | 0.10 | 20 | $CH_3CHOHCH_3$ | 27 | 73 |
| $C_6H_5COCH_3$ (42) | 0.20 | 40[d] | $C_6H_5CH(OH)CH_3$ | 87 | 9 |
| | | | $C_6H_{11}COCH_3$ | 4 | |
| $C_6H_5COCH_3$ (42) | 0.20 | 50 | $C_6H_5CH(OH)CH_3$ | 50 | 5 |
| | | | $C_6H_{11}COCH_3$ | 19 | |
| | | | $C_6H_{11}CH(OH)CH_3$ | 26 | |
| $(C_6H_5CH_2)_2CO$ (24) | 0.20 | 134 | C=O | 20[e] | 0 |
| | | | CHOH | 80 | |
| $CH_3COCH_3/C_6H_6$ (27/56) | 0.20 | 24[f] | $C_6H_{12}$ | 99 | excess $C_6H_6$ and $CH_3COCH_3$ |
| | | | $CH_3CH(OH)CH_3$ | trace | |

[a] All reactions were carried out at 100 °C with 650 psi of $H_2$, pressurized at 25 °C. Yields by $^1H$ NMR integration and GLC. [b] Catalyst from run 1 reused. [c] Cyclohexane (20 mL) was used as solvent. [d] 200 psi $H_2$ at 25 °C. [e] Four products were obtained, all containing carbonyl absorption (IR). [f] 100 psi $H_2$ at 25 °C. All the hydrogen was consumed in this reaction. Yields based on hydrogen.

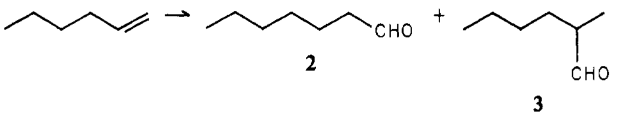
**Catalyst Preparation.** As expected, the cyclopentadiene anion of either soluble or cross-linked polystyrene could be generated in THF by the reactions of *anti*-7-chloronorbornene-containing polymers, **9c** and **9d**, respectively, with butyllithium at ambient temperature. Although the reaction of soluble *syn*- and *anti*-7-methoxynorbornene-containing polymer (**9a**) with sodium-potassium alloy also gave polymer-attached cyclopentadiene anion, the cross-linked *syn*- and *anti*-7-methoxynorbornene-containing polymer (**9b**) failed to react with the alloy.



Once the anion was generated, the rhodium complexes (**12a,c,d**) were obtained by the reaction of bis(chlorodicarbonylrhodium) with the anion. Quenching the polymer-bound anion followed by the reaction of the polystyrene-attached cyclopentadiene unit with dicobaltoctacarbonyl in refluxing methylene chloride gave the cobalt complexes **13a,c,d**. Rhodium analysis showed that ~75% of the theoretical amount of rhodium had complexed on cross-linked polymer **10d** to give **12d**. However, cobalt analysis showed that slightly greater than 100% of the theoretical amount of cobalt had complexed onto **11d**. Since excess cobalt carbonyl was used in the reaction, this is possibly a result of insoluble cobalt metal or clusters becoming trapped in the polymer. The infrared spectra of these polymers containing rhodium and cobalt carbonyls showed carbonyl stretching at 2045, 1980 cm$^{-1}$ [$Rh(CO)_2$] and 2015, 1970 cm$^{-1}$ [$Co(CO)_2$].

**Catalytic Reactions.** Using the cross-linked polymer-bound cyclopentadienyldicarbonylcobalt catalyst (**13d**), we attempted the Fischer–Tropsch synthesis of hydrocarbons under the conditions reported.[7] The reduction of carbon monoxide in a 3:1 $H_2$:CO mixture (75 psi at 25 °C) at temperatures of 150 and 200° C with catalyst **13d** in octane did not give the expected hydrocarbon mixture.

