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## The Formation and Chemistry of New Functionally Substituted $\eta^5$ -Cyclopentadienyl-Metal Compounds: Routes to New Vinyl Monomers

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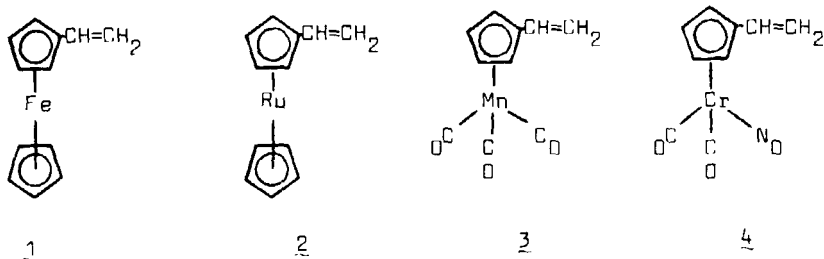
### ABSTRACT

Reactions of cyclopentadienylsodium with ethyl formate, methyl or ethyl acetate, or dimethyl carbonate in THF solution have produced high yields of the functionally substituted organosodium compounds  $[\text{C}_5\text{H}_4\text{C}(\text{O})\text{R}]^-\text{Na}^+$ , where  $\text{R} = \text{H}, \text{CH}_3$  or  $\text{OCH}_3$ . These organosodium reagents have proved to be valuable intermediates in the formation of functionally substituted cobaltocene, nickelocene, etc., sandwich complexes as well as for other  $\eta^5$ -cyclopentadienyl-metal systems such as  $(\eta^5\text{-C}_5\text{H}_4\text{CHO})\text{M}(\text{CO})_2$  ( $\text{M} = \text{Co}, \text{Rh}$ ) and  $(\eta^5\text{-C}_5\text{H}_4\text{CHO})\text{W}(\text{CO})_3\text{CH}_3$ . The latter aldehydes can be readily converted into corresponding acrylate and vinyl derivatives. The polymerization chemistry of these new organometallic monomers has been initiated.

### INTRODUCTION

Soon after the discovery of bis- $(\eta^5\text{-cyclopentadienyl})$ iron (ferrocene) in 1951, it was demonstrated that this unique organometallic compound could undergo typical aromatic-type ring-substitution reactions [1,2]. The ability to introduce functional groups onto the  $\eta^5$ -cyclopentadienyl rings of ferrocene made possible the synthesis of vinylferrocene (1) in 1955, and its

polymerization reactions were studied by Arimoto and Haven [3]. A limited number of other  $\eta^5$ -vinylcyclopentadienyl-metal compounds have been synthesized and their polymerization chemistry investigated, including vinylruthenocene (2)[4], vinylcymantrene (3)[5], and vinylcynichrodene (4)[6,7]. Monomers 2-4 can be



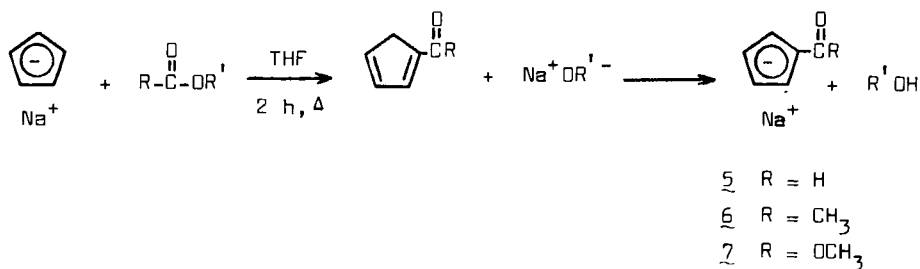
prepared by virtue of the fact that the parent  $\eta^5$ -cyclopentadienyl-metal compounds, like ferrocene (1), can be acetylated under Friedel-Crafts conditions and converted into vinyl analogs by standard organic procedures. The topic of vinylic organotransition metal monomers and polymers has recently been reviewed by Pittman [8].

It would seem worthwhile to investigate the formation and polymerization chemistry of still other  $\eta^5$ -vinylcyclopentadienyl-metal compounds, since the products might possess unusual and potentially useful properties. Unfortunately, however, the ability to functionalize  $\eta^5$ -cyclopentadienyl-metal compounds by means of electrophilic aromatic substitution reactions is severely limited, including the iron, ruthenium, manganese and chromium systems mentioned above plus only a few other analogs [9,11]. The failure of most  $\eta^5$ -cyclopentadienyl-metal compounds to undergo ring substitution may be ascribed either to their inherent lack of aromatic character or to more facile reaction pathways under the reaction conditions involved. In any event, the inability of most  $\eta^5$ -cyclopentadienyl-metal compounds to form functionally substituted derivatives by ring-substitution routes has greatly impeded the development of  $\eta^5$ -cyclopentadienyl-metal chemistry of the type shown by ferrocene. This result in turn has also greatly hampered the growth of vinylic organotransition metal monomers and polymers.

