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SYNTHETIC AND CATALYTIC STUDIES OF POLYMER-BOUND METAL CARBONYLS*

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Summary

The reactions of polymeric analogs of benzyl-diphenylphosphine and -triphenylphosphine with a variety of metal carbonyls have been examined using both thermal and photochemical techniques. Metal derivatives of both linear polymers and swellable cross-linked resins have been synthesized in this manner. The catalysis of hydroformylation and isomerization reactions have been studied using a polymeric derivative of dicobalt hexacarbonyl. The catalyst could be very easily recycled and gave product yields in the hydroformylation of pentenes quite similar to those reported earlier using the corresponding homogeneous species. The cyclization of ethyl propiolate has also been carried out using a new polymeric nickel complex. Benzene isomers are isolated during the initial use of this catalyst whereas cyclooctatetraene isomers, in addition, are observed using the recycled catalyst.

Introduction

A survey of the very recent literature dealing with organometallic catalysts quickly reveals that possibly the most exciting new area of endeavor in this field concerns the enormous synthetic utility of homogeneous catalysts bound to polymeric matrices. Indeed, these new systems, although heterogeneous in nature, display many of the desirable characteristics indigeneous to homogeneous catalytic systems.

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Although a number of biochemical studies have appeared in the last decade in which the action of enzymes (i.e. biochemical catalysts) bound to organic polymeric or glass supports have been studied [1], the concept of binding known homogeneous catalysts to solid-phase supports was introduced more recently by the work of Haag and Whitehurst, of Mobil Oil, who demonstrated the catalytic utility of salts of $Pt(NH_3)_4^{2+}$ with polymeric sulfonate counterions [2] and more recently the catalytic applications of heterogeneous species obtained by the coordination of $RhCl_3$ to polymers containing pendant phosphine units [3].

Other advances in this area have been recorded by Moffat, who in 1969, reported the catalysis of hydroformylation reactions utilizing a poly-2-vinylpyridine/$Co_2(CO)_8$ system [4]. A more recent report has emphasized the use of this system as a "catalyst reservoir" suitable for the release of small amounts of cobalt carbonyl under hydroformylation conditions followed by its uptake after completion of the reaction [5].

Manassen, in addition, has reported the catalysis of hydroformylations and hydrogenations using polymeric phosphine ligands coordinated to rhodium complexes [6]. The catalysis of hydrosilation, hydrogenation, and hydroformylation reactions has been described by Capka et al. also by employing rhodium complexes coordinatively bonded to polymeric phosphine ligands [7].

Grubbs and co-workers [8] uniquely demonstrated the hydrogenation selectivity as a function of substrate molecular bulk afforded by a form of Wilkonson's catalyst [i.e. $ClRh(PPh_3)_3$] when bonded to a rigid polymeric matrix. More recently, they have prepared an unusual monomeric titanium catalyst generated and stabilized by coordination to a polymer matrix [9]. Bailar's group has also reported the selective hydrogenation of soybean methyl ester to monoene and diene products effected by the use of palladium(II) and platinum(II) chlorides bound to a polymer with pendant phosphine units [10].

Collman and co-workers [11] have examined coordination characteristics and catalytic activity of numerous homogeneous complexes of iridium, rhodium, and cobalt bound to polymeric resins and have, in addition, prepared a very novel arene hydrogenation catalyst through the aerial oxidation of a polymer-supported polynuclear rhodium carbonyl.

That research efforts in this field have received much emphasis may be further concluded from the publication of several recent reviews [12 - 14] discussing the ramifications of research in this nebulous "grey" region which promises to bridge the gap between the formerly distinct areas of homogeneous and heterogeneous catalysis. Hopefully, these will provide a clearer understanding of the molecular function of the truly heterogeneous systems.

We would now like to report recently completed work dealing with the preparation of numerous metal carbonyl derivatives of both linear and crosslinked polymeric phosphine ligands. Three of these derivatives have been found to display very useful hydroformylation, isomerization and oligomerization catalytic properties which compare favorably with those of the corresponding purely homogeneous species, although several distinct differences have been noted.

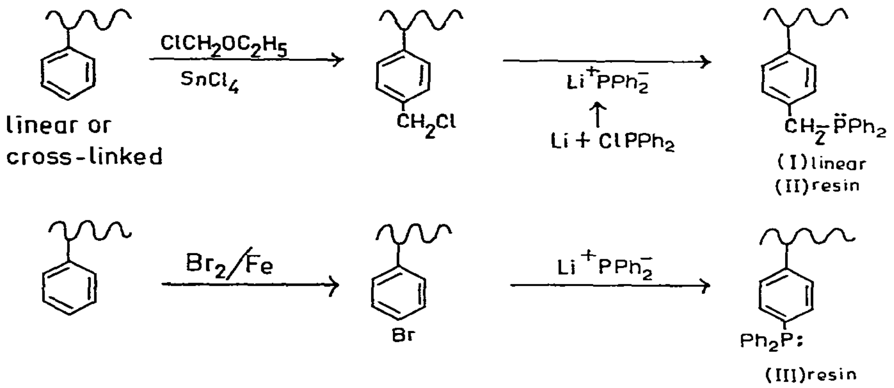
Results and discussion

Due to the wide variety of known transition metal organometallic species containing coordinated phophines, a vast array of polymer-bound catalysts may be envisioned in which the active metal is directly coordinated to an insoluble polymeric phosphine ligand. However, since the paths of a number of these homogeneously catalyzed reactions are known to be very dependent upon the amount of free ligand (i.e. phosphine) present, it was of foremost interest to study the coordination properties (i.e. substitution and exchange) of a variety of preformed metal complexes in the presence of polymeric ligands.

Hence, we have examined a large number of reactions of metal carbonyls with polymeric analogs of both benzyl-diphenylphosphine and -triphenylphosphine in terms of the extent of metal incorporation onto the polymers and the properties of several of these species as catalysts in organic reactions.

Preparation of polymeric ligands

Both the linear and cross-linked polymeric analogs of benzyldiphenylphosphine (I and II) were synthesized by the reaction of lithium diphenylphosphide ($LiPPh_2$) with the corresponding chloromethylated polystyrene and styrene/divinylbenzene resin, respectively (Scheme 1 and Table 1). Elemental analyses of the products indicated that the reactions proceeded nearly to completion with typically only a small amount of residual chlorine (i.e. $\leqslant$ 0.08%) remaining on the polymer. A sample of the corresponding polymeric analog of triphenylphosphine, III, had been prepared by the reaction of $LiPPh_2$ and brominated styrene/divinylbenzene resin* but was found to contain a significant amount of residual bromine, indicative of the greater difficulty inherent in carrying out nucleophilic displacements on halogenated arenes.



