

Polymerization of Propadiene. IV. Kinetics and Mechanism of Polymerization under the Influence of Rhodium(I) Complexes

J. P. SCHOLTEN and H. J. VAN DER PLOEG,* *Polymer Chemistry Laboratory, Twente University of Technology, Enschede, The Netherlands*

Synopsis

The kinetics and mechanisms of propadiene polymerization under the influence of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, $\text{Rh}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3\text{Cl}$, $\text{Rh}(\text{CO})_3\text{Cl}$ are reported. The reaction rates are first-order in $\text{Rh}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3\text{Cl}$ and $\text{Rh}(\text{CO})_3\text{Cl}$ and half-order in $[\text{Rh}(\text{CO})_2\text{Cl}]_2$. They are second-order in the substrate for $\text{Rh}(\text{CO})_3\text{Cl}$ and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and first-order for $\text{Rh}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3\text{Cl}$. The data are interpreted in terms of a common intermediate mechanism. The formation of this common intermediate is the rate-determining step. A solvent effect is also discussed.

Introduction

During the last five years extensive work has been carried out on the kinetics of vinyl and 1,3-diene polymerization by use of Ziegler-Natta catalysts.¹⁻³ The dimerization of olefins and dienes by organometallic compounds has also received considerable attention.⁴⁻⁶ The homogeneous hydrogenation of unsaturated bonds has also been the object of detailed studies.^{7,8} Extensive research in the literature, however, revealed that hardly any research had been carried out on the kinetics and mechanism of polymerization reactions of propadiene catalyzed by rhodium complexes. This paper is part of a series dealing with the polymerization of propadiene. In part III⁹ we described this polymerization by some rhodium(I) complexes and proposed a possible reaction mechanism. In this publication we will report on the kinetics of the polymerization of propadiene catalyzed by the rhodium complexes: $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (α), $\text{Rh}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3\text{Cl}$ (β), and $\text{Rh}(\text{CO})_3\text{Cl}$ (δ). We were able to relate the observed kinetic data to a mechanism that confirms the one proposed earlier.

Experimental

The coordination complexes and starting materials were prepared as described in our previous publication.⁹

* To whom inquiries should be addressed.

Nomenclature

The nomenclature used is also the same, but for the sake of clarity we will repeat here as Table I the table published in part III of this series.⁹

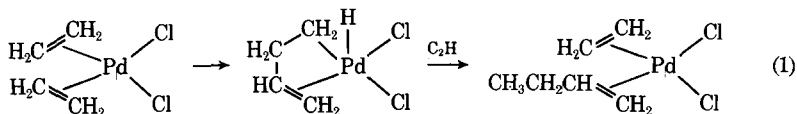
Procedure

The procedure for kinetic studies involved measurements of polymer yields in relation to various reaction parameters. The reactions were carried out in glass autoclaves with a volume of ± 250 ml. The catalysts were weighed and dissolved. From the solution the desired amounts were pipetted into the autoclaves. In the case of β and δ the catalysts were prepared in solution with known amounts of α , assuming 100% conversion. The reaction mixture volume was filled to 100 ml, and the autoclaves were closed. Then propadiene was added under its own pressure and the overshoot was gently blown off, while weighing the autoclave plus contents, until the desired amount was left behind. Four identical autoclaves were used for the polymerization experiments. These reactions were all allowed to proceed for the same amount of time. Then the remaining propadiene was blown off and the autoclaves were opened. The polyallene formed was filtered from the reaction medium and washed with acetone to remove catalyst residues, filtered again, and dried at room temperature at a pressure of 10 torr.

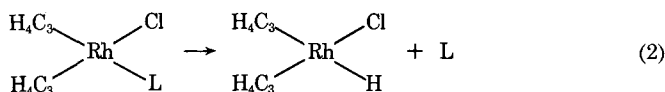
The temperature experiments were carried out identically in a double-walled, 500-ml glass autoclave which was thermostatted.

Results and Discussion

In our previous publication we proposed a kinetic scheme for both a binuclear (α) and mononuclear (β and δ) species. The aim of this work is to support and prove this scheme. As is known from the literature on isomerization,^{10,11} hydrogenation,^{7,8} and polymerization, these reactions can take place via a hydride intermediate. Ketley⁵ in his work on the dimerization of alkenes by Pd and Rh chloride, assumes in the mechanism proposed a hydride shift [eq. (1)]:



In analogy, we assume a hydride shift to take place with the coordinated propadiene leading to the reaction shown in eq. (2).



