

Isolation and Characterization of Reactive Intermediates and Active Catalysts in Homogeneous Catalysis

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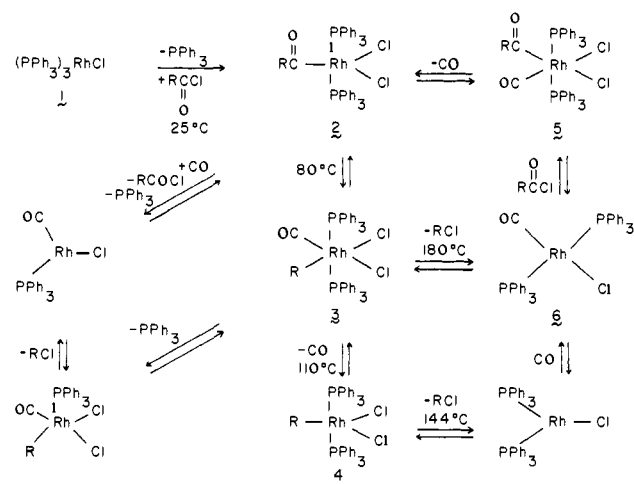
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Abstract: A new method has been developed for the isolation and characterization of highly reactive intermediates and of active catalysts in homogeneous catalysis by transition-metal complexes. Using the principles of steric exclusion type chromatography, a method has been devised for the isolation of highly reactive intermediates on the surface of porous polymer films. Analysis of these surface-isolated intermediates by X-ray photoelectron spectroscopy (ESCA) provided detailed information about the transition-metal complexes that resided on the surface of the polymer film. The utility of this process was demonstrated by a reanalysis of the decarbonylation of acid chlorides using chlorotris(triphenylphosphine)rhodium(I) (Wilkinson's catalyst). Through the utilization of the concepts and techniques described above, the active catalytic intermediate involved in the metathesis-promoted polymerization of cyclopentene to polypentenamer by oxotetrachlorotungsten-ethylaluminum dichloride was isolated on the surface of porous polystyrene film. This technique was viable because the active catalyst had to be attached to the end of the growing polymer chain. Analysis of the surface-isolated catalyst by X-ray photoelectron spectroscopy showed a ratio of W:O:Al:Cl of 1:1:1:4-5. The tungsten showed a binding energy of 36.0 and 38.2 eV [W(4f_{7/2}) and W(4f_{5/2}), respectively]. This intermediate species was very labile. On treatment with trimethylphosphine, this catalyst was converted into a new tungsten complex (nonspecific) that showed binding energies of 34.0 and 36.2 eV for W(4f_{7/2}) and W(4f_{5/2}), respectively. These values can be compared to values of 34.1 and 36.3 eV for Schrock's stable tungsten-alkylidene complex, W(O)(CHCMe₂)Cl₂(PEt₃)₂.

A major problem associated with the study of catalytic processes is the difficulty of determining the nature of reactive intermediates or of the "active" catalyst. Often, when a catalyst is added to a reaction mixture, the experimentalist has little knowledge as to whether the bulk of the added material is the catalyst, whether only a trace amount of the added accelerator is the active catalyst, or whether all or part of the added material is converted to a new material that is the active catalyst.² This problem is particularly acute in homogeneous catalysis by transition-metal complexes, where the active catalytic intermediate is often extremely unstable and highly reactive.³ This report outlines a method for the selective isolation and characterization of the "active" catalyst in certain homogeneous catalytic processes.

We have developed a single probe that achieves both rapid isolation and purification of an active catalytic intermediate. This probe consists of a small, thin aluminum sheet that is coated with a porous polystyrene (or other polymeric) film. The underlying principle was to use this film as a unidirectional steric exclusion type chromatograph⁴ where the direction of the solvent travel is from the surface of the film toward the surface of the aluminum chip. Those molecules in the reaction mixture that have large appendages in the form of macromolecular ligands would be retained on the surface of the film, while the capillary action of the reaction solvent would carry any *small* precatalyst molecules, *low molecular weight* organic substrates, and *small* product molecules into the interior of the film. Analysis of the material on the surface of the film (typically <50 μg) was performed by X-ray photoelectron spectroscopy (ESCA),⁵ which provided in-

Scheme I



formation on what elements were present, the approximate oxidation state of the composite elements, and an insight into the nature of any attached ligands.

In order to demonstrate that our conceptual approach to the isolation and characterization⁶ of reactive intermediates was feasible, we chose to test our methods on a process that other workers had studied in detail in order to demonstrate the advantages of our approach. In addition, we sought to examine a reaction in which the intermediates had reasonable stability. Such a reaction was the decarbonylation of organic acid chlorides by chlorotris(triphenylphosphine)rhodium(I) (Wilkinson's catalyst; 1).

Scheme I illustrates much of what has been presented in terms of mechanistic speculation concerning the details of this decarbonylation reaction. Intermediates 2-6 have been isolated by

(1) Graduate School Dissertation Fellow, University of Minnesota, 1979-1980; SOhio Fellow, 1980-1981.

(2) Kinetic studies carried out in our laboratory on a wide variety of catalytic processes indicated that ca. 75% of those studied had induction periods. Thus, for those reactions with induction periods, it is likely that the transition-metal complexes that were added were "precatalysts". An alternate possibility, which must be considered for certain cases, is that the reaction mixture contained an inhibitor which had to be destroyed (or used up) prior to the start of the desired catalytic process.

(3) These properties may be due to a rapid rate of spontaneous decomposition, oxygen sensitivity, water sensitivity, thermal sensitivity, or a combination of these factors. Additional problems were associated with active catalysts that are formed after *variable* induction periods, present in only trace amounts, and extremely short-lived.

(4) For the use of polymer membranes in the separation of metal complexes containing macromolecular ligands, see: Gosser, L. W.; Knoth, W. H.; Parshall, G. W. *J. Mol. Catal.* 1977, 2, 253. Bayer, E.; Schurig, V. *Angew. Chem., Int. Ed. Engl.* 1975, 14, 493.

(5) We have constructed an efficient drybox onto one of the ports of our Physical Electronics, Inc. Auger-ESCA-SIMS spectrometer. This was equipped with a series of pressure locks that permitted us to go from the atmospheric pressure of the drybox to the 10⁻⁹ mm of the spectrometer without exposure to oxygen or moisture. With this apparatus, a reaction mixture can be probed and a preliminary ESCA measurement made in less than 30 min.

(6) We stress at this point that we do not fully understand all of the details involved in the separations which occur on the "porous" polystyrene films that have been swollen by the solvents (benzene, toluene, or chlorobenzene) used in our experiments.

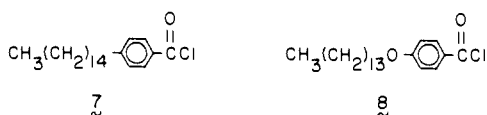
Table I. Binding Energies (eV) of Rhodium Derivatives Studied by ESCA^a

compd	Rh(3d _{5/2})	Cl(2p _{3/2})	P(2p)
A. PPh ₃ Derivatives			
(PPh ₃) ₃ RhCl (1)	307.2	197.8	131.0
[(PPh ₃) ₂ RhCl] ₂	307.3	198.5	131.2
(PPh ₃) ₂ (CO)RhCl (6) ^b	308.2	197.8	131.0
B. Derivatives 2a,b , 3a,b , and 4a,b ^c			
2a	309.2	197.7	131.1
3a	309.6	198.0	131.2
4a	309.0	197.8	131.0
2b	308.9	197.5	131.0
3b	309.4	197.8	131.2
4b	308.6	197.7	130.9
C. Derivatives 2c,d , 3c,d , and 4c,d ^c			
2c	309.2	197.7	131.1
3c	309.6	198.0	131.2
4c	309.0	197.8	131.0
2d	308.9	197.5	131.0
3d	309.4	197.8	131.2
4d	308.6	197.7	130.9
D. Derivatives 4c,d ^c Heated to 180 °C			
4c	<i>d</i>	197.6	<i>e</i>
4d	<i>d</i>	197.5	<i>e</i>

^aAll values are calibrated vs. C(1s) (284.6 eV) and are reproducible to ±0.1 eV. ^bThe O(1s) binding energy for **6** was 532.6 eV. ^c**a**, C₆H₅; **b**, 4-CH₃OC₆H₄; **c**, 4-*n*-C₁₅H₃₁C₆H₄; **d**, 4-*n*-C₁₄H₂₉OC₆H₄. ^dNo rhodium was detectable. ^eNo phosphorus was detectable.

various groups⁷⁻¹² and characterized by classical methods after tedious purification. We have repeated the literature preparations and produced pure samples of **2**, **3**, and **4**¹³ where (a) R = C₆H₅ and (b) R = 4-CH₃OC₆H₄. Table IA lists the binding energies for a series of rhodium derivatives for comparison purposes. Table IB lists the binding energies of the relative atoms of the authentic samples that we prepared by the literature methods and isolated by classical techniques. The samples examined in parts A and B of Table I were mounted on polyethylene film and all data were calibrated vs. the C(1s) binding energy. In this way, binding energies could be routinely reproduced on various samples by different workers on different instruments, since shifts due to variance in sample charging were minimized by correcting for sample charging to the same reference.