SCHEME 1. Methods used in the preparation of polymeric ligands of types I, II, and III.

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* Kindly provided by R. Hanes of this laboratory.

TABLE 1

PROPERTIES AND ELEMENTAL ANALYTICAL DATA FOR POLYMERIC LIGANDS

Compound[a]	Per cent cross-linking	Mesh	Exclusion limit	Elemental analyses found		
				P	Cl	Br
I	0 (linear)			4.95	0.07	
IIa	2	200 - 400	2700	2.47	0.06	
IIb	1	200 - 400	14000	3.43	0.08	
IIc	1	200 - 400	14000	3.00	0.05	
IId	1	200 - 400	14000	1.76	0.30	
III	1	200 - 400	14000	3.22		1.15

[a] Compounds I and II are diphenylphosphinomethylpolystyrene derivatives while III is diphenylphosphinopolystyrene.

Reactions of polymeric ligands with metal carbonyls

In all systems studied (Table 2, Scheme 2) the reactions of the metal carbonyls with the polymeric ligands were found to proceed smoothly in a manner not unlike the reations between the carbonyls and monomeric phosphines themselves. Both the linear polymer, I, and the cross-linked resins, II, were found to be quite reactive and, in general, a high percentage of metal was incorporated onto the polymers based upon the available phosphine present (Table 2).

Although thermal methods have previously been shown to be effective in the preparation of polymeric substitution products, we now report the first instances in which metals have been bound within the pores of a transparent swollen resin, utilizing photochemical techniques. Reactions of $Mo(CO)_6$ and $W(CO)_6$ with IIa were carried out both thermally and photochemically and the latter method appears to have been at least equally as efficient in incorporating the metal. Similar results were observed when $Cr(CO)_6$ was reacted thermally and photochemically with the linear polymer, I.

All polymers were characterized by their infrared spectra recorded in KBr pellet form, and elemental analytical data. The form of the CO stretching spectra of these polymeric derivatives, as expected, were found to be quite similar to the related derivatives earlier prepared using monomeric phosphines. Although the reactions were carried out using a molar excess of the metal carbonyl, the CO stretching spectra of the resin-bound derivatives of the Group VI hexacarbonyls and iron pentacarbonyl (Fig. 1) clearly indicated that significant amounts of the *trans*-disubstituted derivatives had formed. This observation attests to the high degree of mobility of the coordination sites within these matrices containing a low degree of crosslinking. Collman and co-workers [11] earlier emphasized this mobility and the general tendency toward chelation in the reactions of resin-substituted triphenylphosphine with $IrCl(CO)(PPh_3)_2$ and $RhCl(CO)(PPh_3)_2$.

This tendency toward chelation was more clearly pronounced in the reaction of $Co_2(CO)_8$ with the cross-linked polymeric ligand, IId. The initial product in this reaction, which forms very rapidly, was found to be the brown polymeric analog (XXIII) (Scheme 2) of $[Co(CO)_3(PPh_3)_2]^+[Co(CO)_4]^-$ which is known to form in the reaction of PPh_3 and $Co_2(CO)_8$ [15]. In analogy to the latter compound, the polymeric ionic derivative could easily be

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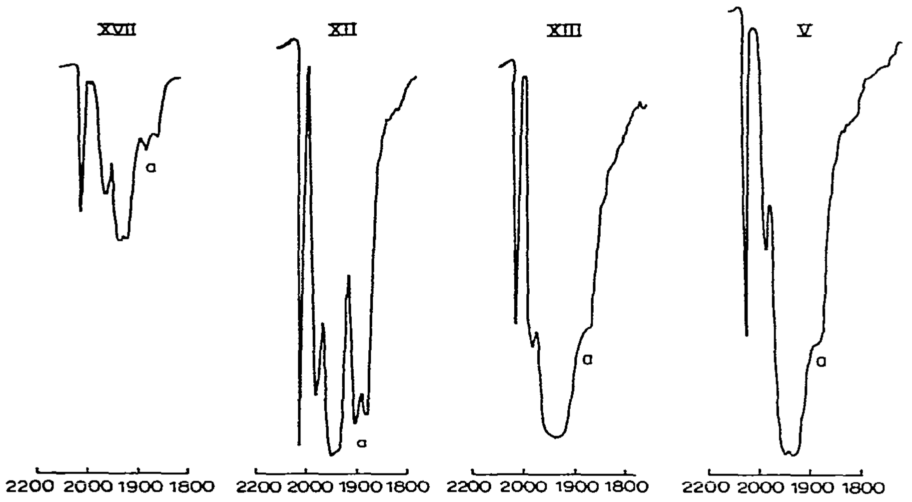
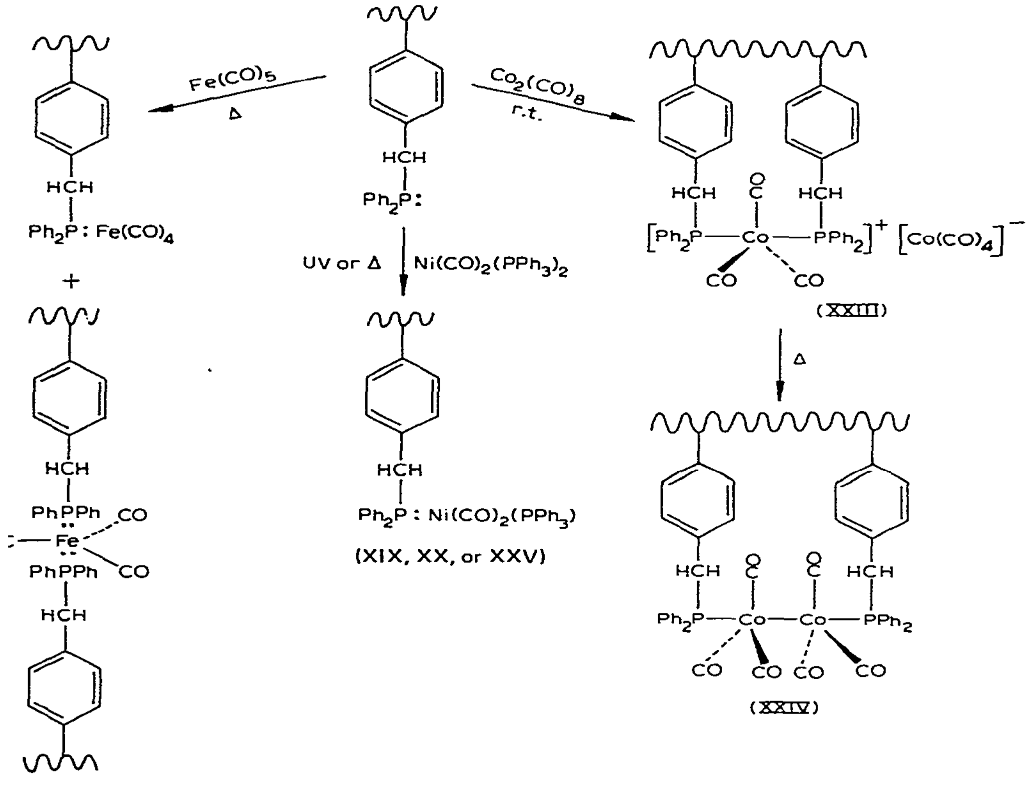


