

Mechanism of Poly(methyl Methacrylate) Fire Retardation by Wilkinson's Salt

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Synopsis

The reaction of Wilkinson's salt, $\text{ClRh}(\text{PPh}_3)_3$, and poly(methyl methacrylate) (PMMA) has been studied. Char formation is observed, and some 30% of the reaction product is nonvolatile at 600°C. In order to understand the pathway of this reaction, the reaction of dimethylglutarate (DMG) and $\text{ClRh}(\text{PP}_3)_3$ has been studied. A pathway is proposed in which the initial step is the oxidative addition of the rhodium species into a carbon—oxygen bond of the DMG molecule. Six different products have been isolated from this reaction and can be seen to result from the oxidative insertion. This pathway also seems to apply to the PMMA reaction and leads to an interpretation of the results of this reaction and permits one to understand the role of this, and similar, compounds as flame retardants.

INTRODUCTION

The desirable characteristics displayed by poly(methyl methacrylate) (PMMA) have made it one of the important commercial polymers. It has been widely accepted that PMMA invariably breaks down at elevated temperatures to give large amounts of monomer.¹⁻⁷ The mode of polymerization, i.e., free radical or anionic, determines the threshold temperatures for decomposition of PMMA.^{8,9} An increase in these respective threshold temperatures has little effect on the identities of the products of pyrolysis.^{10,11}

Starnes points out in his review article¹² on polymer degradation that technological advances have preceded the basic understanding of many aspects of this area and that additives to protect polymers have been largely developed on an empirical basis. Important fundamental questions need to be answered and the answers will lead the way for the design of suitable additives for polymer stabilization.

Recent work in this laboratory has shown that Wilkinson's salt is an effective flame retardant for poly(methyl methacrylate) (PMMA).¹³ The interaction of these two materials leads to crosslinking of the polymer. Crosslinking increases the threshold temperature for decomposition and simultaneously decreases the formation of flammable small molecules. Crosslinking of PMMA was shown to proceed by the formation of anhydride linkages; the literature cites evidence¹⁴ that the formation of these linkages increases the threshold temperature for decomposition.

The present paper describes the mechanistic details of the reaction of PMMA with Wilkinson's salt. The goal of this work is to understand the reaction of PMMA and the rhodium compound and to use that understanding in the design of additives as flame retardants for PMMA.

RESULTS AND DISCUSSION

In order to use an additive for a thermal process, it is imperative that first there be a clear understanding of the thermal behavior of the additive alone. The literature¹⁵ indicates that biphenyl and benzene are the only non-rhodium-containing species produced by pyrolysis or $\text{ClRh}(\text{PPh}_3)_3$, either in solution or as neat compound. Benzene is believed to arrive from an ortho-metallation reaction, the formation of biphenyl has been attributed to an oxidative addition reaction. The other products of the reaction have not been isolated and their structures have been only speculatively assigned. In the previous work,¹⁵ it was noted that the solvent and the atmosphere play an important role in the production of biphenyl. When benzene is used as the solvent, a small amount of air is required to ensure production of biphenyl. In this work all reactions were performed under high vacuum conditions by pyrolysis of the neat rhodium compound, and benzene is the only simple organic compound that is produced; we are unable to observe the formation of biphenyl. The lack of biphenyl formation can only be attributed to the absence of air and must suggest that air plays an important role in its formation. Previous work¹⁵ has shown, by the use of radical scavengers, that a radical process is not important for biphenyl formation and an oxidative addition process has been suggested. Further work to clarify the formation of biphenyl and its pathway is indicated.

No other products have previously been identified as arising from the pyrolysis of $\text{RhCl}(\text{PPh}_3)_3$. In this work, we have observed triphenylphosphine, triphenylphosphine oxide, and a rhodium-containing species. Since the workup of the reaction has been carried out entirely in air, it is not surprising that the phosphine is produced. Augustine and Van Peppen¹⁶ have shown that dissociation of Wilkinson's salt occurs in the presence of air and that aerial oxidation of these ligands may also occur. The rhodium containing material is no doubt the product of ortho-metallation which has undergone further reaction with the air. An elemental analysis is available which leads to a formula. No other information is available that would permit some structural assignment.