To test of our technique, we synthesized 4-*n*-pentadecylbenzoyl chloride (**7**) and 4-*n*-tetradecyloxybenzoyl chloride (**8**).¹⁴ These



(7) Blum, J. *Tetrahedron Lett.* **1966**, 1605. Blum, J.; Oppenheimer, E.; Bergmann, E. D. *J. Am. Chem. Soc.* **1967**, *89*, 2338. Blum, J.; Kraus, S.; Pickholtz, Y. *J. Organomet. Chem.* **1971**, *33*, 227.

(8) Tsuji, J.; Ohno, K. *J. Am. Chem. Soc.* **1966**, *88*, 3452. Tsuji, J.; Ohno, K. *Tetrahedron Lett.* **1966**, 4713. Tsuji, J.; Ohno, K. *J. Am. Chem. Soc.* **1968**, *90*, 99.

(9) Stille, J. K.; Regan, M. T.; Fries, R. W.; Huang, F.; McCarley, T. "Homogeneous Catalysis-II"; Foster, D., Roth, J. F., Eds.; American Chemical Society: Washington, DC, 1974; Adv. Chem. Ser. No. 132. Stille, J. K.; Regan, M. T. *J. Am. Chem. Soc.* **1974**, *96*, 1508. Stille, J. K.; Fries, R. W. *Ibid.* **1974**, *96*, 1514. Stille, J. K.; Huang, R.; Regan, M. T. *Ibid.* **1974**, *96*, 1518.

(10) Kampmeier, J. A.; Rodehorst, R. M.; Philip, J. B., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 1847. See also: Kampmeier, J. A.; Harris, S. H.; Mergelsberg, I. *J. Org. Chem.* **1984**, *49*, 621.

(11) Baird, M. C.; Mague, J. T.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 1347.

(12) Chatt and Shaw (Chatt, J.; Shaw, J. *J. Chem. Soc. A* **1966**, 1437) have isolated a closely related version of **5** in which two of the phenyl groups on each of the phosphines have been replaced by ethyl groups.

(13) Using a stoichiometric amount of **1**, we obtained 50% of **2a** and 52% of **2b** after 3 min at 30 °C. Heating of **2a** and **2b** to 80 °C for 30 min gave 63% of **3a** and 65% of **3b**. Heating of **3a** and **3b** at 80 °C for 18 h gave 65% of **4a** and 57% of **4b**. These yields are of purified material that had been chromatographed. Spectral data were identical with those that were available in the literature.⁷⁻¹¹

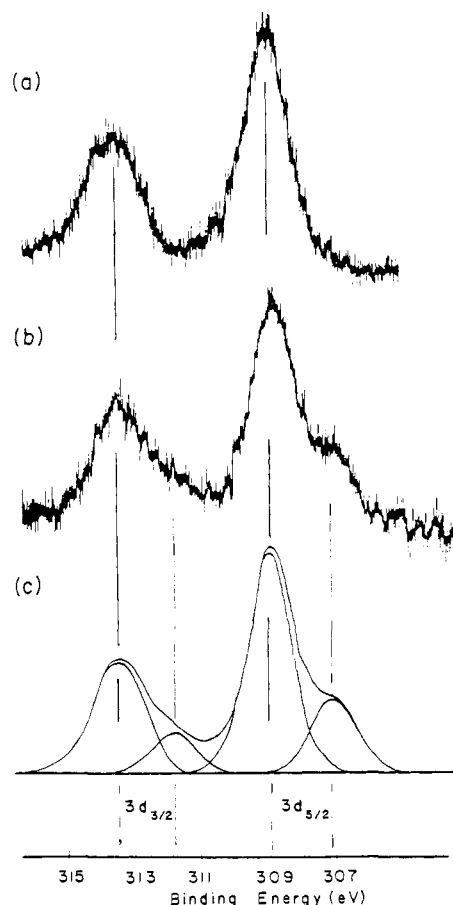


Figure 1. (a) ESCA spectrum of a mixture of **2c** and **1** resulting from the reaction of **7** with excess **1** and sampled on polystyrene film. (b) ESCA spectrum of a mixture of **2c** and **1** resulting from the reaction of **7** with excess **1** and sampled on polyethylene film. (c) Deconvolution of curve b into the two components **2c** and **1**.

compounds were treated with **1** for the same times and at the same temperatures as were used to prepare **2-4**. However, instead of classical isolation techniques being used, a polystyrene-coated probe was dipped into the reaction mixture and immediately removed, and the solvent was pumped off under reduced pressure. ESCA of the surface of the film gave the values listed in Table IC. The values obtained by this rapid method for **2c**, **3c**, and **4c** were identical with those of **2a**, **3a**, and **4a**. Similarly, the values obtained for **2d**, **3d**, and **4d** were identical with those of **2b**, **3b**, and **4b**. This demonstrated the utility of our technique for the rapid isolation, purification, and partial characterization of organometallic intermediates.

Several additional features of this study merit comment. When an excess of **1** was used with **7**, ESCA revealed only **2c** on the surface of the polystyrene film. However, if a relatively nonporous polyethylene film was used, both **2c** and **1** could be observed by ESCA. This is illustrated in Figure 1. In general, on relatively nonporous, nonswellable films, such as polyethylene, all of the species present in 10% or greater concentration could be detected. In contrast, with swellable films, such as polystyrene, only those species with large ligands remained on the surface when solvents such as benzene, chlorobenzene, and toluene were used. The results obtained with a mixture of **1** and **2c** on polystyrene point up a special phenomenon which we do not currently understand. In the reaction of **1** with **7** to form **2c**, a triphenylphosphine ligand (*M_r* = 262) was lost while chlorine and the 4-*n*-pentadecylbenzoyl

(14) The acid chloride **7** showed Cl(2p_{3/2}) and O(1s) binding energies of 200.0 and 532.0 eV, respectively. The acid chloride **8** showed Cl(2p_{3/2}) at 200.2 eV and O(1s) binding energies at 532.9 and 531.7 eV for the two different oxygens.

Table II. Binding Energies (eV) of Tungsten Derivatives

compd	W(4f _{7/2}) ^a	W(4f _{5/2}) ^a
Part A ^b		
WOCl ₄	37.0	39.2
WO ₂ Cl ₂	36.9	39.1
WCl ₆	36.4	38.5
WO ₃	36.3	38.5
WO(O- <i>t</i> -Bu) ₄	36.0	38.1
WCl ₅	35.9	37.9
WCl ₃ (OC ₂ H ₅) ₂	35.3	37.3
WOCl ₃ (PEt ₃) ₂	34.8	36.9
WCl ₄	34.7	36.9
WCl ₄ [P(C ₆ H ₅) ₃] ₂	33.5	35.7
WO ₂	33.2	35.4
Part B ^b		
WOCl ₄ + 2EtAlCl ₂	36.0	38.2
WOCl ₄ + 2EtAlCl ₂ after 45-min X-ray exposure	34.5, 35.5	36.7, 37.7
WOCl ₄ + 2EtAlCl ₂ after 24 h	34.5, 35.5	36.7, 37.7
WOCl ₄ + 2EtAlCl ₂ + air	36.2	38.4
WOCl ₄ + 2EtAlCl ₂ + 4P(CH ₃) ₃	34.0	36.2
Part C ^c		
WOCl ₄ + 2EtAlCl ₂ + cyclopentene (30 min) (9)	36.0	38.2
9 after 24 h	34.5, 35.5	36.7, 37.7
9 after 45-min exposure to X-ray	34.5, 35.5	36.7, 37.7
9 immediately after exposure to O ₂	36.2	38.5
9 after treatment with excess P(CH ₃) ₃	34.0	36.2
Part D ^b		
WO[CHC(CH ₃) ₃]Cl ₂ (PEt ₃) ₂ (10)	34.1	36.3
WO[CHC(CH ₃) ₃]Cl ₂ (PEt ₃) ₂ ^d	34.4	36.5
WO[CHC(CH ₃) ₃]Cl(PEt ₃) ₂ +EtAlCl ₃ ⁻	34.7	36.8
Part E ^c		
10 + 1EtAlCl ₂ + cyclopentene	34.9	37.0