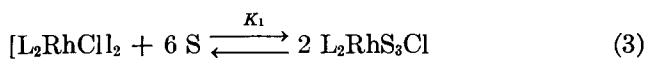
A mechanism shown in eqs. (3)–(9) for the polymerization of propadiene with a binuclear complex is now proposed. In this mechanism the original

TABLE I
Symbols Used for the Various Rhodium(I)-Complexes

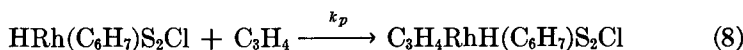
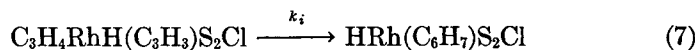
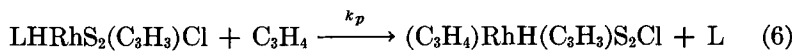
Symbol		
α	$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	Tetracarbonyl- μ, μ' -dichlorodirhodium (I)
β	$\text{Rh}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{Cl}$	Triphenylphosphine- <i>cis</i> -dicarbonylchlororhodium (I)
γ	$\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{CO})\text{Cl}$	Carbonyl- <i>trans</i> -bis(triphenylphosphine) chlororhodium (I)
δ	$\text{Rh}(\text{CO})_3\text{Cl}$	Tricarbonylchlororhodium (I)
ϵ	$\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{Cl}$	Tris(triphenylphosphine)chlororhodium (I)

ligands are all replaced. Indeed, infrared spectroscopy of complexes isolated from the reaction medium indicate the absence of CO absorption.

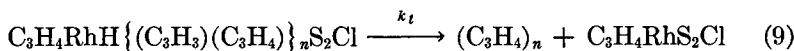
Initiation:



Propagation:



Termination:



From this reaction scheme we find for the propagation step (6)

$$v_p = -d(\text{C}_3\text{H}_4)_p/dt = k_p[\text{LHRhS}_2(\text{C}_3\text{H}_3)\text{Cl}][\text{C}_3\text{H}_4] \quad (10)$$

and from the initial equilibrium (3)

$$K_1 = [\text{L}_2\text{RhS}_3\text{Cl}]^2/([\text{L}_2\text{RhCl}]_2[\text{S}]^6) \quad (11)$$

or

$$[\text{L}_2\text{RhS}_3\text{Cl}] = K_1^{1/2}([\text{L}_2\text{RhCl}]_2)^{1/2}[\text{S}]^3 \quad (12)$$

The equilibrium (4) gives:

$$K_2 = [\text{S}][\text{L}_2\text{RhS}_2(\text{C}_3\text{H}_4)\text{Cl}]/([\text{L}_2\text{RhS}_3\text{Cl}][\text{C}_3\text{H}_4]) \quad (13)$$

or

$$[\text{L}_2\text{RhS}_2(\text{C}_3\text{H}_4)\text{Cl}] = K_2[\text{C}_3\text{H}_4][\text{L}_2\text{RhS}_3\text{Cl}]/[\text{S}] \quad (14)$$

Substituting eq. (12) in eq. (14) we find:

$$[\text{L}_2\text{RhS}_2\text{C}_3\text{H}_4\text{Cl}] = K_1^{1/2}K_2[\text{C}_3\text{H}_4][(\text{L}_2\text{RhCl})_2]^{1/2}[\text{S}]^2 \quad (15)$$

On assuming the hydride shift to be of first order, there is a direct relation between $\text{L}_2\text{RhS}_2(\text{C}_3\text{H}_4)\text{Cl}$ and $\text{LHRhS}_2(\text{C}_3\text{H}_3)\text{Cl}$ at a fixed time which can be written as

$$[\text{LHRhS}_2(\text{C}_3\text{H}_3)\text{Cl}] = \text{const.} [\text{L}_2\text{RhS}_2(\text{C}_3\text{H}_4)\text{Cl}] \quad (16)$$