Fig. 1. CO stretching spectra (cm^{-1}) of linear and cross-linked polymeric derivatives of $Fe(CO)_5$ (XII and XVII, respectively) and $Cr(CO)_6$ (V and XIII, respectively) indicating the relative amounts of monosubstituted (unlabeled bands) and disubstituted (bands labeled a) species.



SCHEME 2. Typical reactions which occurred between metal carbonyls and polymeric ligands

PREPARATIVE CONDITIONS, PROPERTIES, AND ELEMENTAL ANALYSES OF POLYMER-BOUND METAL CARBONYLS

Compound	Reactants[a]	Solvent	Conditions[b]	Color	ν(CO)[c]	Elemental Analyses	
						P (%)	Metal (%)
IV	I + $Cr(CO)_6$ (0.48) (3.2)	toluene	u.v./22.7	green	2040m 1980w 1940s, br 1880w-m	3.80	3.86
V	I + $Cr(CO)_6$ (0.80) (4.1)	diglyme	100/1.25	grey	as above	3.80	4.35
VI	I + $Mo(CO)_6$ (0.80) (3.6)	diglyme	100/1.2	off-white	2045m 1995w 1940s, br 1890sh		
VII	I + $W(CO)_6$ (0.80) (3.1)	diglyme	100/1.25	grey-blue	2042m 1985w 1940s, br 1880m	3.23	18.55
VIII	I + $Co_2(CO)_8$ (1.60) (3.5)	toluene	r.t./0.5	light tan	2045m 1992s 1886s, br		
IX	VIII	DME	70/4	tan	1982sh 1958s	4.22	8.07
X	I + $MeCpMn(CO)_3$ (0.63) (4.9)	toluene	u.v./21.5	light brown	1935s 1866s	5.84	7.75
XI	I + $Mn_2(CO)_{10}$ (0.80) (3.1)	diglyme	118/21	yellow	2060m 1988s 1930m	2.89	7.83
XII	I + $Fe(CO)_5$ (0.80) (5.7)	diglyme	115/11	off-white	2015s 1972m 1940s 1892 1870^{d}, s	3.96	3.39
XIII	IIa + $Cr(CO)_6$ (0.40) (4.6)	toluene	u.v./24	light yellow	2040m 1978w 1930s, br 1880sh	2.38	3.43
XIV	IIa + $Mo(CO)_6$ (0.40) (3.8)	diglyme	100/1.5	grey	see VI	2.11	2.34
XV	IIa + Mo(CO) (0.40) (3.8)	toluene	u.v./22	grey	see VI	2.28	5.59

XVI	IIa + W(CO)$_6$ (0.40) (3.6)	toluene	u.v./21	pale yellow	2040m 1975w 1928s, br 1880sh	2.02	11.63
XVII	IIa + W(CO)$_6$ (0.40) (3.6)	diglyme	100/1	light green	see XVI	2.12	7.51
XVIII	IIa + Fe(CO)$_5$ (0.40) (3.7)	diglyme	122/21	light green	see XII	2.36	3.95
XIX	IIa + Ni(CO)$_2$(PPh$_3$)$_2$ (0.24) (1.4)	THF	u.v./21.5	off-white	1998s 1940s, br	2.53	6.66
XX	IIa + Ni(CO)$_2$(PPh$_3$)$_2$ (0.24) (1.9)	diglyme	100/23	light yellow	see XIX	2.22	2.97
XXI	IIa + Mn$_2$(CO)$_{10}$ (0.28) (1.8)	diglyme	115/21	brown	seeXI	2.27	4.89
XXII	IIa + MeCpMn(CO)$_3$ (0.40) (4.9)	toluene	u.v./23	yellow-brown	see X	2.31	4.37
XXIII	IId + Co$_2$(CO)$_8$ (7.3) (29.3)	toluene	r.t./1	brown	2045m 1997s 1888s, br		
XXIV	XXIII	DME	72/25	red-brown	1980sh 1955s	1.71	3.73
XXV	IIb + Ni(CO)$_2$(PPh$_3$)$_2$	benzene	90/24	yellow	see XIX	3.67	5.07
XXVI	IIb + Co$_2$(CO)$_8$ (16.6) (38.0)	toluene	r.t./2	brown	see XXIII		
XXVII	XXVI	DME	69/29	red-brown	see XXIV	2.81	5.68
XXVIII	IIc + RhCl(CO)(PPh$_3$)$_2$ (4.7) (1.5)	benzene	r.t./72	yellow	1972	3.05	1.04
XXIX	IIc + RhCl(CO)(PPh$_3$)$_2$ (4.7) (1.5)	benzene	60/120	yellow	see XXVIII	2.82	0.79
XXX	III + Co$_2$(CO)$_8$	toluene	r.t./2	dark-brown			
XXXI	XXX	DME	65/24		1932s, br	4.34	9.01

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[a] Mmol of reactants in parenthesis. [b] Conditions specify the use of photochemical (u.v./hours reacted) or thermal (°C/hours reacted) reactions. [c] In cm^{-1}.

converted, upon heating in dimethoxyethane at 70°, to a neutral derivative (XXIV), which is an analog of $Co_2(CO)_6(PPh_3)_2$. This was confirmed by the similarity of the CO stretching spectra of these two compounds [16]. Both exhibit a single major absorption, although it is found to be quite broad in the case of XXIV. XXVII and XXXI were prepared in a similar manner.