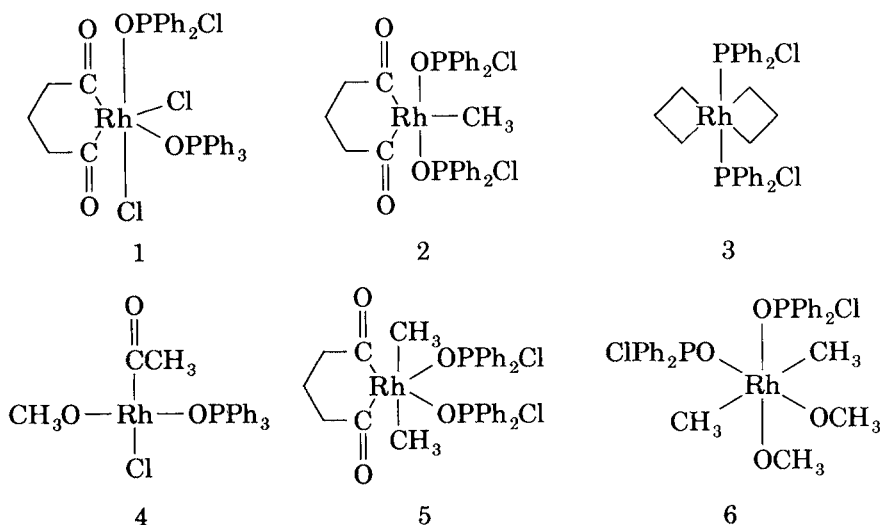
As previously reported,¹³ the reaction of PMMA and $\text{RhCl}(\text{PPh}_3)_3$ results in the formation of anhydrides both in the soluble fraction and in the char, and rhodium is present in both fractions. In the soluble fraction, some simple rhodium-containing compounds may be identified. These rhodium compounds have methyl and/or methoxy, in addition to triphenylphosphine and chloride, as ligands attached to rhodium. Since the bulk of the material is intractable char, it is not possible to delineate a pathway for the reaction. GPC analysis of the polymer fraction present in this soluble fraction indicates that the molecular weight of the polymer is unchanged by reaction. In order to understand this reaction, a model, dimethylglutarate (DMG) was used. This model was chosen both because its structure is similar to the substructure of PMMA and because its boiling point is above the pyrolysis temperature.

The pyrolysis of DMG with Wilkinson's salt results in the formation of about 30 compounds as shown by HPLC. Several of these are present in very small concentration and have not been isolated. Only those compounds that may be isolated in analytical amounts are considered in the delineation of the reaction pathway. The only volatile product that has been observed is ben-

zene: the formation of benzene presumably does not involve reaction with DMG but rather results from the pyrolysis of the rhodium compound.

Two major products are triphenylphosphine and triphenylphosphine oxide. The formation of triphenylphosphine may be the result of dissociation of Wilkinson's salt.¹⁵ The formation of Ph_3PO could be due to (i) aerial oxidation of phosphine ligands to the metal atom rhodium¹⁷ or (ii) the abstraction of an oxygen atom of the ester moiety from DMG by liberated Ph_3P .¹⁸ The production of triphenylphosphine oxide may occur by either or both of these routes or by other pathways. Extrapolation of this argument would mean that other phosphorus ligands attached to the metal atom should be able to abstract oxygen from the ester moiety or be subject to aerial oxidation.