^aAll values are calibrated against the C(1s) binding energy of the polymer film and are reproducible to ± 0.1 eV. ^bSamples mounted on polyethylene. ^cSamples collected on polystyrene. ^dPrepared through the reaction of 10 with bis(benzonitrile)palladium chloride.²⁰

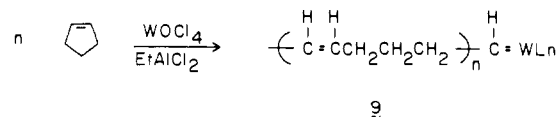
ligand ($M_r = 350.5$) were added. Thus, the overall molecular weights of 1 and 2c differ very little. However, on polystyrene film, 2c remains on the surface of the film while 1 is not detected on the surface even when 1 is known to be present in concentrations that would be easily detected if it were on the surface of the film. This would appear to indicate that the C₁₅-alkyl chain provided a property to the rhodium complex 2c that helped to maintain it on the surface of the film. Whether this was due to the extended nature of the chain or whether there exists an attractive force between the C₁₅-alkyl chain and the surface of the film is not known at this time and will be the subject of future study.

The same complex phenomenon noted above also appeared to be involved in additional experiments that were carried out with the rhodium complexes. When a solution of 4c or 4d was heated to 180 °C and then analyzed with our probe system, the surface showed no rhodium or phosphorus but did show chloride (Table ID). This indicated that the chlorine was attached to a long-chain species but that none of the rhodium catalyst was attached to the chain after heating to 180 °C. Here again, the rhodium complexes that were present in solution were carried into the swollen polymer film. The presence of organic chloride on the surface attested to the retention of the long alkyl chain substituted aromatic halide on the surface. This observation is interesting in view of recent discussions of the mechanism of decarbonylation of acid chlorides by Wilkinson's catalyst.⁷⁻¹⁰

Having demonstrated the feasibility of using a porous polymer film for the isolation of transition-metal complexes in the example outlined above, we turned our attention to a more complex reaction where less definitive evidence exists for the mechanistic detail. This new study involved the details of the mechanism of olefin metathesis. Although extensive circumstantial evidence exists for the intermediacy of metal-carbene complexes and metallocyclobutanes in the olefin metathesis reaction,¹⁵ such intermediates have

not been isolated from metathesis reactions where metal-carbene complexes have not been added as initiators.^{16,17} Because of our interest in this important and mechanistically intriguing reaction, we have applied the techniques outlined above for the isolation and characterization of active catalytic species to the olefin metathesis reaction. In particular, we attempted the isolation of a highly reactive intermediate from the metathesis of olefins in the presence of oxotetrachlorotungsten-ethylaluminum dichloride.

Our described technique for the isolation of metal complexes with attached macromolecular ligands on the surface of polymer films through a type of "steric exclusion" chromatography appeared ideally suited to the study of olefin metathesis. It is well established that cyclopentene reacts with a variety of olefin metathesis catalysts (generally derivatives of molybdenum or tungsten) to yield polypentene.¹⁸ Since this is a "growing" or "living" polymer, the active metathesis catalyst must be attached to the end of the growing chain as represented by 9.¹⁹ This attached



polymer chain was chosen to serve as a macromolecular ligand that would retain the active catalyst on the surface of a porous polymer film. This material could then be analyzed by ESCA.

In order to establish a set of reference data for binding energies of tungsten derivatives, a series of known compounds were run on polyethylene film. The observed values for these compounds are listed in Table II, part A. In anticipation of data to be discussed below, it is of interest to compare tetrachlorotungsten with tetrachlorobis(triphenylphosphine)tungsten, where complexation of tetrachlorotungsten with two triphenylphosphine ligands resulted in a decrease in binding energy of the tungsten 4f electrons of 1.2 eV.

With reference data in hand, the oxotetrachlorotungsten-ethylaluminum dichloride catalyst system was examined. As shown in Table II, part B, treatment of oxotetrachlorotungsten with 2 equiv of ethylaluminum dichloride in benzene gave a highly reactive, relatively short-lived intermediate. Sampling of the material with a polyethylene-coated aluminum foil chip followed by ESCA showed the presence of a single tungsten species with binding energies for W(4f_{7/2}) = 36.0 eV and W(4f_{5/2}) = 38.2 eV. The solution containing this material rapidly metathesized 2-heptene to 2-butene and 5-decene. This material was readily destroyed by the X-ray bombardment used in the ESCA. After 45 min of exposure to the X-ray flux, the compound that was initially present was converted into two new compounds having binding energies of W(4f_{7/2}) = 34.5 and 35.5 eV and W(4f_{5/2}) = 36.7 and 37.7 eV. The initially formed complex was converted into these same two complexes on standing in solution. After 24 h, only the two compounds with binding energies of 34.5 and 35.5

(15) Banks, R. L.; Bailey, G. C. *Ind. Eng. Chem. Prod. Res. Dev.* **1964**, *3*, 170. Dixon, R. E. Belg. Pat. 633 483; *Chem. Abstr.* **1965**, *62*, P4446. For selected recent reviews, see: Mol, J. C.; Monlijn, J. A. *Adv. Catal.* **1975**, *24*, 131. Katz, T. J. *Adv. Organomet. Chem.* **1978**, *16*, 283. Grubbs, R. H. *Prog. Organomet. Chem.* **1978**, *2*, 1. Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449. Haines, R. J.; Leigh, G. J. *Chem. Soc. Rev.* **1975**, *4*, 155. Hughes, W. B. *CHEMTECH* **1975**, 486. Hocks, L. *Bull. Soc. Chim. Fr.* **1975**, 1893. Banks, R. L. *Catal. Org. Synth.* **1978**, 233.

(16) For examples of exchange of the alkylidene portion of metal-carbene complexes, see: Burkhardt, T. J.; Casey, C. P. *J. Am. Chem. Soc.* **1973**, *95*, 5833. Burkhardt, T. J.; Casey, C. P. *Ibid.* **1974**, *96*, 7808. Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *Ibid.* **1978**, *100*, 3611. Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *Ibid.* **1979**, *101*, 5074. Lee, J. B.; Ott, K. C.; Grubbs, R. H. *Ibid.* **1982**, *104*, 7491.

(17) For an example of data gathered on a sample in solution, see: Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514. Osborn and co-workers have observed a reactive intermediate by NMR spectroscopy. However, this involved the initial addition of a tungsten-carbene complex to the reaction mixture.

(18) Natta, G.; Dall'Asta, G.; Mazzanti, G.; Mortoni, G. *Makromol. Chem.* **1963**, *69*, 163. Natta, G.; Dall'Asta, G.; Mazzanti, G. *Angew. Chem.* **1964**, *76*, 765. Natta, G.; Dall'Asta, G.; Bassi, I. W.; Carella, G. *Makromol. Chem.* **1966**, *91*, 87.

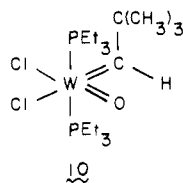
(19) Ln is used in structure 9 to represent undefined ligands.

eV were observed on sampling of the solution with the polyethylene-coated aluminum foil chip probe. As the first formed complex decreased in concentration and the two new components increased in concentration, the rate of metathesis of 2-heptene decreased. When the species having a binding energy of 36.0 eV had completely disappeared, the solution would no longer promote the metathesis of 2-heptene. Exposure to air of either the initially formed complex or the two new complexes formed from the initially formed complex resulted in the immediate conversion of all of these materials to a new material with $W(4f_{7/2}) = 36.2$ eV and $W(4f_{5/2}) = 38.4$ eV. This material was X-ray stable and did not change with time. We believe this material to be tungsten trioxide.