Both hydroformylation reactions and hydrogenation reactions could be effected with the polymer-bound rhodium catalyst **12d**. The hydroformylation of 1-hexene in benzene was carried out with $CO/H_2$ (1/1) at 1300 psi (25 °C) and 110 °C to yield heptanal and 2-methylhexanal (2:3). The conversion was complete in less than an hour, representing a turnover on rhodium of >148/h. This catalyst could be reused in subsequent hydroformylation without loss in activity.



This selectivity, linear/branched (2/3), is lower than that observed in the hydroformylation of 1-pentene and 1-hexene with a catalyst prepared from a commerical polystyrene that had been chloromethylated and subsequently allowed to react with cyclopentadiene anion.[5]

Rhodium catalyst **12d** was also an effective hydrogenation catalyst (Table II). Generally the hydrogenation of aromatic rings took place relatively rapidly compared to the hydrogenation of ketones, although the hydrogenation of acetophenone gave predominately 1-phenylethanol. Hydrogenation of benzene containing electron-donating substituents took place faster than hydrogenation of benzene itself ($OCH_3$ > $CH_3$ > H), in accord with the results of acetophenone hydrogenation. Thus, the aromatic ring containing the electron-withdrawing acetyl group is not hydrogenated rapidly and the generation of the hydroxyethyl group also retards ring hydrogenation. When the catalyst was reused for the hydrogenation of benzene, a higher activity was observed. The polymer itself is partially hydrogenated during these reactions.

## Experimental Section

$^1H$ NMR spectra were recorded on a Varian EM360 and $^{13}C$ NMR spectra were measured on a JEOL FX-100 spectrometer. IR spectra were obtained on a Beckman IR4240 and an Acculab 3. Melting points are uncorrected.

**Materials.** *p*-Bromostyrene (Aldrich Chemical Co.), styrene, and divinylbenzene (Matheson Coleman & Bell) were purified by vacuum transfer techniques to separate the polymer and inhibitor before use.

Norborn-2-en-7-one was prepared by using previously published methods.[15] Sodium–potassium alloy was made from sodium and po-

**Table III.** Elemental Analyses of Monomers and Polymers

| compd | | % C | % H | % Cl |
|---|---|---|---|---|
| **4** | found | 76.64 | 6.45 | 16.95 |
| | calcd | 76.28 | 6.40 | 17.32 |
| **6** | found | 84.62 | 7.64 | |
| | calcd | 84.87 | 7.60 | |
| **7** | found | 77.70 | 6.59 | 14.99 |
| | calcd | 78.08 | 6.55 | 15.37 |
| **8** | found | 85.03 | 8.19 | |
| | calcd | 84.91 | 8.02 | |
| $(C_6H_5\text{-}C_5H_5)_2Fe$ | found | 78.48 | 5.69 | |
| | calcd | 78.12 | 5.37 | |
| **9a** | found | 90.37 | 7.88 | |
| | calcd | 90.89 | 7.79 | |
| **9c** | found | 88.96 | 7.35 | 3.34 |
| | calcd | 89.49 | 7.85 | 3.00 |
| **9d** | found | 88.76 | 7.46 | 3.35 |
| | calcd | 89.48 | 7.51 | 3.01 |

tassium metal in a 1:3 molar ratio. Tetrahydrofuran (THF) was distilled under nitrogen atmosphere from a sodium–benzophenone complex.

**Reactions of Aryllithium with Cyclopent-2-enone.** To a solution of 1.0 g (6.4 mmol) of bromobenzene in 5 mL of hexane, under nitrogen, was added 15 mL of a 2.5 M (37.5 mmol) solution of *n*-butyllithium in hexane at 25 °C. During the 36-h reaction period, the white phenyllithium that precipitated was removed by filtration and washed with hexane. The precipitate was dissolved in 15 mL of THF and 0.8 g (9.7 mmol) of cyclopentanone in 2 mL of THF was added at 0 °C. After 6 h, the solution was poured into water and extracted with ether. The white solid, insoluble in ether, was removed by filtration and dried to yield 0.2 g (25%) of polycyclopentanone; $^1$H NMR no aromatic; mp 180 °C dec.