Combining eqs. (16), (15), and (10) we find for the propagation

$$v_p = \text{const.} k_p K_1^{1/2} K_2 [\text{C}_3\text{H}_4]^2 [(\text{L}_2\text{RhCl})_2]^{1/2} [\text{S}]^2 \quad (17)$$

In ethanolic solution one finds thus:

$$v_p = K_\alpha [\text{C}_3\text{H}_4]^2 [\alpha]^{1/2} \quad (18)$$

In the case of β and δ the mechanism is slightly different. The starting reaction is reaction (4) of the initiation, where $\text{L}_2\text{RhS}_3\text{Cl}$ should be read as $\text{L}_3\text{RhS}_2\text{Cl}$ and direct replacement of one ligand by propadiene takes place.

By an analogous derivation, one finds for β [assuming (4) to be a very fast reaction]:

$$v_p = K_\beta [\text{C}_3\text{H}_4]^1 [\beta]^1 \quad (19)$$

and for δ

$$v_p = K_\delta [\text{C}_3\text{H}_4]^2 [\delta]^1 \quad (20)$$

Although it seems obvious that α dissociates in a polar solvent, viz., $\text{C}_2\text{H}_5\text{OH}$, into two solvated mononuclear species, it seemed more complete to prove this aspect by determining the order with respect to ethanol. This was performed by adding to a hexane solution of α for each experiment a different amount of ethanol. Thus, a second-order reaction in ethanol was firmly established (see Fig. 1).

On treating β in the same way, the rate of polymerization seemed to be second-order in ethanol, as can be seen in Figure 2. We assume, that in a preponderantly nonpolar mixture β does not exist as a mononuclear but as a dimeric species, as described by Poilblanc et al.¹² This was confirmed by the finding of a zero order in ethanol in a benzene medium, suggesting benzene to be strong enough to split the chlorine bridge.

A separate experiment proved this conclusion, because a second order in benzene is found when the reaction is carried out in hexane with different amount of benzene, although the reaction rates were very small. In the case of δ no reaction took place in hexane, even for prolonged times (up to one week).

At this point some additional remarks with respect to the structure of δ seems appropriate, in view of the work of Morris and Tinker¹³ and a personal comment of the latter author to one of us (van der Ploeg). He disputes the presence of $\text{Rh}(\text{CO})_3\text{Cl}$ in the solution we obtained on treating α with carbon monoxide under pressure and suggests that according to

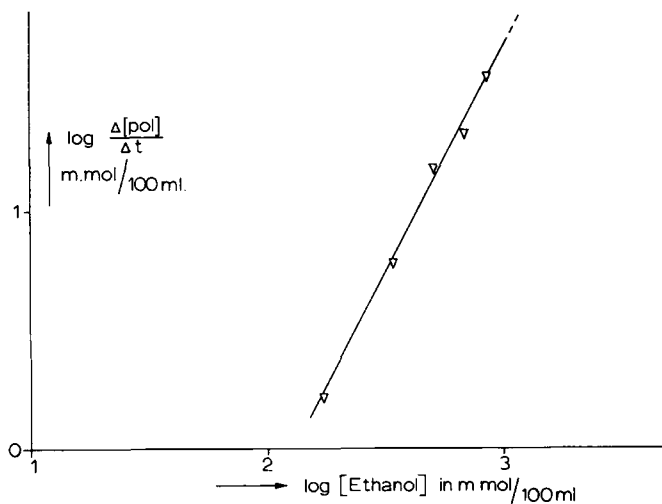
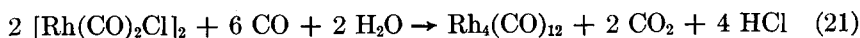


Fig. 1. Dependence of reaction order on solvent with α .

Chini¹⁴ the reaction (21) could take place under our conditions or that α does not react at all.