The major question that needs to be answered at this point is whether any of the materials isolated above are related to the active catalyst or whether the active catalyst is merely some minor component that is associated with the isolated materials but does not contribute significantly to the observed ESCA values. Through the use of a polystyrene-coated aluminum chip probe this question could be tested. When the solutions described above were probed with a polystyrene-coated aluminum chip, only trace amounts of tungsten could be detected (C:W ratio > 500:1). Thus, the tungsten species that were present in solution were not held on the surface of the polystyrene film. However, if the intermediates characterized above were the active species, they should remain on the polystyrene film surface if a large macromolecular ligand were attached, while, as demonstrated above, materials without a large ligand attached would not appear on the surface of the film.

When the metathesis reaction of cyclopentene, as illustrated above, was run and a polystyrene-coated aluminum chip was dipped into the solution, an intense tungsten concentration was shown to be present on the surface of the film by ESCA. This material had $W(4f_{7/2}) = 36.0$ eV and $W(4f_{5/2}) = 38.2$ eV. As shown in Table II, part C, its behavior in all respects was identical with the material characterized on polyethylene as part of the study documented in Table II, part B. However, it should again be stressed that the materials discussed in relation to part B were not retained on the surface of polystyrene. Thus, the ability to detect these materials when cyclopentene was the olefin would appear to be associated with the attachment of the tungsten species to the polypentenomer that was formed. As shown in Table II, part C, the isolated tungsten derivative decayed on standing and was rapidly decomposed by the Mg $K\alpha$ X-rays used in the ESCA measurements. It was instantly decomposed on exposure to oxygen. ESCA also indicated the presence of oxygen, aluminum, and chlorine. The approximate ratio of tungsten:oxygen:aluminum:chlorine was 1:1:1.4-5. It appeared that at least two types of chlorines were present. In addition, the oxygen content appeared to vary.

Schrock and co-workers have recently prepared the stable tungsten-carbene complex **10**.²⁰ This material showed binding



energies for tungsten of 34.1 and 36.3 eV [$W(4f_{7/2})$ and $W(4f_{5/2})$, respectively] as shown in Table II, part D.²¹ Since this tungsten-carbene complex showed binding energies quite different from those of our sample, it raised the question of the effect of the aluminum halide associated with our catalyst vs. the phosphine ligands associated with **10**. Presumably, the aluminum chloride either would be complexed through the oxygen or would be present

as a salt through removal of a chloride, while in **10**, the phosphines are associated with tungsten.²⁰ Treatment of our isolated intermediate with excess trimethylphosphine transformed **9** into a new material with tungsten binding energies of 34.0 and 36.2 eV (see Table II, parts B and C). These values were within experimental error (± 0.1 eV) of the values observed for Schrock's tungsten-carbene complex. In an attempt to assess the effect of the various ligands on the binding energy of **10**, we repeated the literature reaction of **10** with bis(benzonitrile)palladium dichloride.²⁰ This gave a pentacoordinate tungsten species (**10** minus PEt_3) with tungsten binding energies of 34.4 and 36.5 eV ($4f_{7/2}$ and $4f_{5/2}$, respectively). Thus, removal of one phosphine ligand resulted in ca. a 0.3-eV shift to higher binding energy. Recall that the addition of two triphenylphosphine ligands to tetrachlorotungsten resulted in a 1.2-eV shift to lower binding energy for a 0.6-eV shift per triphenylphosphine. In addition, we reacted **10** with ethylaluminum dichloride, which by analogy to the literature²⁰ should result in the removal of a chloride ion from **10** to produce a cationic tungsten species. Binding energies of 34.7 and 36.8 eV were obtained for this fairly unstable material.²² Thus, removal of a chloride (presuming correctness of the literature) resulted in an increase in binding energy for tungsten of 0.8 eV. It could be postulated that removal of both phosphines and a chloride from **10** would result in a material whose binding energy would be very similar to that of **9**.

In order to show that the material withdrawn from the polymerization of cyclopentene to polypentenomer still had active catalyst attached, a control reaction was run in which two identical probes were exposed to the reaction mixture;²³ both were treated identically except one was examined by ESCA while the other was immersed in a new olefin-containing solution. In order to determine whether any olefin from the new solution was added to the polymer chain, the olefinic component used was 1-tritio-cyclooctene.²⁴ In this manner, olefin incorporation could be measured by counting the tritium. Polyethylene film²⁵ and polyethylene film impregnated with ethylaluminum dichloride incorporated 2940 and 2885 counts/min, respectively. In contrast, the active complex on polyethylene [$W(4f_{7/2}) = 36.0$ eV] incorporated 64 390 counts/min, or approximately 20 times the background.²⁶

In summary, we have demonstrated that a highly reactive intermediate could be removed from an olefin metathesis reaction mixture and partially characterized. We caution that the agreement in binding energy between **9** treated with trimethylphosphine and **10** does not prove that they have the same structure

(22) The material obtained from the reaction of **10** with ethylaluminum dichloride was a mild metathesis catalyst. Polymerization of cyclopentene with this metathesis catalyst and isolation of the active species on polystyrene film showed this tungsten catalyst to have binding energies of 34.9 and 37.0 eV [$W(4f_{7/2})$ and $W(4f_{5/2})$, respectively] (Table II, part E). This demonstrated that this catalytic species was different from that obtained from oxotetra-chlorotungsten and ethylaluminum dichloride (as it should be, since it should retain the phosphorus ligands).

(23) Two different methods of sampling were used. One involved the dipping of the chromatography chip into the solution. The other involved the addition of 20-50 μ L of the solution to the surface of the chromatography chip with a syringe. Both methods gave the same end result, although the latter technique was often more convenient. In the first technique, small amounts of the polymer film were redissolved in the solvent, resulting in a thinner film. In experiments where "redipping" was desired, the technique of adding new material by syringe was often used to prevent the loss of both polymer and material already deposited on the surface of the polymer film.

(24) 1-Tritiocyclooctene was prepared from 1-bromocyclooctene by exchange of the bromide with *tert*-butyllithium followed by quenching with tritium oxide. A 0.4- μ L sample of this material showed 553 890 counts/min (see Experimental Section).

(25) Polyethylene film was used in place of polystyrene film, since the decomposed metathesis catalyst appeared to be a very active Friedel-Crafts catalyst. The same binding energies (± 0.1 eV) were obtained on polyethylene as on polystyrene for the tungsten derivatives.

(26) Curiously, the "inactive" complex on polyethylene [$W(4f_{7/2}) = 34.5$ and 35.5 eV] showed 13 208 counts/min. It was demonstrated that this material would not metathesize 2-heptene but would polymerize 2-heptene into higher molecular weight oligomers. In contrast, it was demonstrated that as long as **9** [$W(4f_{7/2}) = 36.0$ eV] was present, 2-heptene would give 5-decene. As the ratio of **9** to the other tungsten species decreased, the rate of metathesis of 2-heptene to 5-decene also decreased.

(20) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4516. Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148.

(21) We thank Professor R. R. Schrock for generously providing a sample of **10** and of trimethylphosphine.

but does indicate that the tungsten atoms of these materials are in a similar electronic environment.

We are continuing to use this technique to study other catalytic systems for olefin metathesis and are extending this work to the investigation of Ziegler-Natta polymerization.

Experimental Section²⁷

Preparation of ESCA Samples. (A) Cross-Linked Polystyrene Films.

A small amount of solution of polystyrene ($M_{av} = 25000$, Aldrich Chemical Co.) in dry benzene (1 g/50 mL) was placed on a 1-cm² aluminum foil chip. The chip was cut from a "heavy-duty" aluminum foil that had previously been cleaned with methylene chloride and methanol in an ultrasonic bath, and all manipulations of the chip were done without contact with bare fingers. When the solution of polystyrene was tacky, a 1-cm² piece of cross-linked polymer film^{28,29} was pressed into the polystyrene "glue". The sample was then dried under vacuum for >12 h at <0.01 mm. For air-sensitive samples all of these operations were conducted in a nitrogen-atmosphere drybox.

(B) Analysis of Crystalline Materials. An aluminum foil chip, prepared as in part A, was coated with a solution (approximately 0.1 mL) of a polystyrene in benzene (1 g/50 mL) so that the front surface of the chip was completely coated. The solution was allowed to air-dry (under nitrogen for air-sensitive samples). Then the crystalline material to be examined was pressed onto the surface of the polystyrene coat. The sample was then examined by ESCA.