Six rhodium-containing compounds have been isolated from the experiment of $\text{RhCl}(\text{PPh}_3)_3$ and DMG. These are shown below:



Structures of all these compounds are based $^1\text{H-NMR}$ and $^{31}\text{P-NMR}$, infrared analysis, and elemental analysis. The proton NMR spectra were assigned following Landgrebe.¹⁹ The chemical shift of a methyl attached to rhodium is 0.3 ppm.²⁰ The infrared spectra of rhodium carbonyl and carboxyl species show the carbonyl stretching frequency in the range $1620\text{--}1720\text{ cm}^{-1}$.^{21,22} The P—O stretching vibration occurs in the range $1200\text{--}1300\text{ cm}^{-1}$,³ while the P—Cl stretching frequency in OPPh_2Cl occurs at 521 cm^{-1} . The $^{31}\text{P-NMR}$ spectra of $\text{ClRh}(\text{PPh}_3)_3$ shows peaks at 24.6, 32.0, and 50.2 ppm.²⁴ The first two are assigned to the two phosphines that are trans to each other; the peak at 50.2 is assigned to the phosphine trans to the chlorine. It is clear that the phosphine experiences a downfield shift upon coordination and a larger downfield shift when trans to an electronegative substituent. This data allows the assignment and structural characterization of all of the compounds isolated from the reaction.

Compound 1. The proton resonance at 1.3 ppm is attributed to the center ring CH_2 and 2.1 ppm is attributed to the CH_2 adjacent to the carbonyl. The infrared bands at 1651 , 1224 , and 515 cm^{-1} may be attributed to the carbonyl,

the P—O stretch, and the P—Cl stretch, respectively. The ^{31}P -NMR spectrum shows two peaks at 64.5 and 45.5 ppm. All compounds which contain the OPPh_2Cl group show a resonance near 45 ppm; this then must be attributable to that moiety. The OPPh_3 must be assigned to 64.5 ppm; it is shifted downfield, relative to the parent Wilkinson's salt, both because of the trans chloride and the presence of a phosphine oxide rather than a phosphine. The resonance for OPPh_2Cl is only a little shifted from the position of the free ligand. These data all lead to the structure depicted above.

Compound 2. The proton resonance at 0.1 ppm may be attributed to the methyl on rhodium, all other spectral data are quite similar to that of compound 1. The ^{31}P resonance is at 47.0 ppm, in the range observed for OPPh_2Cl in all other compounds.

Compound 3. The proton resonance at 1.0 ppm may be assigned to the methylenes attached to rhodium; the resonance at 1.3 ppm corresponds to the inner methylene. The infrared spectrum shows no carbonyl or P—O vibrations but does show P—Cl at 515 cm^{-1} . The ^{31}P -NMR spectrum shows only resonance at 29.7 ppm, this must be attributed to the chlorodiphenylphosphine. Free chlorodiphenylphosphine appears at 80 ppm; this indicates a great downfield shift upon coordination and may be attributed to the presence of the rhodacycle.

Compound 4. The two aliphatic proton resonances may be assigned to the two methyl groups in the structure. The infrared spectrum indicates both carbonyl and P—O vibrations. Not enough sample was available for a ^{31}P -NMR spectrum.