The ether was removed under reduced pressure to yield 0.6 g of an oil that showed carbonyl stretching in the infrared. $^1$H NMR showed aryl and vinyl protons. The vinyl proton chemical shifts did not correspond to the shifts of authentic phenylcyclopentadiene. GLC of the oil showed two major and two minor fractions.

When the reaction of 3.14 g (20 mmol) of bromobenzene with 21 mmol of *n*-butyllithium was carried out in THF at 25 °C and a solution of 2.5 g (30 mmol) of cyclopentenone in THF was added at 0 °C, 1.8 g (72%) of polymer and 1.8 g (67%) of butylbenzene was isolated.

*tert*-Butyllithium in place of *n*-butyllithium gave 0.7 g (28%) of polymer and an oil composed of 13 different products (GLC) that showed carbonyl stretching in the infrared.

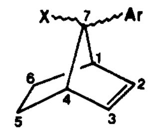
The reaction was also carried out with 3.14 g (20 mmol) of bromobenzene and excess lithium metal at 25 °C in THF, after which the excess lithium was removed by filtration. Addition of 2.5 g (30 mmol) of cyclopentenone in THF at 0 °C gave 1.4 g (56%) of polymer and an oil that did not contain vinyl protons ($^1$H NMR) that corresponded to those of authentic sample.

**7-(*p*-Styryl)- and Phenylnorborn-2-en-7-ol (6 and 3) (Tables III and IV).** *p*-Styrylmagnesium bromide was prepared from 3.6 g (20 mmol) of *p*-bromostyrene and 0.53 g (22 mmol) of magnesium in 20 mL of THF at ambient temperature. The unreacted magnesium was separated by decantation under nitrogen. To the Grignard solution at 0–10 °C was added 2.2 g (20 mmol) of norbornen-7-one. After being stirred for 20 min the reaction solution was poured into 150 mL of 20% aqueous ammonium chloride solution. The small amount of polymer which formed during the reaction was filtered. The product was extracted with three 50-mL portions of ether. To the combined ether solutions was added 0.035 g of *tert*-butylcatechol and the solution was dried ($MgSO_4$). After evaporation of the ether, the residue was distilled to give 2.9 g (68%) of 7-styrylnorborn-2-en-7-ol (**6**); bp 96–105 °C (0.2 mmHg). The distillation residue was a colorless polymer (1.3 g).

7-Phenylnorborn-2-en-7-ol[13] (**3**) was prepared in THF in a similar way in a 90% yield: bp 110–115 °C (13.8 mmHg).

**Preparation of 7-Chloro-7-(*p*-styryl)- and 7-Chloro-7-phenylnorborn-2-ene (7 and 4) (Tables III and IV).** To a solution of 2.3 g (10.8 mmol) of 7-styrylnorborn-2-en-7-ol in 5 mL of ether was added 10 mL of a 35% aqueous hydrochloric acid and the mixture was stirred at 25 °C for 15 h. Then it was extracted with ether and the ethereal extract was washed with aqueous potassium bicarbonate. After drying ($MgSO_4$) the mixture was evaporated. The residue was recrystallized from ether to yield 2.2 g (88%) of 7-chloro-7-styrylnorborn-2-ene (**7**): mp 67–71 °C. Further recrystallization produced the pure antiisomer: mp 78.0–78.5 °C.