(C) Supported Linear Polymers. About 0.1 mL of a solution of the appropriate polymer in benzene (1 g/50 mL) was allowed to dry on a 1-cm² aluminum foil chip. The chip was dried under vacuum. If the polymer was air sensitive, the drying was conducted under nitrogen.

(D) Polystyrene on Aluminum Chip for the Dip-Probing Experiments.

A solution (approximately 0.1 mL) of polystyrene in benzene (1 g/50 mL) was allowed to dry on a 1-cm² aluminum foil chip. The solvent was allowed to evaporate in the air or under nitrogen for 24 h. The ESCA sample was prepared by dipping the aluminum chip into the reaction solution for approximately 5–10 s,³⁰ allowing the bulk of the solvent to evaporate while the sample was being mounted, followed by evacuation of the sample in the ESCA antechamber.

(E) Polyethylene on Aluminum Chip for the Dip-Probing Experiments.

An aluminum chip (1 cm²) was coated with a layer of low-density polyethylene (Aldrich Chemical Co.) by evaporation of a hot solution (approximately 0.1 mL) of polyethylene in *o*-xylene (0.25 g/25 mL) in an oven at 110 °C. Then the polymer was dried under vacuum for 24 h. The ESCA sample on aluminum coated with polyethylene was prepared in the same manner as for the polystyrene samples.

Chlorotris(triphenylphosphine)rhodium(I) (1). The method of Wilkinson³¹ was used. To a hot solution of 3 g of triphenylphosphine in 88 mL of ethanol was added a hot solution of 0.5 g of rhodium trichloride trihydrate (Engelhard) in 32 mL of ethanol under nitrogen. The solution was refluxed for an additional 0.5 h and filtered hot, and the red crystals

(27) All melting points were determined on a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Boiling points are uncorrected. All ¹H NMR spectra were taken on a Hitachi R24B or Varian HFT-80 nuclear magnetic spectrometer. All ¹³C NMR spectra were taken on a Varian CFT-20 nuclear magnetic spectrometer. All NMR spectra were referenced to tetramethylsilane (δ 0.00) or benzene-*d*₆ (δ 7.15). All infrared spectra were taken on a Beckman Model 4240 infrared spectrometer. All mass spectra were taken on a AEI MS30 (electron impact) mass spectrometer. All chemical analyses were done by Scandinavian Microanalytical Laboratory, Herlev, Denmark, except for that of tungsten complexes which were conducted by M-H-W Laboratories, Phoenix, AZ. All ESCA were conducted on a Physical Electronics Model 548/2500 ESCA-AES-SIMS spectrometer equipped with a magnesium X-ray source and a Physical Electronics Model 2100 rapid introduction system that had a nitrogen-atmosphere drybox attached. All binding energies were referenced to C(1s) = 284.6 eV unless otherwise stated. Benzene was distilled from sodium benzophenone ketyl. Chlorobenzene was distilled from calcium hydride. All other solvents were reagent grade and used as received unless otherwise specified. Solvents were deoxygenated by three freeze-thaw cycles using liquid nitrogen and a vacuum system of <0.01 mm. All other reagents were used as received unless otherwise specified. Nitrogen was purified by passing it through two chromous chloride solutions (100 mL), two concentrated sulfuric acid solutions (100 mL), and a 1 in. diameter, 2 ft long column of 4-Å molecular sieves.

(28) Cross-linked polystyrene films were prepared according to the literature procedure: Jarrel, M. S.; Gates, B. C. *J. Catal.* **1975**, *40*, 255. Zundel, G. "Hydration and Intermolecular Interaction, Infrared Investigations with Polyelectrolyte Membranes"; Academic Press: New York, 1969.

(29) Cross-linked polystyrene films of approximately 7 and 20 μ m were prepared.

(30) An alternate procedure, which gave identical results, involved the transfer of 20–50 μ L of the reaction mixtures (solution) to the surface of the film using a syringe.

(31) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

were washed with 50 mL of deoxygenated anhydrous diethyl ether under nitrogen. The crystals were dried under vacuum to give 1.4 g (74%) of **1**: IR (Nujol mull) 1480, 1429, 1087, 741, 694 cm⁻¹. ESCA on polyethylene of a sample of **1** prepared from a benzene solution gave Rh(3d_{5/2}) = 307.2 eV, Cl(2p_{3/2}) = 197.8 eV, and P(2p) = 131.0 eV referenced to C(1s) = 284.6 eV [lit.³² Rh(3d_{5/2}) = 307.6 eV vs. C(1s) = 285.0 eV].

Chlorobis(triphenylphosphine)rhodium(I) Dimer. The method of Wilkinson³¹ was used. A saturated solution of chlorotris(triphenylphosphine)rhodium(I) (**1**) in dry, deoxygenated benzene (50 mL) was refluxed under nitrogen for 2 h. The salmon pink precipitate was collected by filtration under nitrogen and was washed with 50 mL of dry, deoxygenated diethyl ether. The product was dried in vacuo and was obtained in quantitative yield (70 mg). An ESCA sample was prepared on polyethylene and gave the following binding energies: Rh(3d_{5/2}) = 307.3 eV, Rh(3d_{3/2}) = 312.0 eV, Cl(2p_{3/2}) = 198.5 eV, P(2p) = 131.2 eV.

Chlorocarbonylbis(triphenylphosphine)rhodium(I) (6). This material was purchased from Strem Chemicals and used without purification. An ESCA sample was prepared on polyethylene and gave the following binding energies: Rh(3d_{5/2}) = 308.2 eV, Cl(2p_{3/2}) = 197.8 eV, P(2p) = 131.0 eV, O(1s) = 532.5 eV.

4-Bromobenzyl Bromide. A mixture of 50 g of 4-bromotoluene, 43 g of *N*-bromosuccinimide, 0.5 g of benzoyl peroxide, and 250 mL of carbon tetrachloride was refluxed for 1.5 h and then filtered. The solution was extracted with an aqueous sodium bisulfite solution (10 g/100 mL). The organic layer was separated and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed in vacuo. The residue crystallized on standing. Recrystallization from ethanol gave 44 g (60%) of product: mp 62–63 °C [lit.³³ mp 63 °C]; ¹H NMR (CDCl₃) δ 7.5–7.2 (4 H, m), 4.4 (2 H, s).

1-(4-Bromophenyl)pentadecane. In a 250-mL, round-bottomed flask equipped with a reflux condenser, a magnetic stirring bar, a rubber septum, and a nitrogen inlet for static pressure was placed 2.0 g of magnesium turnings. The system was evacuated and backfilled with nitrogen. Then 10 mL of dry tetrahydrofuran was added, followed by two drops of 1,2-dibromoethane. After the reaction was initiated, 13.85 g of 1-bromotetradecane in 40 mL of dry tetrahydrofuran was added slowly over a 0.5-h period. The reaction was then refluxed for an additional hour. The Grignard solution was then added to a solution of 11.25 g of 4-bromobenzyl bromide in 100 mL of dry tetrahydrofuran containing 12 mg of lithium chloride and 20 mg of cupric chloride in a 250-mL, round-bottomed flask under nitrogen, while the temperature was maintained at 0 °C. The reaction was stirred for 3 h at 0 °C. Then 50 mL of a 10% aqueous ammonium chloride solution was added. The organic layer was separated, and washed with 100 mL each of water and brine. After the solvent was removed in vacuo, the resulting solid was extracted with 100 mL of acetone. The acetone was removed in vacuo. The resulting solid was recrystallized from methanol to give 6.5 g (39%) of 1-(4-bromophenyl)pentadecane: mp 40–41 °C; ¹H NMR (CDCl₃) δ 7.5 (2 H, d), 7.1 (2 H, d), 2.6 (2 H, t), 1.3 (26 H, br s), 0.95 (3 H, t); ¹³C NMR (CDCl₃) δ 145.74 (s), 135.19 (d), 134.07 (d), 123.23 (s), 39.31 (t), 35.89 (t), 35.25 (t), 34.36–32.13 (several carbons), 26.65 (t), 18.04 (q); IR (melt) 2960, 2930, 2860, 1495, 1475, 1410, 1075, 1015, 850, 820, 797, 720 cm⁻¹; mass spectrum, 366.1903 (calcd for C₂₁H₃₅Br, 366.1922), *m/e* 366 (M⁺), 368 (100%).