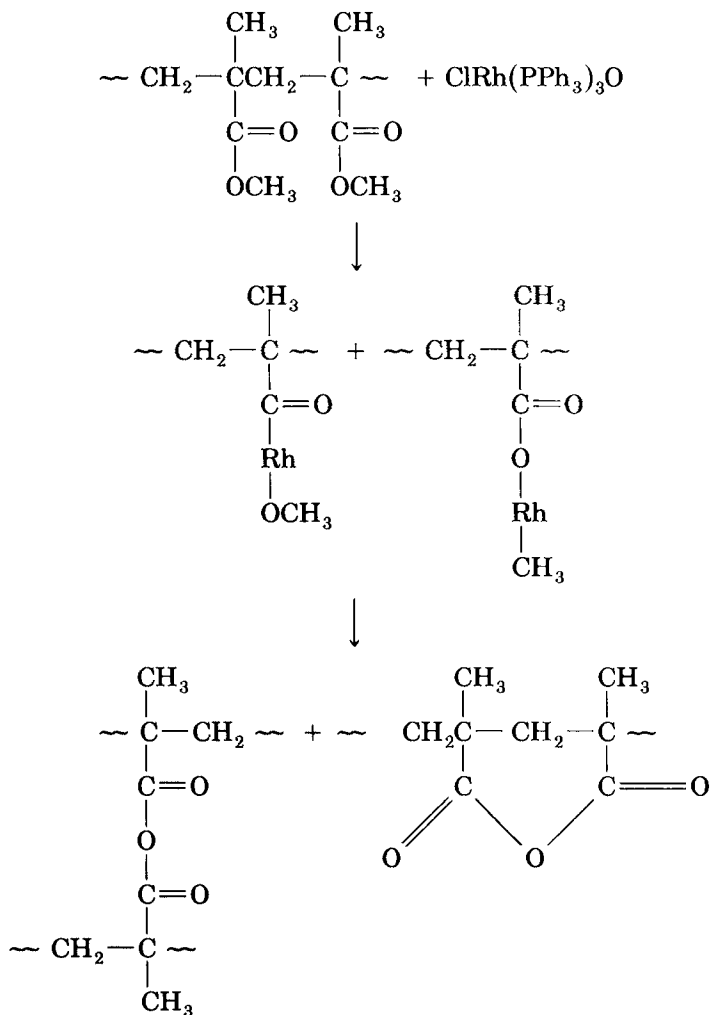
Compound 5. All of the proton resonances and IR data may be assigned in the same manner as above. The ^{31}P -NMR shows only a peak at 47.5 ppm, a region that is consistently observed for OPPh_2Cl .

Compound 6. Assignments follow from the above data. The two ^{31}P resonances, 50.3 and 63.5 ppm, may be assigned to the inequivalent OPPh_2Cl groups. These are shifted downfield from the usual 46 ppm because they are trans to methoxide.

Based upon the structures of these compounds 1–6, it seems most likely that the initial step in the reaction is oxidative addition into some bond of the DMG molecule. Oxidative addition to alkyl and acyl halides is well known for Rh^+ species,²⁵ and there are reports of oxidative addition to formate esters.^{26,27} Such oxidative additions no doubt occur into a carbon—oxygen bond of the DMG and subsequent reactions lead to the observed products. The subsequent reactions include ligand exchange as well as other reactions. Compounds 1, 2, and 5 involve an insertion into the carbonyl—oxygen bond, giving an intermediate in which an acyl and a methoxy are initially bound to the rhodium. If this is then followed by a ligand exchange, the ring may be formed with the transfer of methoxy to another rhodium. Compounds 4 and 6 are the species to which methyl and methoxy have been transferred. No easy route to compound 3 is obvious. It also should be noted that the only products shown here arise from insertion into the carbonyl—oxygen bond, thus liberating a methoxy for ligation. In compounds 2, 5, and 6, the presence of methyl ligands may perhaps indicate that some of the minor products that have not been isolated here involve insertion into the O— CH_3 bond and ligand exchange from these produces these products. The presence of phosphine oxides, rather than simple phosphines, may be attributed to the ease of air oxidation of

these phosphines.¹⁸ It is not clear why chlorophosphines are produced in the reaction; the phenyls that are replaced by chloride probably show up as benzene, which is found among the volatiles in the reaction.

Mechanism for the Formation of Char from PMMA. The results of the DMG reaction may now be used to explain the reaction of Wilkinson's salt with PMMA. About 60% of the product isolated from the reaction between PMMA and Wilkinson's salt is insoluble in routine solvents and is identified as char. Solid state ¹³C-NMR and IR spectra of this char reveal the presence of anhydride linkages¹³ as well as esters. A mechanism similar to that proposed for the dimethylglutarate model compound would require an initial oxidative addition into a C—O bond of the polymer. Since there are two C—O bonds, carbonyl—O, and O—CH₃, both may be utilized as in DMG. A simple elimination of the rhodium methyl and rhodium methoxide species may then occur. This process leads to both interchain and intrachain anhydride formation. A schematic is shown below (Scheme 1):