Moreover, the reaction between $Co_2(CO)_8$ and the linear soluble polymeric ligand, I, gave rise to an analogous brown ionic complex, VIII, which rapidly precipitated upon mixing the reagents, presumably due, in part, to the cross-linking introduced by the coordination of the $Co(CO)_3$ moiety to different chains. This compound could also be converted to the neutral form, IX, which displayed low solubility in organic solvents.

In addition to carbonyl substitution reactions, phosphine exchange reactions were employed in binding both $Ni(CO)_2(PPh_3)_2$ and $RhCl(CO)(PPh_3)_2$ to polymeric resins. Both species were of interest due to their potential catalytic applications. With the former compound, both photochemical and thermal means were found to be effective in promoting the exchange reactions with the polymeric ligand IIa giving XIX and XX, respectively. The rhodium compound which, in a report by Collman [11], had been attached to a polymeric analog of triphenylphosphine, was bound to IIc by stirring the reactants at room temperature for three days yielding XXVII. Heating the reactants at 60° for five days was found to only slightly affect the rhodium content.

The polymeric nickel and rhodium derivatives displayed two and one CO stretching bonds respectively, indicative in the former case that very little of CO substitution had occurred giving a monocarbonyl derivative. Measurements of the amount of phosphine displaced per mole of metal incorporated, however, were not made, although Collman has reported that the degree of chelation was very high in his rhodium derivative [11].

Hydroformylation reactions using polymeric cobalt and rhodium catalysts

It has long been known that $Co_2(CO)_8$ is a very useful catalyst for the hydroformylation of olefins [17]. However, much attention has been directed recently towards the conditions required and the yields obtained when phosphine substitution products of this catalyst were used [18 - 22]. In general, it has been found that, although the rate of hydroformylation is decreased, the use of $Co_2(CO)_6(PR_3)_2$ (where R = alkyl or aryl) leads to significantly greater ratios of linear/branched aldehydes and alcohols. In addition, it has also recently been shown that the disubstituted derivatives are catalytically active under much lower pressures [21] than the unsubstituted form. Furthermore, based on the very similar linear/branched product ratios observed when 1-hexene and 2-hexene have been studied, the substituted catalysts appear to be very effective isomerization agents, presumably due to the formation of $HCo(CO)_3(PR_3)$ intermediates [18,19]. Likewise, $HCo(CO)_4$ has long been known to be an active isomerization catalyst [23]. We have thus examined the hydroformylation of 1- and 2-pentene using the new polymeric cobalt derivatives XXIV, XXVII, and XXXI with a view toward determining any significant differences in catalytic behavior between these and their purely homogeneous analogs.

Reactions typically carried out at total pressures of approximately 1000 psi (1/1; H_2/CO) for about 7 hours using XXVII as the catalyst, revealed

TABLE 3

RESULTS OF HYDROFORMYLATION EXPERIMENTS[a]

Catalyst (g)	Substrate (ml)	Solvent (ml)	Temp (°C)	Time (h)	Pressure[b] (psi)	Products[c]			
						Aldehydes		Alcohols	
						Linear	Branched	Linear	Branched
XXVII (1.0)	1-pentene (4.0)	benzene (8.0)	150	7	980	62.5	32.9	0.0	0.0
Recycled[d]	1-pentene (4.0)	benzene (8.0)	147	7	995	65.2	29.4	0.0	0.0
Recycled[d,e]	1-pentene (4.0)	benzene (8.0)	149	7.5	985	62.0	34.1	0.0	0.0
XXVII (1.0)	1-pentene (4.0)	benzene (8.0)	150	7	1000	61.4	24.6	0.0	0.0
Recycled[d,f]	1-pentene (4.0)	benzene (8.0)	172	6	1000	26.8	14.9	28.1	18.4
XXVII (1.0)	1-pentene (4.0)	benzene (8.0)	164	7	1000	35.1	25.8	22.0	15.5
XXVII (1.0)	1-pentene (2.0)	benzene (4.0)	147	7	400	50.2	40.2	0.0	0.0
XXIV (0.5)	1-pentene (2.0)	benzene (4.0)	145	7	975	63.5	29.4	0.0	0.0
XXXI (1.0)	1-pentene (5.0)	benzene (5.0)	146	7	1000	56.0	38.6	2.2	1.9
XXXI (1.0)	1-pentene (5.0)	benzene (5.0)	165	7	995	39.5	35.7	12.0	9.4
XXVII (1.0)	2-pentene (4.0)	benzene (8.0)	144	7	960	63.8	30.8	0.0	0.0

[a] Reactions carried out in a 150 ml stainless steel autoclave with continous rocking in a heated oil bath. [b] H_2/CO = 1/1. [c] Mole per cent based upon the amount of 1-pentene used. [d] Catalyst recycled from preceding reaction. ν(CO) 2050(m), 1990(d, s), 1955(o), 1870(m-s). [e] Elemental analysis of the recovered resin: P(2.78%), Cl(0.06%), Co(4.30%), O(4.69%). [f] Elemental analysis of the recovered resin: P(2.25%), Cl(0.05%), Co(3.32%), O(3.17%).

that at temperatures in the range of 145 - 150° 1-pentene undergoes nearly complete conversion to a mixture of isomeric aldehydes accompanied by a small amount of pentane ($\leq$ 4%) (Table 3). Under these conditions the linear/branched ratio of products is generally of the order of 2/1, a result not unlike that found using homogeneous phosphine-substituted cobalt carbonyls. Very similar results were obtained when polymer XXIV, containing a smaller amount of phosphorus and cobalt, was used.

The polymeric catalysts, which may be recovered simply by filtering the reaction mixture in air and washing with benzene, may be immediately recycled in subsequent reactions with essentially no change in catalytic behavior (Table 3). However, washing of the resin must be completed rather hastily; otherwise, the recovered polymer oxidizes readily to a greenish-colored compound which exibits no CO stretching bands.

Moreover, XXVII has been found to be active in the hydroformylation of 1-pentene at the relatively low pressure of 400 psi (1/1; H_2/CO) much below that required for $Co_2(CO)_8$ and similar to results reported for $Co_2(CO)_6(PR_3)_2$ [21]. However, the majority of reactions were carried out at 1000 psi because of the excessive pressure drop during the reaction. When the reaction temperature was increased above 150 - 155° catalyst XXVII was found to promote the formation of the corresponding linear and branched alcohols. This, however, is not surprising in view of the fact that Slaugh and Mullineaux [21] have reported high conversions of 1-pentene to alcohols using $Co_2(CO)_6$-$(PR_3)_2$ derivatives in the range of 150 - 195°. The ratio of linear/branched products appears to decrease considerably at higher temperatures and was found to be only about 1.4/1.0 at 171°. The formation of high molecular weight compounds, presumably due to condensation reactions, also becomes noticeable at higher temperatures.