4-*n*-Pentadecylbenzoic Acid. To a stirred solution of *tert*-butyllithium in pentane (2 M, 16.3 mL) cooled to –78 °C under nitrogen was added slowly a solution of 6 g of 1-(4-bromophenyl)pentadecane in 50 mL of dry tetrahydrofuran to maintain a temperature of less than –65 °C. The reaction was stirred at –78 °C for an additional 15 min and then the reaction was transferred onto dry ice (100 g) under nitrogen with a syringe. After all the dry ice evaporated, the reaction was treated with 50 mL of 5% hydrochloric acid. The reaction was extracted with 50 mL of diethyl ether and washed twice with 50-mL portions of water and brine. The organic layer was dried over anhydrous sodium sulfate. After filtering, the solvent was removed in vacuo and the resulting solid was recrystallized from 95% ethanol to give 4.8 g (89%) of the desired acid: mp 97–98 °C; ¹H NMR (CDCl₃) δ 8.15 (2 H, d), 7.35 (2 H, d), 2.75 (2 H, t), 1.3 (26 H, br s), 0.95 (3 H, t); ¹³C NMR (CDCl₃) δ 172.11 (s), 149.50 (s), 130.20 (d), 128.46 (d), 126.69 (s), 36.01 (t), 31.83 (t), 30.98 (t), 30.37–28.77 (several carbons), 22.58 (t), 13.98 (q); IR (thin film on NaCl) 3080 (br), 2960, 2920, 2850, 2660 (br), 2550 (br), 1690, 1615, 1580, 1475, 1430, 1320, 1295, 1185, 1130, 1120, 1020, 945, 860, 757,

(32) Nefedov, V. I.; Schubochnina, E. F.; Kolomnikov, I. S.; Baranovskii, I. B.; Kukolev, V. P.; Golubnichaya, M. A.; Shubochkin, L. K.; Porai-Koshits, M. A.; Vol'pin, M. E. *Zh. Neorg. Khim.* **1973**, *18*, 845. For an English translation, see: *Russ. J. Inorg. Chem. (Engl. Transl.)* **1973**, *18*, 444.

(33) Shoosmith, J. B.; Slate, R. H. *J. Chem. Soc.* **1926**, 214.

748, 718, 690 cm^{-1} ; mass spectrum, 332.2693 (calcd for $\text{C}_{22}\text{H}_{36}\text{O}_2$, 332.2715), m/e 332 (M^+), 136 (100%).

Anal. Calcd for $\text{C}_{22}\text{H}_{36}\text{O}_2$: C, 79.46; H, 10.91. Found: C, 79.68; H, 11.15.

4-*n*-Pentadecylbenzoyl Chloride (7). A mixture of 2 g of 4-*n*-pentadecylbenzoic acid, 1 mL of freshly distilled thionyl chloride, and 10 mL of benzene was refluxed while being protected from moisture with a calcium sulfate drying tube for 1 h. The solvent was distilled and the residue was distilled (Kugelrohr distillation, 8×10^{-6} mm, 100 °C) to give 1.9 g (90%) of the desired acid chloride (7) as a low-melting solid: mp 27–28 °C; $^1\text{H NMR}$ (CDCl_3) δ 8.05 (2 H, d), 7.3 (2 H, d), 2.7 (2 H, t), 1.3 (26 H, br s), 0.95 (3 H, t); $^{13}\text{C NMR}$ (CDCl_3) δ 167.83 (s), 151.52 (s), 131.50 (d), 130.67 (s), 128.89 (d), 35.96 (t), 31.84 (t), 30.78 (t), 30.50–22.57 (several carbons), 22.57 (t), 13.97 (q); IR (melt) 2920, 2850, 1780, 1750, 1610, 1575, 1480, 1420, 1210, 1170, 875, 840, 790, 640, 625, 610 cm^{-1} ; mass spectrum, 350.2376 (calcd for $\text{C}_{22}\text{H}_{33}\text{ClO}$, 350.2376), m/e 350 (M^+), 315 (100%).

Anal. Calcd for $\text{C}_{22}\text{H}_{33}\text{ClO}$: C, 75.29; H, 10.05. Found: C, 75.55; H, 10.23.

4-(*n*-Tetradecyloxy)benzoic Acid. To a solution of 5.7 g of potassium hydroxide in 60 mL of diethylene glycol was added 6 g of 4-hydroxybenzoic acid. The solution was heated to 50 °C until a homogeneous solution was obtained. Then 13.3 g of 1-bromotetradecane was added. The reaction was vigorously stirred for 12 h at 120 °C. After the reaction cooled to room temperature, 30 mL of 10% hydrochloric acid was added and the reaction mixture was extracted with 100 mL of diethyl ether. The organic layer was washed with 100 mL each of water and brine and dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo and the resulting solid was recrystallized from 95% ethanol to yield (after drying under vacuum) 14.5 g (92%) of 4-(*n*-tetradecyloxy)benzoic acid as a white waxy crystalline solid: mp 95–96 °C; $^1\text{H NMR}$ (CDCl_3) δ 8.00 (2 H, d), 6.95 (2 H, d), 4.05 (2 H, t), 1.90–1.40 (6 H, m), 1.3 (20 H, br s), 1.9 (3 H, t); $^{13}\text{C NMR}$ (CDCl_3) δ 170.78 (s), 163.55 (s), 132.20 (d), 121.17 (s), 114.09 (d), 68.19 (t), 29.52–28.34 (multiple carbons), 25.86 (t), 22.55 (t), 13.98 (t); IR (thin film on NaCl) 2960, 2920, 2850, 2650, 2580, 1690, 1610, 1580, 1518, 1470, 1435, 1335, 1310, 1260, 1170, 1065, 940, 845, 770, 715, 690 cm^{-1} ; mass spectrum, 334.2511 (calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3$, 334.2508), m/e 334 (M^+), 69 (100%).

Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3$: C, 75.41; H, 10.25. Found: C, 75.42; H, 10.26.

4-(*n*-Tetradecyloxy)benzoyl Chloride (8). A mixture of 2 g of 4-(*n*-tetradecyloxy)benzoic acid, 1 mL of freshly distilled thionyl chloride, and 10 mL of benzene was refluxed while being protected from moisture with a calcium sulfate drying tube for 1 h. The solvent was removed, and the residue was distilled (Kugelrohr distillation, 8×10^{-6} mm, 110 °C) to give 2.0 g (95%) of 8 as a white solid: mp 44–45 °C; $^1\text{H NMR}$ (CDCl_3) δ 8.07 (2 H, d), 6.90 (2 H, d), 4.05 (2 H, t), 1.9–1.3 (6 H, m), 1.3 (20 H, br s), 0.9 (3 H, t); $^{13}\text{C NMR}$ (CDCl_3) δ 167.01 (s), 164.96 (s), 133.83 (d), 125.05 (s), 114.50 (d), 68.51 (t), 31.78 (t), 29.50–28.84 (multiple carbon peaks), 25.77 (t), 22.54 (t), 13.95 (q); IR (melt) 2920, 2850, 1760, 1740, 1605, 1575, 1510, 1470, 1425, 1330, 1280, 1220, 1175, 1165, 1120, 1035, 1020, 1005, 995, 975, 880, 840, 810, 730, 710, 660, 620 cm^{-1} ; mass spectrum, 352.2196 (calcd for $\text{C}_{21}\text{H}_{33}\text{O}_2\text{Cl}$, 352.2196), m/e 352 (M^+), 69 (100%).

Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{O}_2\text{Cl}$: C, 71.47; H, 9.42. Found: C, 71.27; H, 9.50.

ESCA of 7 and 8. ESCA samples of 7 and 8 were prepared by method E, which was described earlier in the Experimental Section, from a 7×10^{-2} M solution of 7 and 8 in benzene. For 8, the following binding energies were obtained: $\text{Cl}(2p_{3/2}) = 200.2$ eV and two $\text{O}(1s)$ species = 532.9 and 531.7 eV. For 7, the sample only showed carbon on the surface. However, if the sample was gently rubbed with a glass rod and then examined by ESCA, chlorine and oxygen could be detected; $\text{Cl}(2p_{3/2}) = 200.0$ eV and $\text{O}(1s) = 532.0$ eV.