A close examination of this mechanism indicates that whenever rhodium-inserted moieties are adjacent to each other, elimination may occur with the

formation of the anhydride. This allows both intrachain anhydride formation, if moieties in the same chain should be adjacent, as well as interchain anhydride formation, should the rhodium-inserted species be from different chains. It is also expected that not all of the rhodium will be eliminated, since it is unreasonable to expect that all of these species will necessarily encounter a partner for the elimination reaction to proceed. In agreement with this, the char does contain rhodium. Also the char contains the starting ester, this indicates that not all of the starting ester moieties undergo the insertion reaction. The insertion into the C—O bond also requires that either a methyl or methoxy be a ligand to the rhodium; among the soluble portions of the reaction mixture there are several rhodium compounds in which methyl and/or methoxy is observed, by NMR spectroscopy, ligated to the metal. The exact identity of these materials has not been completely probed; however, HPLC analysis shows the presence of materials with retention times identical to those of **4** and **6** above in the reaction of $\text{ClRh}(\text{PPh}_3)_3$ and PMMA. The presence of anhydrides in the PMMA reaction and their absence in the DMG reaction must be explained. In the DMG system, we assume that the free rotation that is allowed in that molecule renders ligand exchange a more likely reaction than in the PMMA system. In the latter case, elimination of the rhodium species with concomitant formation of anhydride seems to be the preferred pathway.

Char formation has previously been observed for PMMA upon reaction with ammonium polyphosphate.²⁸ In that work, a variety of volatile products were produced; these include methanol, carbon monoxide, dimethyl ether, carbon dioxide, and hydrocarbons. In both the work of Camino et al.²⁸ and this work, the stabilization of the PMMA occurs as a result of anhydride formation. In that work it is stated that the anhydrides that are produced inhibit chain depolymerization reactions and allow other reactions to proceed. Mechanistically the reactions are quite different, Camino et. al.²⁸ suggest that the reaction produces a copolymer of methacrylic acid and methyl methacrylate. This copolymer is known to eliminate methanol in a cyclization reaction involving adjacent ester and acid units.

CONCLUSION

The efficacy of Wilkinson's salt as a flame retardant for PMMA may be attributed to the ability of this rhodium compound to oxidatively insert into a carbon—oxygen bond of the polymer. While this material is a poor choice for a flame retardant, due to problems with cost, color, and toxicity, the results of this study may lead the way to the discovery of materials that function by a similar process without these limitations. Materials that may be suitable as PMMA flame retardants by a mechanism such as this would have to undergo an oxidative insertion into a C—O bond, leading to a bond from the additive to methyl or methoxy. We are actively engaged in the search for such species.

EXPERIMENTAL

Pyrolysis reactions were performed in vessels with a volume of about 80 cm^3 . These were thoroughly evacuated on the high vacuum line for about 12 h, then loaded with 0.50 g of Wilkinson's salt (Aldrich) and 1.0 g of the polymer

(PMMA), both of which were obtained from Aldrich Chemical Co. The vessel was then thoroughly evacuated for at least 12 h before it was sealed off from the vacuum line. The vessel was heated in a muffle furnace at 260°C for 2 h. The oven was turned off, the vessel allowed to cool to room temperature and then removed from the oven and cooled in liquid nitrogen. *Vessels have been known to explode from gas pressure. Caution must be used in these manipulations.* The tube was then opened and attempts were made to dissolve the product in solvents such as chloroform, acetone, tetrahydrofuran, etc. Only 40% of the crude product was soluble.

Some vessels were equipped with a break-seal; these were reattached to the vacuum line, the break-seal was broken, and the gases present in the sample were determined by PVT measurements and identified by infrared spectroscopy. The reaction vessel was then removed from the vacuum line and treated as above.