Use of catalyst XXXI, the cobalt carbonyl derivative of the polymeric analog of triphenylphosphine, was found to give results similar to those observed for catalyst XXVII (Table 3). The ratio of linear/branched products at 146° was observed to be about 1.5/1, somewhat lower than that observed for XXVII. It also is observed to decrease with increasing reaction temperatures (Table 3). Furthermore, this ratio is significantly less than that reported by Slaugh and Mullineaux [21] using $Co_2(CO)_6(PPh_3)_2$ at 195° (3.0/1.0). This latter observation is somewhat surprising in view of the fact that a sterically hindered polymer-bound cobalt hydride intermediate, in contrast to the purely homogeneous species, would be expected to exhibit an even greater preference for the formation of a normal alkyl intermediate and thus a greater linear/branched product ratio. Furthermore, the presence of the polyethylene backbone bound to the triphenylphosphine ligands would be expected to reduce the acidity of a cobalt hydride intermediate somewhat, leading to more anti-Markownikov addition in the heterogeneous species, also favoring the linear products. Reasons for the observed behavior are not presently understood.

The hydroformylation of 2-pentene using XXVII as the catalyst was also found to proceed quantitatively and result in a linear/branched product ratio of 2.1/1.0, very similar to that observed using 1-pentene as the substrate. This result is not unexpected in view of Tucci's report that nearly identical product distributions were obtained from 1-hexene (3.0/1.0) and 2-hexene (3.0/1.0) using $HCo(CO)_3(PBu_3)$ as a catalyst [18]. Indeed, this strongly suggests that the active intermediate in our reactions, most probably a polymeric cobalt hydride (i.e. polymer—$Co(CO)_3H$), can function as an effective isomerization catalyst (see *isomerization reactions*).

The form of the organometallic moiety on the recovered catalyst was of foremost interest to us since it exhibited a CO spectrum (five bands; see Footnote *d*, Table 3) significantly different than that of the starting polymers, which exhibit a single major broad band. Although there is some chance that the catalyst may be isolated from the reaction mixture at least partially in the form of a cobalt hydride (i.e. polymer—$Co(CO)_3H$), previous work with monomeric species of this type has shown that they are generally unstable at room temperature. However, the fairly rapid oxidation of our resins if left standing in the atmosphere for short periods of time before washing may, indeed, suggest the initial presence of hydrido species stabilized by pockets of H_2 and CO within the matrix. Moreover, it has been shown that $Co_2(CO)_6(PPh_3)_2$ is readily converted under a CO atmosphere to $Co_2(CO)_7(PPh_3)$ which reportedly exhibits CO stretching bands at 2079 m, 2026 m, 2010 sh 1996 s and 1964 m cm^{-1} [24]. Furthermore, direct evidence has been reported for this species under hydroformylation condition when $Co_2(CO)_6(PPh_3)_2$ was introduced as the catalyst [25,26]. Hence, we strongly feel that, on the basis of the similarity of the CO stretch spectrum of our recovered catalyst with that of $Co_2(CO)_7$-(PPh_3), that it consists primarily of a mixture of the dicobalt heptacarbonyl (i.e. polymer—$Co_2(CO)_7$) derivative along with some of the initial disubstituted species. This, however, does not rule out the possibility that a hydrido species is initially present upon isolation of the resin from the autoclave.

Conversion of the original disubstituted complex to a monosubstituted under CO immediately suggests that some cobalt carbonyl may in fact be released from the support under reaction conditions. Indeed, in nearly all of the experiments described above, a small amount of $Co_2(CO)_8$ is found to be released, resulting in the formation of yellow to yellow-brown product solutions. This, in fact, does become more apparent in the reactions carried out at elevated temperatures. Accordingly, the cobalt content of XXVII was reduced from 5.68% to 3.32% during its use in three sequential reactions (Table 3, Footnote *e*). It seems feasible that this loss of $Co_2(CO)_8$ could be minimized by the equilibration of the reaction mixture following release of the CO and H_2 pressure. In this way the $Co_2(CO)_8$ could rapidly recoordinate with free phosphine sites within the polymer in much the same manner described by Moffat [5] in a poly-2-vinylpyridine/cobalt carbonyl system. Such studies are in progress.

Preliminary hydroformylation studies of 1-pentene utilizing polymeric catalyst XXVIII, derived from $RhCl(CO)(PPh_3)_2$ [27] and the polymeric ligand IIc, revealed that this species is quite active under considerably milder conditions. Reactions carried out at 70° and 400 psi total pressure (H_2 / CO; 1/1) have resulted in complete conversion of 1-pentene to a mixture of aldehydes. The linear/branched product ratio was observed to be about 3.0/1.0 with no alcohols observed. Both the unaltered CO stretching spectrum of the recovered catalyst and the clear reaction solutions suggest that the rhodium moiety remains firmly bound to the polymer during the reaction.

The major drawback to the widespread use of homogeneous rhodium catalysts, although often active under mild conditions [27], has been their initial expense coupled, of course, with the loss of metal during recovery. The latter problem, it seems, may now be largely circumvented using this matrix technique, very possibly signaling the advent of widespread usage of more costly metal species in such systems.

Oligomerization of ethyl propiolate with polymeric catalyst XXV

$Ni(CO)_2(PR_3)_2$ (R = alkyl or aryl) complexes serve as active catalysts for the oligomerization (i.e. cyclotrimerization and polymerization) of a wide variety of acetylenic compounds [28,29]. Ethyl propiolate has been found to be one of the most reactive substrates with $Ni(CO)_2(PPh_3)_2$, reportedly being converted in 95% yield to a mixture consisting of 6% 1,3,5-tricarbethoxybenzene and 89% of the 1,2,4-trisubstituted isomer [30]. In reactions of this type, the spent catalyst has been reportedly recovered in the form of nickel oxides and phosphine oxides during work-up of the reaction mixtures. Hence, we have examined the oligomerization of ethyl propiolate in the presence of resin XXV, containing bound nickel dicarbonyl phosphine units, in view of its possible recycling characteristics and to examine the product yields.