However, we feel that our conclusions are justified on the following grounds. The reaction (21) can be rejected, for we used ethanol with less than 0.1% water. The conversion, as Chini found, would be very low under such conditions. Moreover, our reaction times were about 5 hr, whereas

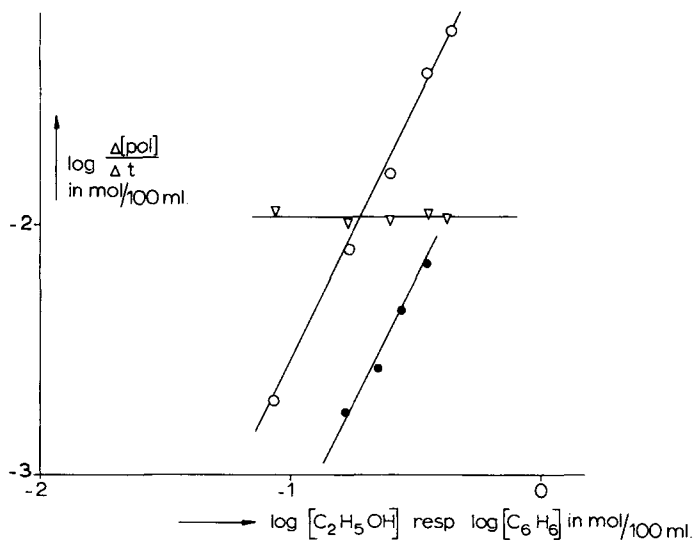


Fig. 2. Solvent dependence with α : (O) ethanol in hexane; (▽) ethanol in benzene; (●) benzene in hexane.

Chini's reactions took 24–48 hr. The rhodiumcarbonyls $\text{Rh}_4(\text{CO})_{12}$ and $\text{Rh}_6(\text{CO})_{16}$ are not soluble in ethanol. We obtained clear solutions. Also we can recover α from the solution and γ is formed quantitatively on treating the solution with the appropriate amount triphenylphosphine. These observations exclude, in our view, the formation of rhodiumcarbonyls.

Therefore, only the second suggestion could be true. We find however, a marked change in color from yellow to red and two main infrared absorptions (2075 and 2000 cm^{-1}) which are slightly but significantly different from those of α in an ethanolic solution (2070 and 1995 cm^{-1}). The fact that in our case the differences in the infrared spectrum between α and δ are less pronounced than in Morris and Tinker's work¹³ may be attributed to a difference in effect of a polar (EtOH) and a nonpolar ($\text{CICH}_2\text{CH}_2\text{Cl}$) solvent on the infrared spectrum.

As is described in this publication, we find a first-order dependence of δ in the polymerization of propadiene, indicating a mononuclear species, different from α . The polymer yield in this case is lower, corroborating the presence of a different active complex.

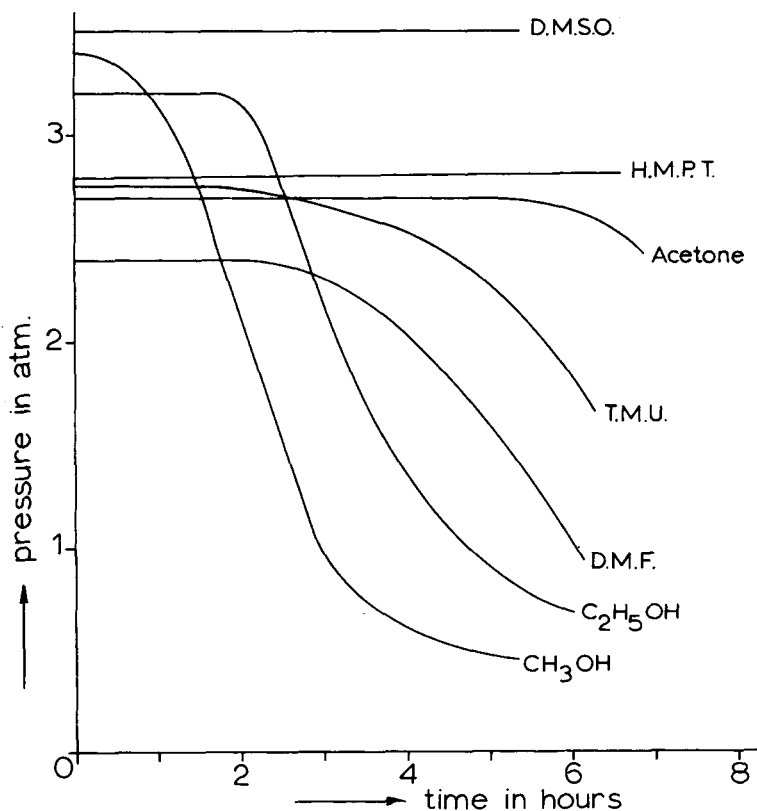


Fig. 3. Dependence of rate of polymerization on solvent with α at 40°C .