**Table IV.** $^{13}$C NMR Spectra[a]



| carbon | isomer | **6**[b] | X = $OCH_3$[b]<br>Ar = $C_6H_5$<br>syn, anti | **8**[b] | **4**[c] | **7**[b] | **9c**[c] |
|---|---|---|---|---|---|---|---|
| 2 and 3 | syn | 22.9 | 22.3 | 22.2 | | | |
| | anti | 23.4 | 23.4 | 23.3 | 24.4 | 23.8 | 24.4 |
| 1 and 4 | syn | 48.9 | 45.8 | 45.8 | | | |
| | anti | 48.5 | 46.6 | 46.5 | 50.9 | 50.4 | 50.9 |
| $CH_3O$ | syn | | 52.5 | 52.4 | | | |
| | anti | | 50.7 | 50.6 | | | |
| 7 | syn | 93.4 | 98.4 | 98.1 | | | |
| | anti | 92.3 | 97.3 | 97.0 | 86.2 | 85.4 | 86.2 |
| styryl | syn | 113.6 | | 113.2 | | | |
| $=CH_2$ | anti | 113.2 | | 112.7 | | 113.6 | |

[a] ppm from $Me_4Si$. [b] $CDCl_3$. [c] $C_6D_6$.

7-Chloro-7-(*p*-phenyl)norborn-2-ene (**4**) also was obtained from 7-(*p*-phenyl)norborn-2-en-7-ol in a similar way. The chlorinated product was separated by distillation, 73–82 °C (0.15 mmHg) (80% yield).

An alternate procedure for the synthesis of **7** was by the reaction of 13 mmol of 7-arylnorborn-2-en-7-ol in 7 mL of ether and 7 mL of acetyl chloride under a nitrogen atmosphere. The reaction solution was poured into water and worked up as described above.

**7-Methoxy-7-(*p*-styryl)norborn-2-ene (8).** Methylation of 7-(*p*-styryl)norborn-2-en-7-ol (**6**) was carried out by a procedure similar to that described[16] with the use of 4.3 g (20 mmol) of **6**, 2.3 mmol of sodium hydride, and an excess of methyl iodide in dimethoxyethane. After the reaction was complete, the mixture was poured into 250 mL of pentane (dried over sodium), and the precipitated sodium chloride and excess sodium hydride were removed by filtration. To the filtrate was added 0.03 g of *tert*-butylcatechol, and the solvent was removed under reduced pressure. The residue was distilled under reduced pressure to yield 4.2 g (93%) of **7**: bp 105 °C (0.5 mmHg). The distillation residue was polymer (Tables III and IV).

**Polymerization Reactions: Preparation of 9.** Polymerizations were carried out by charging the molar ratios of monomer indicated by **9**. To a charge of 1.67 g (16.0 mmol) of styrene and 1.78 mmol of the norbornene-containing monomer (**7** or **8**) in 8 mL of benzene was added 0.048 g of benzoyl peroxide. The polymerization was carried out for 72 h (linear) or 48 h (cross-linked) under nitrogen at 60 °C. The reaction mixture was poured into pentane and the precipitated polymer was removed by filtration. The polymer was washed repeatedly with pentane and dried in vacuo to give ~75% yield of the soluble, linear polymers (**9a,c**) and ~95% of the insoluble, cross-linked polymer. Anal. Calcd for **9c**: Cl, 3.0. Found: Cl, 3.3. Anal. Calcd for **9d**: Cl, 3.0. Found: Cl, 3.3 (Table IV).

**Generation of Cyclopentadiene Anion from 7-Substituted Norbornenes: Catalyst Preparation.** The reaction of the polymer-supported 7-chloronorbornene derivatives with butyllithium was carried out in THF. A representative procedure for 10% cross-linked–10% 7-chloronorbornene attached polymer is as follows: To a suspension of 0.5 g (0.43 mmol) of chloronorbornene in 10 mL of THF was added, under nitrogen, 1.9 mL, (2.24 M, 4.3 mmol) of *n*-butyllithium at 0 °C. After 1 h, the polymer became red.