RESULTS AND DISCUSSION

We have recently developed a new and apparently general route for the formation of a wide variety of functionally substituted  $\eta^5$ -cyclopentadienyl-metal compounds [11]. The method provides a convenient means of introducing functional substituents onto  $\eta^5$ -cyclopentadienyl rings in systems which are incapable of undergoing electrophilic aromatic substitution. In the present paper, we shall discuss the general procedures by which new functionally substituted  $\eta^5$ -cyclopentadienyl-metal compounds can be synthesized, and especially the application of this method for the formation of new organometallic monomers.

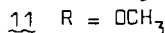
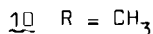
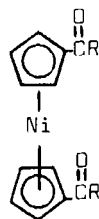
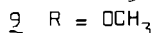
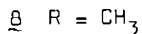
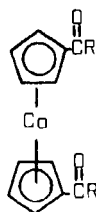
Reactions of cyclopentadienylsodium with either ethyl formate, methyl acetate or dimethyl carbonate in refluxing THF solution for 2 h produce 70-95% yields of the respective compounds formyl-(5), acetyl-(6) or methoxycarbonylcyclopentadienylsodium (7) [12]. These reactions likely proceed via the intermediate formation of the respective 1-substituted cyclopentadienes, which react readily with the sodium alkoxide concurrently produced to afford the functionally substituted cyclopentadienylsodium derivatives 5-7.



These organosodium reagents are moisture sensitive, but are generally stable in air for short periods of time, in contrast to cyclopentadienylsodium itself. Their proton nmr spectra recorded in  $\text{D}_2\text{O}$  solution consist of two pairs of unresolved multiplets representing the ring protons as well as singlet resonances for the substituent protons [11].

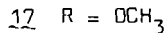
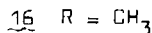
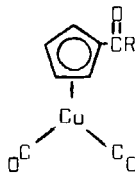
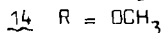
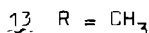
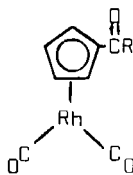
Reactions of 5-7 with various transition metal halides have proved useful in the synthesis of functionally substituted sandwich compounds which are generally unattainable by other means.

Thus, reactions of 6 or 7 with either  $\text{CoCl}_2$  or  $\text{NiBr}_2 \cdot 2\text{DME}$  in THF solution afforded 1,1'-diacetylcobaltocene (8), 1,1'-dicarbomethoxycobaltocene (9), 1,1'-diacetylnickelocene (10), and 1,1'-



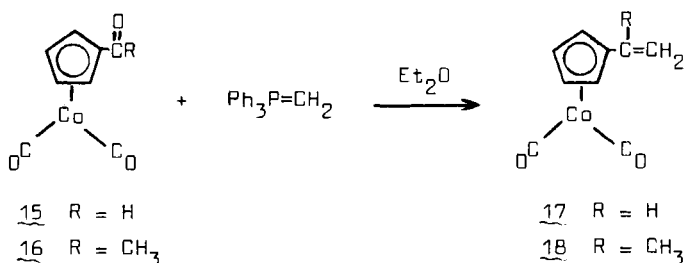
dicarbomethoxynickelocene (11), respectively, in yields of 30-50% [13]. The ester derivatives 9 and 11 are currently being evaluated as potential monomers for the production of organocobalt- and organonickel-containing condensation polymers [14]. Similar routes to organometallic condensation polymers which contain the ferrocene unit have been examined previously, although only relatively low  $M_n$  molecular weight products could be obtained [15,16].

Organosodium reagents 5-7 are also convenient precursors to functionally substituted  $\eta^5$ -cyclopentadienyldicarbonylmetal derivatives, products which have likewise been unavailable through electrophilic substitution reactions of the parent compounds. Thus, reactions of 5-7 with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  in THF readily produce the corresponding formyl (12), acetyl (13) and

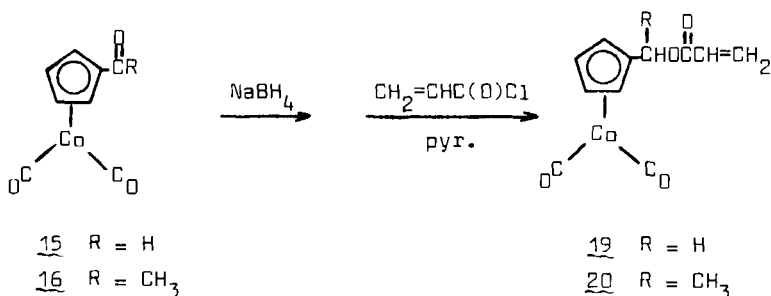


methoxycarbonyl (14) analogs, whereas the respective cobalt counterparts (15-17) are available via reactions of 5-7 with an equimolar mixture of  $\text{Co}_2(\text{CO})_8$  and  $\text{I}_2$  in THF solution. These products are obtained in yields of 50-98% as dark red liquids which are distillable under reduced pressure.