Reactions were carried out by stirring a suspension of the catalyst beads in the presence of ethyl propiolate using either benzene or THF as a solvent under N_2. In either case, the catalyst (initially light yellow) gradually acquired a dark brown color during a 15 - 20 minute induction period. However, when benzene was used as the solvent, this culminated in a highly exothermic reaction accompanied by considerable gas evolution presumably caused by rapid displacement of the CO ligands. The solutions were then heated for eight hours at about 70°. Work-up of the THF reaction mixture led to a yield of 5.8% 1,3,5-tricarbethoxybenzene and 74.5% of the 1,2,4-tricarbethoxybenzene by weight based on the amount of ethyl propiolate used (Table 5). The use of benzene as solvent led to lower yields as did the use of THF when stirred at room temperature.

The dark brown catalyst recovered under N_2 from the initial THF reaction mixture was found to be active in a second reaction converting only a slightly lower percentage of ethyl propiolate. However, now the product mixture surprisingly consisted of cyclooctatetraene isomers, identified by NMR and mass spectrometry, in addition to the two benzene isomers. Further recycling of the catalyst led to significantly decreased conversions of the substrate but the yield of the cyclooctatetraenes relative to the benzene isomers increased. Moreover, recovery of the resin in the air from an initial THF reaction led to large reductions in the conversion in subsequent reactions using this catalyst although the cyclooctatetraene products were still observed. Yields of sequential reactions carried out in benzene, in contrast to THF, seemed to be little influenced by the method used for catalyst recovery, but the 8-membered rings were still observed in these systems in the second and succeeding runs.

An attempt to elucidate the structure of the organometallic moiety on the recovered catalysts has met with little success. These dark brown resins contain no coordinated CO ligands but do exhibit intense ester CO absorptions in the IR. No evidence is observed in the IR for a C=C stretching vibration. Most

RESULTS OF OLIGOMERIZATION EXPERIMENTS USING POLYMERIC NICKEL CATALYSTS[a]

Catalyst (g)	Reactant (ml)	Solvent (ml)	Temp (°C)	Time (h)	Conversion[b]	Products[c]		
						sym. benzene	unsym. benzene	cyclo-octatetraenes
XXV (0.50)	ethyl propiolate (2.0)	THF (5.0)	68	7	80.5	5.8	74.5	0.0
Recycled[d]	ethyl propiolate (2.0)	THF (5.0)	69	7	75.0	6.0	45.5	23.5
Recycled[d]	ethyl propiolate (2.0)	THF (8.0)	71	7	31.3	2.3	16.8	12.2
Recycled[d,e]	ethyl propiolate (2.0)	THF (5.0)	69	7	37.3	1.7	18.6	16.8
XXV (0.50)	ethyl propiolate (2.0)	THF (5.0)	70	6	79.5	8.0	71.5	0.0
Recycled[f]	ethyl propiolate (2.0)	THF (5.0)	71	7	10.5	0.6	5.0	4.9
XXV	ethyl propiolate (2.6)	Benzene (5.0)	70	63	74.5	4.8	69.5	0.0

[a] Analytical data and catalyst description included in Table 2. [b] Per cent by weight converted to cyclized products. [c] Weight per cent based on amount of ethyl propiolate used. [d] Catalyst used was recycled from previous reaction under N_2. [e] Recovered catalyst gave the following elemental analysis (%): P(1.68), Ni(1.57), O(12.69), Cl(0.06). Analysis of XXV was: P(3.67), O(4.75), Ni(5.07), Cl(0.04). [f] Catalyst used was recovered from previous reaction by filtering in the atmosphere.

TABLE 5

RESULTS FROM THE ISOMERIZATION OF ALLYLBENZENE WITH POLYMERIC CATALYST XXVII[a]

Catalyst[b], [d] (g)	Substrate (ml)	Temperature (°C)	Products[c]		
			Allylbenzene	*cis*-Propenyl benzene	*trans*-Propenyl-benzene
0.5	5.0	116	89.5	1.3	9.2
0.5	5.0	136	15.2	6.7	78.1
0.5	5.0	146	13.8	6.8	79.4
none	5.0	176	95.0	1.0	4.0

[a] Reactions carried out in autoclave under 150 psi H_2 for 6 hours. [b] Contains 5.68% Co. [c] Mole per cent. [d] CO stretching spectrum of recovered catalysts: 1988(m–s), 1922(s).

surprisingly, however, elemental analysis of a resin recovered after having recycled it three times in the THF reaction mixtures was found to contain a very high percentage of oxygen compared to that in the initial catalyst (Table 4, Footnote *e*). Analysis of a resin recovered from a single reaction in benzene was also found to have a comparable percentage of oxygen (11.93%). This high oxygen content immediately suggests that each metal must be coordinated in some manner by several of the ethyl propiolate molecules (ca. 4 or 5 molecules). Indeed, these possibly may be bound in the form of a macrocyclic ring system. Work is now proceeding on the study of similar derivatives of the linear polymers in hopes that additional structural information may be obtained in order to understand the reasons for the formation of the cyclooctatetraene derivatives.

Isomerization of allylbenzene

$HCo(CO)_4$ has been known to be an active isomerization catalyst for some time [23], although the exact mechanism by which it acts, whether of the addition-elimination or π-allyl type, is still not certain. Results of our hydroformylation studies using XXVII have suggested that under H_2 this catalyst also may promote olefin isomerization. Hence, we have examined the isomerization of allylbenzene in the presence of XXVII under H_2 at several temperatures (Table 5). We have found that indeed, above 130 - 135° allylbenzene is effectively isomerized over a six hour period to a mixture of *cis*- and *trans*-propenylbenzene with some residual allylbenzene. The yields, of course, are found to be temperature dependent although little difference exists between the results of reactions at 146 and 171°. The form of the organometallic moiety of the recovered olive-colored catalyst is yet unknown. The two carbonyl stretching bands of catalyst XXVII (Table 5, Footnote *d*) are less intense in the spectra of resins recovered from the high temperature reactions.

Experimental

Samples of all organometallic compounds were obtained from Pressure Chemical and used with no further purification. THF and benzene were dried over calcium hydride and distilled immediately before use. Ethyl propiolate (Columbia Organics) was distilled under vacuum and a center cut collected.

Allylbenzene (Columbia Organics), 1-pentene (99%, Chemical Samples) and 2-pentene (Columbia Organics) were used as purchased.

Infrared spectra, recorded on a Beckman IR—33 instrument, were obtained using KBr pellets of both the linear and cross-linked polymer samples. NMR spectra of the products from oligomerization studies were recorded on a Hitachi—Perkin—Elmer R20B (60 MHz) instrument using TMS standards.

Mass spectra of products from the catalytic reactions were recorded on a CEC 21—104 instrument at 70 ev using a direct probe inlet. The molecular weight of the linear polymeric ligand, I, was measured on a Waters Associates GPC/ALC 301 gel permeation chromatograph. A universal calibration technique was used.