The suspension either was quenched by pouring it into methanol to yield the polymer bearing cyclopentadiene-attached units or was allowed to react with bis(chlorodicarbonylrhodium) to yield the polymer-attached $\eta^5$-cyclopentadienyldicarbonylrhodium.[7]

The polymer anion suspension was filtered and the excess *n*-butyllithium was washed from the polymer with dry THF. The polymer was resuspended, under nitrogen, in 10 mL of THF and 0.1 g (0.25 mmol) of bis(chlorodicarbonylrhodium) was added.[5] The suspension was stirred for 48 h at 28 °C during which time the polymer became brown. The polymer was filtered, washed with THF, and dried under reduced pressure for 20 h to give 0.56 g of polymer **12d**; IR 2045 and 1980 cm$^{-1}$. Anal. Calcd for **12d**: Rh, 8.03. Found: Rh, 6.2.

The quenched polymer containing cyclopentadiene was allowed to react with dicobaltoctacarbonyl either in refluxing methylene chloride for 72 h to produce a black catalyst or at 25 °C for 72 h to yield a brown

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catalyst.[7] Anal. Calcd for **13d**: Co, 4.78. Found: Co, 6.5 ($CH_2Cl_2$ reflux); Co, 5.5 ($CH_2Cl_2$ 25 °C).

The reaction of 0.5 g of the soluble polymer-supported 7-methoxynorbornene (**9a**) with 0.3 g of sodium–potassium alloy in 20 mL of THF for 1 h at 28 °C also generated the cyclopentadienyl anion. Cross-linked, insoluble polymer (**9b**) did not react with the alloy. The cobalt and rhodium catalysts were prepared as described above.

**Model Reactions of *syn*- and *anti*-7-Chloro-7-phenylnorborn-2-ene (4).** A solution of phenylcyclopentadiene anion was prepared from **4** by a procedure similar to that described for polymers **9**. The anion was converted to phenylferrocene by using an iron–ferric chloride reagent[14] in a 56% crude yield. Separation of phenyl ferrocene was accomplished by column chromatography ($SiO_2$). Elution with pentane gave 0.5 g (31%) of product: mp 140 °C (lit.[9] mp 154 °C) (Table III).

**Attempted Fischer–Tropsch Reaction.** A mixture of 0.3 g of polymer-supported cobalt catalyst and 20–30 mL of *n*-octane was sealed in a 100-mL Monel Parr pressure reaction vessel under a nitrogen atmosphere. The system was flushed with carbon monoxide three times and finally pressurized with a mixture of hydrogen and carbon monoxide (3:1) to a pressure of 75 psi at 25 °C. The vessel was heated to 150 or 200 °C for 72–168 h. The vessel was then cooled to −78 °C and vented. The volatile components were then transferred to a trap and analyzed by GLC. Only *n*-octane was recovered.

**Hydrogenation.** A 100-mL Monel Parr pressure reaction vessel with a glass liner was charged with substrate and 0.2 g of polymer-bound rhodium catalyst (**12d**) under nitrogen. The reaction vessel was filled with hydrogen and evacuated four times and finally pressurized with hydrogen at 25 °C (Table II). At the end of the indicated reaction time, the catalyst was removed by filtration and the products were determined by $^1H$ NMR, IR, and GLC (Table II).

**Hydroformylation.** Hydroformylation[5] was carried out by charging 0.1 g of polymer-attached catalyst (**12d**), 10 mL of benzene, and 2 mL (17.8 mmol) of 1-hexene into a 100-mL Monel Parr pressure reaction vessel. The system was flushed three times with hydrogen and twice with carbon monoxide. The vessel was pressurized to 200 psi with carbon monoxide and heated to 110 °C in an oil bath. After 40 min, during which time the system achieved equilibrium, a 1:1 carbon monoxide–hydrogen mixture was introduced to 1300 psi and the reaction vessel was heated at 110 °C for 1 h. The pressure dropped to ~1200 psi during this time. The vessel was cooled to 25 °C and the suspension was filtered to remove the catalyst. The solution was analyzed by GLC (SE-30, 10 ft) at 180 °C. The products were identified by comparison with authentic samples. The $^1H$ NMR spectrum of the solution showed no 1-hexene. The turnover rate was >148/h; linear/branched = 0.72.