In order to demonstrate the effect of solvent on the rate of polymerization, we carried out a number of polymerizations using the same amount of catalyst (α) and monomer in the same volume of a number of solvents at the same temperature. Figure 3 shows a compilation of the results. The solvent used must fulfill the following two requirements: (1) it must split the chlorine bridge in α ; (2) it must not form too stable a complex with the rhodium compounds.

In hexamethylenephosphotriamide (HMPT) and dimethyl sulfoxide (DMSO) no polymerization took place. The high complexing ability of these solvents results in stable complexes with the rhodium compounds, too stable to catalyze any further polymerization. Also a reluctancy to

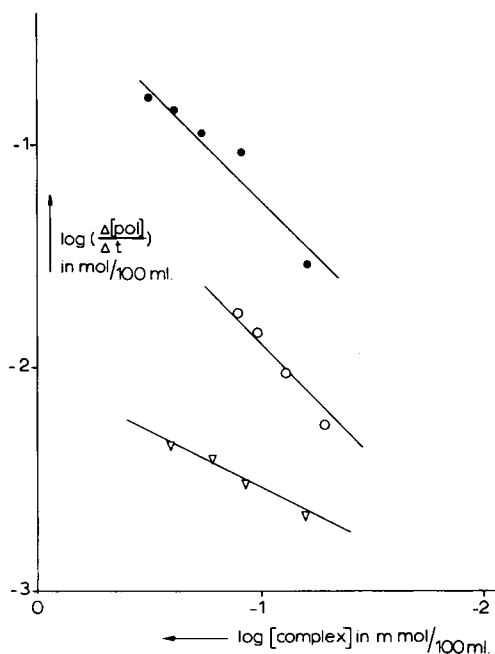


Fig. 4. Dependence of reaction order on catalyst: (∇) α , 8 hr, 20°C, 4 g C_3H_4 ; (\circ) δ , 24 hr, 20°C, 4 g C_3H_4 ; (\bullet) β , 16 hr, 20°C, 4 g C_3H_4 .

react was observed in hexane. In this case however, polymerization could be realized at higher temperature (80°C), indicating the ability of propadiene itself to split the chlorine bridge in α under more drastic conditions. Ethanol and methanol seem to be suited best as a solvents in which to carry out the polymerization.

We did not go further into the nature of the solvent effect, but restricted ourselves to the observation of the phenomenon.

Figure 4 shows the relation between the complex concentration and the polymer yield. The order in α is one half, indicating again the bridge splitting reaction into monomeric species. For β and δ a first-order in the

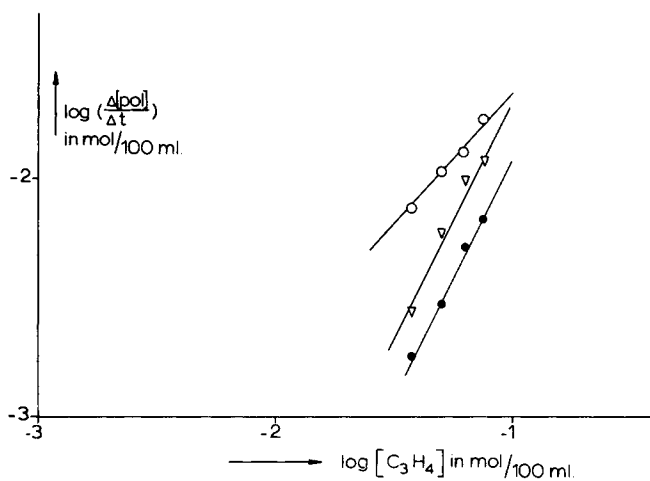


Fig. 5. Dependence of reaction order on propadiene concentration: (∇) α ; (\circ) β ; (\bullet) δ .