VPC chromatograms were recorded for product mixtures from hydroformylation and isomerization reactions on the Varian Aerograph Model 90-P. An 8 ft. column consisting of 15% SE-30 deposited on Chromosorb P (non-acid washed) was used. Mixtures of allylbenzene, *cis*-propenylbenzene, and *trans*-propenylbenzene were effectively separated at a column temperature of 150°. Pentane and 1-pentene were separated at 50° while the mixtures of six-carbon linear and branched aldehydes and alcohols were separated at 125° - 135°.

Preparation of polymeric ligands

Preparation of polymeric ligands was carried out according to methods [7,8,31] very briefly outlined in the literature involving the reaction of lithium diphenylphosphide (i.e. $Li^+PPh_2^-$) with linear and cross-linked chloromethylated polystyrene to give polymers I and II respectively. Polymer III* was prepared by the reaction of $Li^+PPh_2^-$ and brominated polystyrene.

Linear diphenylphosphinomethylpolystyrene. Linear chloromethylated polystyrene ($\bar{M}_n$ = 18,000**) was prepared by the method of Pepper, Paisley, and Young [32] involving the reaction of chloromethylethyl ether with polystyrene using a $SnCl_4$ catalyst. It was purified by precipitating THF solutions of the polymer into large volumes of petroleum ether. The dried polymer (15.9 g, 7.49% Cl; 31.6 mmol Cl) was then stirred with an excess of $Li^+PPh_2^-$ (0.10 mol) for 22 h. Following hydrolysis with 70 ml of saturated NH_4Cl solution, the mixture was transferred to a separatory funnel under N_2 and the aqueous layer removed. The THF layer was then slowly added to 1700 ml of petroleum ether, resulting in the precipitation of the white polymer. After allowing the precipitate to settle overnight the product was collected by filtration and stirred in water for one day and was again filtered and redissolved in 150 ml of THF and reprecipitated in 1200 ml of petroleum ether. A third reprecipitation was carried out and the recovered polymer was dried under vacuum for two days yielding 14.8 g of product.

Cross-linked diphenylphosphinomethylpolystyrene. Chloromethylated styrene/divinylbenzene resin (30 g, Bio-Rad SX—1, 1% cross-linking, 1.29 m. eq. Cl/g) swollen in 200 ml of THF was slowly added to 120 ml of a THF solution of $Li^+PPh_2^-$ (0.14 moles). After stirring for 24 hours, the mixture was added to 500 ml of wet acetone under N_2, hydrolyzing excess

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* Furnished by Ronald Hanes of this laboratory.

** By gel permeation chromatography.

$Li^+PPh_2^-$. After filtration, the resin was washed with 300 ml acetone followed by 200 ml water and 200 ml THF. The final two washings were repeated and finally the resin was washed with liberal amounts of petroleum ether. After drying under vacuum for two days, 33.0 g of dry resin was collected.

Preparation of polymeric metal carbonyl derivatives

Due to the large number of derivatives which have been prepared using both linear and cross-linked polymeric ligands, we have included below descriptions of typical reactions of each type. These reactions are classified accordingly as (i) carbonyl substitution reactions, (ii) phosphine exchange reactions and (iii) the reaction of $Co_2(CO)_8$ with polymeric ligands, somewhat unusual in its behavior. Conditions for other similar reactions are included in Table 2.

(i) Carbonyl substitution reactions

Photochemical reactions

The compounds $M(CO)_6$ (M = Cr,Mo,W), $CpMn(CO)_3$, and $Mn_2(CO)_{10}$ were bound to polymeric ligands by photochemical techniques. Included below are typical reactions of $CpMn(CO)_3$ and $Cr(CO)_6$ with the linear and cross-linked polymers, respectively.

Cross-linked polymeric ligands. IIa (0.50 g; 0.40 mmol P) and $Cr(CO)_6$ (1.0 g; 4.55 mmol) were added to 25 ml of toluene with stirring. After purging the solution with N_2, a water-cooled cold finger was introduced, and the suspension irradiated for 24 h with a Hanovia Type SH mercury arc lamp at a distance of 6 in. After termination of the reaction, the mixture was filtered and washed with liberal amounts of toluene and then strred in 25 ml of toluene overnight. The filtered yellow resin was dried under vacuum (0.55g).

Linear polymeric ligand. $MeCpMn(CO)_3$ (1.0 g; 4.9 mmol) and 0.40 g of the linear polymeric ligand, I (0.32 mmol P), were dissolved in 30 ml of toluene. A water-cooled cold finger was introduced and the N_2 purged solution irradiated for 21.5 h with stirring. After filtering off some decomposition products, the polymer was precipitated by slowly adding the solution to 800 ml of petroleum ether. The light brown polymer, collected by filtration, was redissolved in 25 ml of toluene and reprecipitated into petroleum ether. The polymer was then dried under vacuum for 24 h giving 0.40 g of the light brown powder.

Thermal Reactions

Cross-linked polymeric ligand. $Cr(CO)_6$ (1.00 g; 4.55 mmol) and 0.50 g of cross-linked resin, IIa (0.40 mmol P); were added to 20 ml of diglyme with stirring. The flask was equipped with a reflux condenser and the contents heated under N_2 at 100° for 1.25 h during which time the sublimed carbonyl was manually returned to the flask. After cooling to room temperature the suspension was filtered and washed liberally with toluene. After drying under vacuum 0.75 g of light green resin was recovered.

Linear polymeric ligand. $Cr(CO)_6$ (0.90 g; 2.5 mmol) and 0.50 g of linear polymer, I (0.78 mmol P), were added with stirring to 25 ml of diglyme. This solution was heated for 1.25 h under N_2 at approximately 100° while the sublimed carbonyl was manually returned to the flask periodically. The filtered reaction solution was added to 700 ml of rapidly stirred petroleum ether and the resultant precipitate collected by filtration after settling overnight. The polymer was reprecipitated by adding a 50 ml THF solution to 600 ml of petroleum ether. The precipitate was collected and dried under vacuum for 24 h, yielding 0.64 g of white polymer.

(ii) Phosphine exchange reactions

The two metal carbonyl phosphines, $Ni(CO)_2(PPh_3)_2$ and $RhCl(CO)(PPh_3)_2$, were bound to the cross-linked polymeric ligands by phosphine exchange reactions. With the former, reactions were carried out both photochemically and thermally whereas with the latter, reactions were performed only thermally.