A 0.27 g sample of $\text{ClRh}(\text{PPh}_3)_3$ was placed in a standard reaction vessel and heated to 180°C for 2 h. Upon opening the vessel, the contents (0.25 g) were removed. The weight loss is due both to the formulation of volatile materials and the inherent difficulty of removing all of the material from a tube after a pyrolysis reaction. TLC analysis of the products showed conclusively the absence of biphenyl and the presence of Ph_3P , Ph_3PO , and another compound. Identical results were obtained at 260°C . The phosphorus compounds and the unknown compound were isolated by flask chromatography,²⁹ with 3% ethanol in chloroform as the solvent. The phosphorus compounds were identified by NMR, IR, and mixed melting point. The NMR spectrum of the unknown showed only resonance in the aromatic region; elemental analysis yields the formula $\text{Rh}_2\text{Cl}_3\text{P}_5\text{C}_{90}\text{H}_{97}\text{O}_{20}$. The presence of oxygen in the compound results from the fact that the workup was conducted entirely in air; both phosphine oxides and water of hydration are observed.

In a separate experiment, a 0.54 g sample of $\text{ClRh}(\text{PPh}_3)_3$ was thermolyzed for 2 h in a vessel equipped with a break-seal. When the vessel was opened on the vacuum line, no noncondensable gas could be detected. A total of 1.1 mmol of condensable gas was produced and identified as benzene by IR spectroscopy.

In another experiment, 1.0 g PMMA and 0.50 g $\text{ClRh}(\text{PPh}_3)_3$ were thermolyzed at 260°C for 2 h in a vessel equipped with a break-seal. Upon opening the break-seal on the vacuum line, no noncondensable gases were detected. The only gas produced in the reaction was benzene; 1.3 mmol was determined by PVT measurements and identified by IR spectroscopy. The vessel was removed from the vacuum line and chloroform was added to the tube and the sample filtered. The mass of insoluble material was 1.14 g. This material was heated on the vacuum line at 150°C for 1 h and 0.34 g of chloroform was obtained, identified by IR spectroscopy. Infrared analysis of the insoluble material showed bands at 1805, 1760, 1730, and 1016 cm^{-1} , indicative of anhydride formation and the retention of some ester functionality. Analysis of these insolubles by emission spectroscopy showed the presence of rhodium. The soluble portion (0.56 g) was analyzed by NMR. Resonances at 0.1 and 1.6 ppm were observed; this indicates methyl and methoxy groups on rhodium. HPLC analysis of the soluble fraction gave retention times identical to those of compounds **4** and **6** from the DMG reaction. GPC analysis of the soluble portion shows that the molecular weight is identical with that of starting

material. The vessel was initially charged with 1.50 g of material; 1.46 g was recovered, which includes 0.1 g benzene, 0.80 g insolubles, and 0.56 g solubles. The small weight loss is probably due to the difficulty of removing all of the material from the reaction vessel.

The reaction of DMG and Wilkinson's salt was also studied at 260°C. A 1.0 g sample of $\text{ClRh}(\text{PPh}_3)_3$ (1.1 mmol) was combined with 0.17 g DMG (1.1 mmol) in a vessel equipped with a break-seal and heated for 2 h. No noncondensable gases were found upon opening the vessel on the vacuum line. The condensable gas, 0.2 mmol, was identified as benzene by infrared spectroscopy. The vessel was removed from the vacuum line, and the sample was dissolved and subjected to column chromatography, the solvents used for isolation are indicated below: The materials that were recovered are: compound 1, 48 mg; compound 2, 52 mg; compound 3, 20 mg; compound 4, 19 mg; compound 5, 52 mg; and compound 6, 11 mg. The purity of each fraction was tested by HPLC (Waters Associates, Model M-6000A), the solvent system used was a chloroform/methanol mixture on an Alltech Silica Preparatory column¹⁰ and a UV detector (Waters Lambda-Max Model 481) was employed.

Compound 1 was isolated using 50% ether in chloroform. $^1\text{H-NMR}$: 1.3 (2 H), 2.1 (4 H), 7.1–7.8 ppm (25 H). $^{31}\text{P-NMR}$: 45.5, 64.5 ppm. IR: 1651, 1216, 515 cm^{-1} .

ELEMENTAL ANAL.: Calcd for $\text{RhCl}_3\text{P}_2\text{C}_{35}\text{H}_{31}\text{O}_4$: Rh, 12.5%; Cl, 13.02%; P, 7.5%; C, 52.8%; H, 4.37%. Found: Rh, 12.04%; Cl, 13.46%; P, 7.29%; C, 51.51%; H, 4.1%.