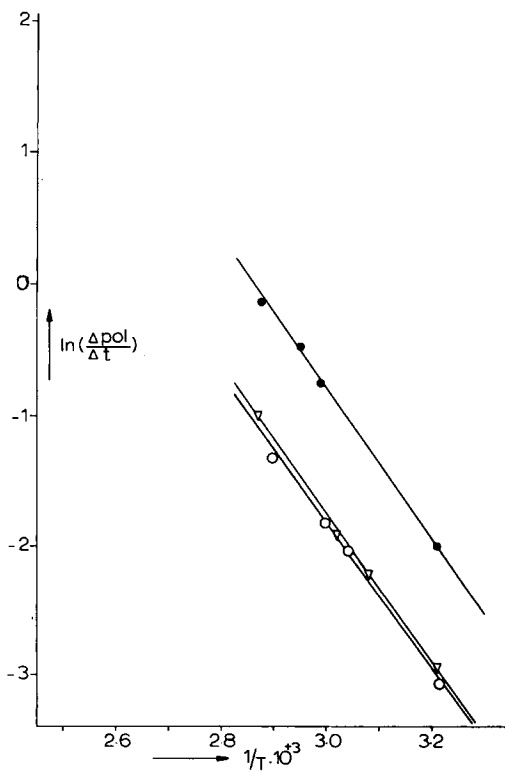
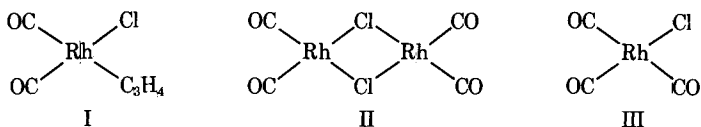


Fig. 6. Activation energies: (\circ) β , 10 mg/200 ml, 20 g C_3H_4 , 2.5 hr; (∇) α , 5 mg/200 ml, 20 g C_3H_4 , 6 hr; (\bullet) δ , 10 mg/200 ml, 20 g C_3H_4 , 6 hr.

complex has been found, confirming the hypothesis that polymerization takes place via a monomeric species.

The order in propadiene itself is shown in Figure 5. A first-order in propadiene is found for β . With α and δ a second-order is found. In part III of this series we stated that polymerization takes place with the three complexes via a common intermediate with the structure I and that its formation might be rate-determining.



We assume that in the case of β the initiation step (4) is not an equilibrium but a very fast reaction, resulting in the formation of a complex with structure I, which is the proper object of the kinetic measurement. In the case of α and δ these are II and III, which give structure I by splitting the chlorine bridge with ethanol followed by replacement of coordinated ethanol by propadiene and direct replacement of a carbon monoxide ligand by propadiene.

Finally we measured the activation energies of the three polymerizations (Fig. 6). All three complexes gave rise to the same energies of activation. As yet we have no satisfactory explanation for this observation.

We thank Prof. Dr. J. Schuyer and Dr. J. W. A. van den Berg of this department and Prof. Dr. P. J. Gellings of the Inorganic Chemistry Department of this University for helpful discussions and critical comments.

References

1. A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *Europ. Polym. J.*, **7**, 289 (1971).
2. N. G. Gaylord, T.-K. Kwei, and H. F. Mark, *J. Polym. Sci.*, **42**, 417 (1960).
3. A. Mazzei, M. Araldi, W. Marconi, and M. de Maldé, *J. Polym. Sci. A-1*, **3**, 753 (1965).
4. B. R. James and L. D. Markham, *J. Catalysis*, **27**, 441 (1972).
5. A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman, and T. R. Steadman, *Inorg. Chem.*, **6**, 657 (1967).
6. R. Cramer, *J. Amer. Chem. Soc.*, **87**, 4717 (1965).
7. J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, **1966**, 1711 (1966).
8. B. R. James and G. L. Rempel, *Can. J. Chem.*, **44**, 233 (1966).
9. J. P. Scholten and H. J. van der Ploeg, *J. Polym. Sci. Polym. Chem. Ed.*, **10**, 3067 (1972).
10. H. Singer and J. D. Umpleby, *Tetrahedron*, **28**, 5769 (1972).
11. R. Cramer, *Accts. Chem. Res.*, **1**, 186 (1968).
12. J. Gallay, D. de Montauzon, and R. Poilblanc, *C. R. Acad. Sci. (Paris)*, **273**, 988 (1971).
13. D. E. Morris and H. B. Tinker, *J. Organometal Chem.*, **49**, C53-C56 (1973).
14. P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 315 (1969).

Received August 6, 1973