Photochemical reactions

$Ni(CO)_2(PPh_3)_2$ (0.90 g; 1.41 mmol) and 0.30 g of ligand IIa (0.24 mmol P) were irradiated for 21 h under N_2 according to the method outlined above in (i). The resin was filtered and washed with 100 ml of toluene and then stirred for one day in 50 ml of THF. It was then recovered by filtration, washed with THF and dried under vacuum, giving 0.35 g of off-white resin.

Thermal reactions

$RhCl(CO)(PPh_3)_2$ (1.0 g; 1.5 mmol) and 4.8 g of IIc (4.7 mmol P) were stirred in 55 ml of benzene at 27° for three days under N_2. The suspension was filtered and after washing with benzene, the resin was stirred twice in 50 ml portions of benzene under N_2 for periods of 1 and 24 h. The filtered resin washed with benzene and petroleum ether, was dried under vacuum yielding 4.47 g of the very light yellow product.

(iii) Reactions of $Co_2(CO)_8$ with polymeric ligands

Cross-linked ligands. IIb (15.0 g; 16.6 mmol P) was suspended in 200 ml of toluene under N_2. To this was slowly added with stirring a 100 ml toluene solution containing 9.0 g of $Co_2(CO)_8$ (26.4 mmol) during a 15 minute period. The dark brown solution was then stirred an additional three h. The dark brown resin (XXVI) was collected by filtration and washed with 300 ml of toluene and 200 ml of petroleum ether. This material was then heated under N_2 at 69° for 27 h. The product was colleted by filtration and washed with 250 ml of petroleum ether. After drying under vacuum 17.7 g of the red-brown material (XXVII) was collected.

Linear polymeric ligand. During a 15 minute period, a 50 ml solution containing 1.20 g of $Co_2(CO)_8$ (3.51 mmol) was added under N_2 to a stirred 100 ml solution consisting of 1.0 g of I (1.6 mmol P) dissolved in 100 ml of toluene. A brown precipitate rapidly formed upon mixing. After stirring an additional 0.5 h, the precipitate was collected by filtration and washed with toluene and petroleum ether. This light tan material, VIII (1.3 g), was collected after drying under vacuum. Compound VIII (1.10 g) was suspended in 100 ml of DME under N_2 and heated at 75° for 4 h. Filtration of the resin followed by washings with toluene and petroleum ether and drying under vacuum led to isolation of 0.60 g of the medium brown resin, IX.

Hydroformylation of pentene

In a typical reaction, 8 ml of dry benzene and 1.0 g of catalyst XXVII (0.97 mmol Co) were introduced into a 160 ml Hoke bomb under N_2. Following the addition of 4.0 ml of 1-pentene (36.4 mmol) and the attachment of the head, the system was evacuated three times while the contents were frozen in liquid N_2. The bomb was then pressurized to 980 psi with H_2 and CO(1/1) and heated in an oil bath at 152° for 7 h. with shaking. During this period a 185 psi pressure drop occurred. After cooling to room temperature the vessel was vented and the contents filtered in the atmosphere, yielding a clear golden filtrate along with the red-brown resin.

A sample of filtrate was injected into the gas chromatograph with the column temperature at 40° in order to separate the pentane reduction product from any unreacted 1-pentene. The column temperature was then increased to 130° and the linear and branched hydroformylation products separated (see Table 3). A column temperature of 250° was used to verify that no higher boiling condensed products were obtained.

Isomerization of allylbenzene

Typically 5.0 ml of allylbenzene (37.9 mmol) and 0.50 g of XXVII (0.48 mmol Co) were charged into a bomb under N_2. The system was then evacuated during three freeze-thaw cycles using liquid N_2. The vessel was then heated for 6 h at 146° after filling with H_2 to a pressure of 155 psi. The bomb was then cooled to room temperature and the pressure released. The contents were then filtered in the atmosphere and the clear filtrate chromatographed at 150° by VPC (Table 4) and the relative amounts of allylbenzene, *cis*-propenylbenzene, and *trans*-propenylbenzene measured by integration.

The olive green catalyst was washed with 25 ml of benzene and 25 ml petroleum ether and the dried under vacuum. An IR spectrum of the recovered resin indicated the presence of two CO stretching bands (Table 5, Footnote *d*).

Oligomerization of ethyl propiolate

Reaction using catalyst in THF. In a typical reaction, 0.50 g of catalyst (0.43 mmol Ni) was introduced into a side-armed flask containing 5.0 ml of THF under N_2. After stirring the resin for about 15 minutes, 2.0 ml of ethyl propiolate (1.91 g; 19.5 mmol) was injected and the solution was further flushed with N_2 for about one minute. During 15 min, the light yellow resin gradually acquired a dark brown coloration. The suspension was then heated at 68° for 8 h. After cooling to room temperature, 100 ml of THF purged with N_2 was introduced to the flask and after stirring for several minutes the suspension was filtered through a glass frit. The recovered resin was dried partially under a stream of N_2 on the frit. The viscous oily material, obtained by concentrating the brown filtrate under vacuum, was then extracted with 320 ml of a refluxing CCl_4/petroleum ether (1/4) mixture. The yellow extract was filtered, the solvents removed under vacuum, and the dark yellow oil collected (1.54 g) corresponding to 80.5% conversion based on the weight of ethyl propiolate used. An integrated NMR spectrum of the oil revealed that the product consisted of 93% 1,2,4-tricaroethoxybenzene and 7% of the symmetrical isomer.

Recycling of catalyst Approximately 10 ml of THF purged with N_2 was used to wash the recovered resin back into the flask. The solvent volume was reduced to 5 ml under a stream of N_2 and 2.0 ml of ethyl propiolate was then injected. After flushing the solution again with N_2 for one minute, the stirred mixture was immediately heated at 69° for 1 hour. After cooling to room temperature, 100 ml of THF was introduced and as above the solution filtered through a frit. The products were worked up in an identical manner, but the NMR of the recovered oil (1.44 g, 75.5% conversion of ethyl propiolate) revealed that the products consisted of 8.1% of the symmetrical benzene derivative, 61% of the unsymmetrical benzene derivative and 30.9% of cyclooctatetraene isomers.

Benzene solution The procedure used was basically the same as that described above for THF solutions. However, approximately 15 - 20 min after the addition of ethyl propiolate, a highly *exothermic reaction occured accompanied by considerable gas evolution* (This however was not observed in reactions using the recycled catalyst). Heating of the system was commenced thereafter. Yields of these reactions are contained in Table 4.

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