Benzoyldichlorobis(triphenylphosphine)rhodium(III) (2a). The method of Stille was followed.⁹ To 0.23 g of chlorotris(triphenylphosphine)rhodium(I) (1) in 15 mL of dry, deoxygenated methylene chloride was added 3.0 mL (3.63 g) of freshly distilled benzoyl chloride under nitrogen. The reaction was stirred at 30 °C for 3 min and then quenched by the addition of 100 mL of dry, deoxygenated pentane. The yellow precipitate was collected by filtration and washed three times with 5 mL of dry, deoxygenated ether. After the yellow precipitate was dried under vacuum, 0.10 g (50%) of 2a was obtained. The infrared spectrum (Nujol) showed carbonyl bands at 1703 (m) and 1659 (s) cm^{-1} , which were in good agreement with the literature.^{9,11}

ESCA of a sample of 2a on polystyrene (prepared by method B) gave the following binding energies: $\text{Rh}(3d_{5/2}) = 309.2$ eV, $\text{Rh}(3d_{3/2}) = 313.9$ eV, $\text{Cl}(2p_{3/2}) = 197.7$ eV, $\text{Cl}(2p_{1/2}) = 198.6$ eV, $\text{P}(2p) = 131.1$ eV, $\text{O}(1s) = 532.1$ eV.

***p*-Anisoyldichlorobis(triphenylphosphine)rhodium(III) (2b).** The complex was prepared in the same manner as 2a from 0.23 g of chlorotris(triphenylphosphine)rhodium(I) (1) and 3.0 mL (3.64 g) of anisoyl chloride in 15 mL of methylene chloride. After the precipitate was vacuum-dried, 0.11 g (52%) of a yellow crystalline product was obtained. The infrared spectrum (Nujol) showed carbonyl bands at 1704 (m) and 1660 (s) cm^{-1} , which were in fairly good agreement with the literature values.⁹

ESCA of a sample of 2b on polystyrene (prepared by method B) gave the following binding energies: $\text{Rh}(3d_{5/2}) = 308.9$ eV, $\text{Rh}(3d_{3/2}) = 313.6$ eV, $\text{Cl}(2p_{1/2}) = 198.4$ eV, $\text{P}(2p) = 131.0$ eV, $\text{O}(1s) = 531.8$ and 532.9 eV.

Phenyldichlorocarbonylbis(triphenylphosphine)rhodium(III) (3a). The method of Stille was used.⁹ To 0.5 g of chlorotris(triphenylphosphine)rhodium(I) (1) suspended in 20 mL of dry, deoxygenated benzene was added 0.5 mL (0.6 g) of freshly distilled benzoyl chloride under nitrogen. The reaction was stirred at 80 °C for 30 min. After the reaction was quenched by addition of 100 mL of pentane, the yellow precipitate that formed was collected by filtration and washed three times with 5 mL of dry, deoxygenated diethyl ether. After the precipitate was vacuum-dried, 0.27 g (63%) of 3a was obtained. The infrared spectrum (Nujol) showed a carbonyl band at 2068 cm^{-1} , which was in good agreement with the literature.^{9,11}

ESCA of a sample of 3a on polystyrene (prepared by method B) gave the following binding energies: $\text{Rh}(3d_{5/2}) = 309.6$ eV, $\text{Rh}(3d_{3/2}) = 314.3$ eV, $\text{Cl}(2p_{3/2}) = 198.0$ eV, $\text{Cl}(2p_{1/2}) = 198.8$ eV, $\text{P}(2p) = 131.2$ eV, $\text{O}(1s) = 532.6$ eV. On long exposure (>3 h) of 3a to X-ray bombardment a new species was formed, which had the following binding energies: $\text{Rh}(3d_{5/2}) = 309.0$ eV, $\text{Rh}(3d_{3/2}) = 313.7$ eV, $\text{Cl}(2p_{3/2}) = 197.8$ eV, $\text{Cl}(2p_{1/2}) = 198.7$ eV, $\text{P}(2p) = 131.0$ eV. These values are in agreement with those found for 4a.

(*p*-Methoxyphenyl)dichlorocarbonylbis(triphenylphosphine)rhodium(III) (3b). This complex was prepared in the same manner as 3a from 0.5 g of chlorotris(triphenylphosphine)rhodium(I) (1) and 0.5 mL (6.0 g) of anisoyl chloride in 20 mL of dry, deoxygenated benzene. After the precipitate was vacuum-dried, 0.29 g (65%) of a yellow crystalline product was obtained. The infrared spectrum (Nujol) showed a carbonyl band at 2060 cm^{-1} , which was in good agreement with the literature.⁹

ESCA of 3b on polystyrene (prepared by method B) gave the following binding energies: $\text{Rh}(3d_{5/2}) = 309.4$ eV, $\text{Rh}(3d_{3/2}) = 314.1$ eV, $\text{Cl}(2p_{3/2}) = 197.8$ eV, $\text{Cl}(2p_{1/2}) = 198.6$ eV, $\text{P}(2p) = 131.2$ eV, $\text{O}(1s) = 532.8$ eV (a broad peak: the half-height width was 2.6 eV, which may be two oxygen species with very similar binding energies). On long exposure (>3 h) of 3b to X-ray bombardment a new species was formed, which had the following binding energies: $\text{Rh}(3d_{5/2}) = 308.6$ eV, $\text{Rh}(3d_{3/2}) = 313.3$ eV, $\text{Cl}(2p_{3/2}) = 197.7$ eV, $\text{Cl}(2p_{1/2}) = 198.5$ eV, $\text{P}(2p) = 130.9$ eV, $\text{O}(1s) = 532.4$ eV. These values are identical with those found for 4b.

Phenyldichlorobis(triphenylphosphine)rhodium(III) (4a). This complex was prepared by the method of Kampmeier.¹⁰ Complex 3a (0.2 g) was heated in refluxing, dry, deoxygenated benzene (10 mL) for 18 h under nitrogen. The reaction was quenched by addition of 100 mL of dry, deoxygenated pentane. The precipitate was collected by filtration to give 0.15 g of crude material. This material was dissolved in 5 mL of methylene chloride with 0.15 g of triphenylphosphine and placed on a column of 20 g of silica gel (Baker, 60–120 mesh). The complex was eluted with methylene chloride. The solvent was removed in vacuo and washed with 5 mL of dry diethyl ether. After the mixture was dried under vacuum, 0.13 g (65%) of 4a was obtained. Infrared spectroscopy showed the absence of any carbonyl absorption.

ESCA of 4a on polystyrene (prepared by method B) gave the following binding energies: $\text{Rh}(3d_{5/2}) = 309.0$ eV, $\text{Rh}(3d_{3/2}) = 313.7$ eV, $\text{Cl}(2p_{3/2}) = 197.8$ eV, $\text{Cl}(2p_{1/2}) = 198.7$ eV, $\text{P}(2p) = 131.0$ eV.

(*p*-Methoxyphenyl)dichlorobis(triphenylphosphine)rhodium(III) (4b). This complex was prepared in the same manner as 4a from 0.2 g of complex 3b in 10 mL of dry, deoxygenated benzene. After workup and chromatography, 0.11 g (57%) of 4b was obtained. Infrared spectroscopy (Nujol) showed the absence of any carbonyl absorption.

ESCA of 4b on polystyrene (prepared by method B) showed the following binding energies: $\text{Rh}(3d_{5/2}) = 308.6$ eV, $\text{Rh}(3d_{3/2}) = 313.3$ eV, $\text{Cl}(2p_{3/2}) = 197.7$ eV, $\text{Cl}(2p_{1/2}) = 198.5$ eV, $\text{P}(2p) = 130.9$ eV, $\text{O}(1s) = 532.4$ eV.

In Situ Preparation and ESCA of Intermediates in the Reaction of 1 with Aryl Chlorides 7 and 8: Complexes 2c, 2d, 3c, 3d, 4c, and 4d. A suspension of 25 mg of chlorotris(triphenylphosphine)rhodium(I) (1) in 5 mL of dry, deoxygenated toluene was treated with 10 mg of 4-*n*-pentadecylbenzoyl chloride (7) or 4-(*n*-tetradecyloxy)benzoyl chloride (8) at room temperature for 15 min under nitrogen. Then a polystyrene-coated aluminum foil chip was dipped into the solution and placed directly into the antechamber of the ESCA system without exposure to air.

For the aryl chloride **7** (for **2c**), the following binding energies were found: Rh($3d_{5/2}$) = 309.2 eV, Rh($3d_{3/2}$) = 313.9 eV, Cl($2p_{3/2}$) = 197.7 eV, Cl($2p_{1/2}$) = 198.6 eV, P(2p) = 131.1 eV, O(1s) = 532.1 eV. For the aryl chloride **8** (for **2d**), the following binding energies were found: Rh($3d_{5/2}$) = 308.9 eV, Rh($3d_{3/2}$) = 313.6 eV, Cl($2p_{3/2}$) = 197.5 eV, Cl($2p_{1/2}$) = 198.4 eV, P(2p) = 131.0 eV, O(1s) = 531.8 and 532.9 eV. These values are in agreement with those found for **2a** and **2b**, respectively.