The reaction was repeated with the use of the same catalyst. Complete conversion of aldehydes, linear/branched = 0.69, was achieved. The catalyst, by IR, showed absorptions at 2045 and 1980 $cm^{-1}$.

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# Alkylation of Tin by Alkylcobalamins. Kinetics and Mechanism

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**Abstract:** The reaction of methylcobalamin with stannous chloride in aqueous hydrochloric acid solution has been examined under aerobic conditions. The reaction occurs with a 1:1 stoichiometry, producing aquocobalamin and methyltin(IV) trichloride. The reaction follows a second-order rate expression: first order in methylcobalamin and first order in stannous chloride. Under anaerobic conditions, the reaction does not occur but does occur in the presence of stoichiometric amounts of aquocobalamin, producing a twofold excess of cob(II)alamin and methyltin(IV) trichloride. This reaction is first order in methylcobalamin, first order in stannous chloride, and zero order in aquocobalamin. Adding cob(II)alamin in large amounts does not affect the kinetics or stoichiometry of this reaction. The kinetics of dealkylation of ethylcobalamin and (chloromethyl)cobalamin by stannous chloride under aerobic conditions are also examined. Second-order rate constants for the dealkylation of methylcobalamin, ethylcobalamin, and (chloromethyl)cobalamin by stannous chloride at 23 °C, [HCl] = 1.0 M, were found to be $1.04 \pm 0.10\ M^{-1}\ s^{-1}$, $(1.66 \pm 0.20) \times 10^{-2}\ M^{-1}\ s^{-1}$, and $7 \times 10^{-3}\ M^{-1}\ s^{-1}$, respectively. The mechanism is described in terms of a direct bimolecular homolytic attack ($S_H2$) by stannous chloride at the saturated carbon center, producing cob(II)alamin and a strongly reducing methylstannyl(III) radical. This radical intermediate then reacts with oxygen or aquocobalamin to produce the stable methyltin(IV) trichloride.

Reactions between alkylcorrinoids and tin are of environmental importance as well as mechanistic interest.[1] Reductive cleavage of alkylcorrinoids and of related $B_{12}$ model compounds by $Sn^{II}$ salts was initially proposed by Schrauzer et al.[2] More recently, it was suggested that tin could be methylated by methylcobalamin through reductive cobalt–carbon cleavage by a species which was generated by one-equivalent oxidation of $Sn^{II}$.[3] In this report, we present kinetic and mechanistic data on the alkylation of stannous chloride by methyl-, ethyl-, and (chloromethyl)cobalamin. Alkyl transfer from cobalt to tin is discussed in terms of a mechanism of $S_H2$ displacement of cob(II)alamin by $Sn^{II}$.

## Experimental Section

**Materials.** Stannous, Stannic, Methyltin(IV), and Dimethyltin(IV) chloride salts were obtained from Ventron, Inc., and were used as received. The stability of $SnCl_2$ solutions against air oxidation at room temperature was determined by standard $S_2O_3^{2-}$–$Br_2$ titration. Stock solutions of $SnCl_2$ were never stored under air for more than 2 h. [$^{13}C$]methyl iodide (90%) was obtained from Stohler Inc. Methylcobalamin ($CH_3$-$B_{12}$) was obtained from Sigma Co. $^{13}CH_3$-$B_{12}$, $C_2H_5$-$B_{12}$, and $CH_2Cl$-$B_{12}$ were synthesized in the dark from cyanocobalamin (Vitamin $B_{12}$) and $^{13}CH_3I$, $C_2H_5I$, and $CH_2Cl_2$, respectively.[4] Cob(II)alamin ($B_{12r}$) was generated by reducing $H_2O$-$B_{12}^+$ with equi-

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