The availability of the functionally substituted organorhodium and -cobalt derivatives 12-17 provides valuable new routes to organometallic monomers of these metals. For example, 15 and 16 react with methylenetriphenylphosphorane in ethyl ether solution to afford ( $\eta^5$ -vinylcyclopentadienyl)dicarbonylcobalt (17) and ( $\eta^5$ -isopropenylcyclopentadienyl)dicarbonylcobalt (18) in moderate

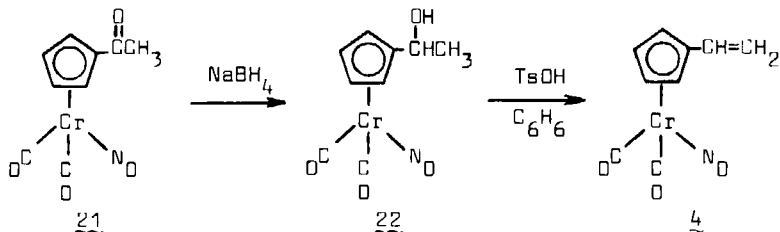


yields, respectively. Reduction of 15 or 16 followed by reaction of the resulting alcohols with acryloyl chloride and pyridine have likewise produced the corresponding acrylate derivatives (19, 20) in good yield.



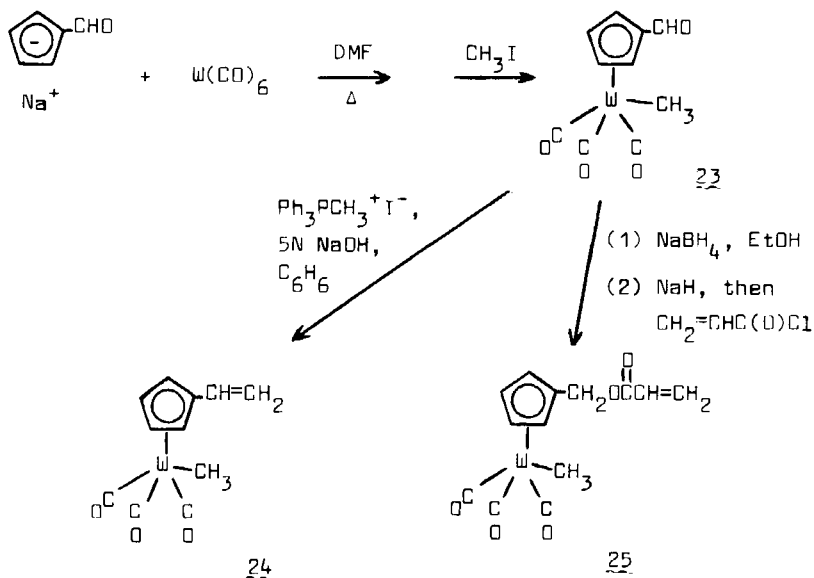
Polymerization studies on these organocobalt vinyl monomers under free radical and cationic conditions are currently in progress, and will hopefully lead to new types of organometallic polymers with potential catalytic properties [8,14,16].

Previous studies in this laboratory have shown that the novel monomer vinylcynichrodene (4) could undergo both homo- and copolymerization. Monomer 4 was prepared from acetylcynichrodene (21) by treatment with sodium borohydride followed by dehydration of the resulting alcohol (22). The value of the Alfrey-Price



parameter  $e$  for 4 was evaluated by reactivity ratio studies to be -1.98, indicating that 4 is an exceptionally electron rich vinyl monomer, resembling vinylferrocene (1) and vinylcymantrene (3) [6,7].

In order to further investigate the formation and reactivity of vinyl monomers of the Group IVB metals, formyl derivative 5 was allowed to react with tungsten hexacarbonyl in refluxing DMF. Treatment of the resulting organometallic anion with iodomethane in THF produced ( $\eta^5$ -formylcyclopentadienyl)-tricarbonylmethyltungsten (23) in 82% yield. Reaction of aldehyde



23 in benzene solution with triphenylmethylphosphonium iodide in the presence of 5N sodium hydroxide under phase transfer conditions afforded ( $\eta^5$ -vinylcyclopentadienyl)tricarbonylmethyltungsten (24) in 80% yield. Attempted formation of 24 under normal Wittig conditions (e.g.,  $\text{Ph}_3\text{P}=\text{CH}_2$  generated in ethyl ether solution from triphenylmethylphosphonium iodide and n-butyl-lithium) also produced 24, although in appreciably lower yield.

Reduction of aldehyde 23 by sodium borohydride in ethanol proceeded smoothly to produce the corresponding alcohol in nearly quantitative yield. Subsequent reaction of this alcohol with sodium hydride followed by acryloyl chloride afforded the acrylate derivative (25) in 65% yield. Homo- and copolymerization reactions of 24 and 25, the first organotungsten vinyl monomers to be synthesized and studied, are under present investigation [17].

It is therefore evident that the development of functionally substituted cyclopentadienyl-metal compounds can lead to many new organometallic monomers which would be unattainable by other means. The polymerization chemistry of these new monomers and evaluation of the properties of the resulting organometallic polymers should be of interest to chemists for many years to come.

#### ACKNOWLEDGEMENT

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