Compound 2 was isolated using 40% EtOH in ether. $^1\text{H-NMR}$: 0.1 (3 H), 1.2 (2 H), 2.1 (4 H), 7.2–7.8 ppm (20 H). $^{31}\text{P-NMR}$: 47.0 ppm. IR: 1651, 1216, 515 cm^{-1} .

ELEMENTAL ANAL.: Calcd for $\text{RhCl}_2\text{P}_2\text{C}_{29}\text{H}_{26}\text{O}_4$: Rh, 15.2%; Cl, 10.5%; P, 9.1%; C, 51.6%; H, 3.8%. Found: Rh, 14.3%; Cl, 11.2%; P, 8.98%; C, 52.17%; H, 4.06%.

Compound 3 was isolated using 50% petroleum ether in ether. $^1\text{H-NMR}$: 1.0 (8 H), 1.3 (4 H), 7.0–7.6 ppm (20 H). $^{31}\text{P-NMR}$: 29.7 ppm. IR: 515 cm^{-1} , no $\text{C}=\text{O}$, no $\text{P}-\text{O}$.

ELEMENTAL ANAL.: Calcd for $\text{RhCl}_2\text{P}_2\text{C}_{30}\text{H}_{32}$: Cl, 11.3%; C, 57.3%; H, 5.09%. Found: Cl, 11.07%; C, 58.02%; H, 5.00%.

Compound 4 was isolated using 5% EtOH in chloroform. $^1\text{H-NMR}$: 1.6 (3 H), 1.8 (3 H), 7–7.6 ppm (15 H). IR: 1633, 1219 cm^{-1} , no $\text{P}-\text{Cl}$.

ELEMENTAL ANAL.: Calcd for $\text{RhCl}_2\text{P}_2\text{C}_{31}\text{H}_{32}\text{O}_4$: Rh, 14.6%; Cl, 10.1%; P, 8.8%; C, 52.8%; H, 4.5%. Found: Rh, 11.88%; Cl, 10.23%; P, 8.86%; C, 52.11%; H, 4.07%.

Compound 5 was isolated using 30% ethanol in ether. $^1\text{H-NMR}$: 0.1 (6 H), 1.3 (2 H), 2.1 (4 H), 7.2–7.6 ppm (20 H). $^{31}\text{P-NMR}$: 47.5 ppm. IR: 1704, 1224, 520 cm^{-1} .

ELEMENTAL ANAL.: Found: Rh, 11.88%; Cl, 10.23%; P, 8.86%; C, 52.11%; H, 4.07%. Calcd for $\text{RhCl}_2\text{P}_2\text{C}_{31}\text{H}_{32}\text{O}_4$: Rh, 14.6%; Cl, 10.1%; P, 8.8%; C, 52.8%; H, 4.5%.

Compound 6 was isolated using 10% EtOH in ether. $^1\text{H-NMR}$: 0.1 (6 H), 1.8 (6 H), 7–7.6 ppm (20 H). $^{31}\text{P-NMR}$: 50.3, 63.5 ppm. IR: 1190, 515, cm^{-1} , no $\text{C}=\text{O}$ absorption.

ELEMENTAL ANAL.: Calcd for $\text{RhCl}_2\text{P}_2\text{C}_{28}\text{H}_{32}\text{O}_4$: Cl, 10.6%; C, 50.2%; H, 4.79%. Found: Cl, 9.8%; C, 49.89%; H, 4.94%.

^1H -NMR spectra were obtained on an EM 360L spectrometer. ^{31}P -NMR spectra were obtained on a Bruker system. IR spectra were obtained on a Analect FX-6200 FT-IR spectrometer.

Chromatograms of products obtained in the case of PMMA were matched with the chromatograms of the individual products of DMG by the use of a solvent programmer (Waters Associates Model 660). An analytical Alltech Silica Column ($5\ \mu\text{m}$) was used for this purpose. Elemental analysis on the samples were performed by Schwartzkopf Laboratories, New York.

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