The reaction mixture was then heated to 60 °C for 30 min under nitrogen. After the reaction cooled to room temperature, a polyethylene-coated aluminum foil chip was dipped into the reaction mixture and placed in the antechamber of the ESCA system without exposure to air. On ESCA for the aryl chloride **7** (for **3c**), the following binding energies were found: Rh($3d_{5/2}$) = 309.6 eV, Rh($3d_{3/2}$) = 314.3 eV, Cl($2p_{3/2}$) = 198.0 eV, Cl($2p_{1/2}$) = 198.8 eV, P(2p) = 131.2 eV, O(1s) = 532.6 eV. For the aryl chloride **8** (for **3d**), the following binding energies were found: Rh($3d_{5/2}$) = 309.4 eV, Rh($3d_{3/2}$) = 314.1 eV, Cl($2p_{3/2}$) = 197.8 eV, Cl($2p_{1/2}$) = 198.6 eV, P(2p) = 131.2 eV, O(1s) = 532.8 eV [a broad peak (half-height width 2.5 eV) may be two oxygen species]. These are in agreement with those found for **3a** and **3b**, respectively.

Next, the reaction was refluxed for 4 h under nitrogen and cooled. Then a polystyrene-coated aluminum foil chip was dipped into the reaction mixture and introduced directly into the ESCA antechamber. On ESCA for the aryl chloride **7** (for **4c**), the following binding energies were found: Rh($3d_{5/2}$) = 309.0 eV, Rh($3d_{3/2}$) = 313.7 eV, Cl($2p_{3/2}$) = 197.8 eV, Cl($2p_{1/2}$) = 198.7 eV, P(2p) = 131.0 eV. For the aryl chloride **8** (for **4d**), the following binding energies were found: Rh($3d_{5/2}$) = 308.6 eV, Rh($3d_{3/2}$) = 313.3 eV, Cl($2p_{3/2}$) = 197.7 eV, Cl($2p_{1/2}$) = 198.5 eV, P(2p) = 130.9 eV, O(1s) = 532.4 eV. These values are in agreement with those found for **4a** and **4b**, respectively.

ESCA of a Mixture of **8 and **1** after Very Short Reaction Time.** A suspension of 25 mg of chlorotris(triphenylphosphine)rhodium(I) (**1**) in 5 mL of dry, deoxygenated toluene was treated with 10 mg of 4-(*n*-tetradecyloxy)benzoyl chloride (**8**) at room temperature for 15 min. Then a polyethylene-coated aluminum foil chip was dipped into the solution and placed directly into the ESCA antechamber without exposure to air. ESCA showed two rhodium complexes having binding energies of Rh($3d_{5/2}$) = 308.9 and 307.2 eV and Rh($3d_{3/2}$) = 313.6 and 311.9 eV in a 3:1 ratio. The higher binding energy species would appear to be **2c** while the lower binding energy species appears to be the starting rhodium complex, **1**.

This was verified by using a 2:3 ratio of **8:1** to ensure some of **1** remained after reacting **8** and **1** together at room temperature for 15 min in 5 mL of toluene. ESCA showed a very similar spectrum (Figure 1) to that found above.

Distinction between Polystyrene and Polyethylene in the Dip-Coating of Reaction Mixtures. A suspension of 25 mg of chlorotris(triphenylphosphine)rhodium(I) (**1**) in 5 mL of dry, deoxygenated benzene was treated with 6 mg of 4-(*n*-tetradecyloxy)benzoyl chloride (**8**, 0.6 equiv of aryl chloride:1.0 equiv of rhodium) for 15 min at room temperature. Then a polyethylene-coated aluminum foil chip was dipped into the reaction and introduced into the ESCA system without exposure to air. ESCA showed **2c** [Rh($3d_{5/2}$) = 308.9 eV] and **1** [Rh($3d_{5/2}$) = 307.2 eV] in a ~2:1 ratio.

When a polystyrene-coated aluminum foil chip was dipped into the reaction and examined by ESCA only **2c** [Rh($3d_{5/2}$) = 308.9 eV] was found (Figure 1).

Thermal Decomposition of **3c, **3d**, **4c**, and **4d**.** The complexes **3c**, **3d**, **4c**, and **4d** were prepared in toluene by the *in situ* technique described above. The solvent was removed under vacuum. The resulting residue was heated at 180 °C for 2 h under vacuum (0.1 mm). Finally 5 mL of dry, deoxygenated toluene was added. ESCA of samples on polystyrene, prepared by dip-coating, showed only chlorine and varying amounts of oxygen. No rhodium or phosphorus was detected, indicating the rhodium was no longer attached to the long-chain-containing organic fragment.

Development of ESCA Standards for Tungsten. A series of tungsten derivatives were deposited on polyethylene-coated aluminum foil chips and their ESCA spectra were recorded. The observed binding energies are listed in Table II, part A. All of the compounds in this section either were commercially available or were synthesized via literature procedures.

ESCA of Oxotetrachlorotungsten-Ethylaluminum Dichloride (2 equiv). To 1.0 mL of a solution of oxotetrachlorotungsten³⁴ in dry, deoxygenated benzene (25 mg/7.0 mL) in a nitrogen drybox was added 14.0 μL of a 1.47 M solution of ethylaluminum dichloride (2 equiv) in hexane with

swirling. A polyethylene-coated aluminum foil chip was dipped into the reaction and immediately placed in the ESCA system.³⁵ ESCA with only 15-min exposure of the sample to X-ray bombardment showed a tungsten complex having binding energies of W($4f_{7/2}$) = 36.0 eV and W($4f_{5/2}$) = 38.2 eV. Chlorine, oxygen, and aluminum were also present.

On longer exposure of the sample to X-ray bombardment (45 min) new peaks were observed having the following binding energies: W($4f_{7/2}$) = 35.5 and 34.5 eV and W($4f_{5/2}$) = 37.7 and 36.7 eV, with the lower binding energy species being the major (ca. 2:1 ratio).

An ESCA sample prepared from the above solution on polyethylene was dried by evacuation in the ESCA system antechamber. Then the sample was exposed to air for 15 min before ESCA. Only one tungsten species, having binding energies of W($4f_{7/2}$) = 36.2 eV and W($4f_{5/2}$) = 38.4 eV, was found. This species was X-ray stable. This species has W(4f) binding energies that are in good agreement with those of tungsten trioxide [W($4f_{7/2}$) = 36.3 eV and W($4f_{5/2}$) = 38.5 eV].

If the solution was allowed to stand for 24 h before an ESCA sample was prepared, two tungsten species having the following tungsten binding energies were found: W($4f_{7/2}$) = 35.5 and 34.5 eV and W($4f_{5/2}$) = 37.7 and 36.7 eV (the lower binding energy species is the major in a ~2.5:1 ratio). These species appear by ESCA to be the same as those found on X-ray decomposition of the initial species, which had W($4f_{7/2}$) = 36.0 eV.

Metathesis of 2-Heptene (WOC₄/2EtAlCl₂). To 1.0 mL of a solution of oxotetrachlorotungsten³⁴ in dry, deoxygenated benzene (25 mg/7.0 mL) in a nitrogen-atmosphere drybox was added 14.0 μL of a 1.47 M solution of ethylaluminum dichloride (2 equiv) in hexane with swirling. Then 67 μL of dry, deoxygenated 2-heptene (50 equiv) and 33 μL of dry, deoxygenated undecane (internal GLC standard) were added. The reaction was swirled for 2 min. Then a polyethylene-coated aluminum foil chip was dipped into the reaction mixture and placed in the ESCA system.³⁵ At the same time a 1-μL aliquot sample was removed from the reaction mixture and analyzed by GLC on a 10 ft × 1/8 in. diameter packed column (10% Carbowax 20M, 5% potassium hydroxide on 80-100-mesh Chromosorb P).

The ESCA showed the same initial species [W($4f_{7/2}$) = 36.0 eV, W($4f_{5/2}$) = 38.2 eV] as that previously described for the reaction of WOC₄ with 2 equiv of EtAlCl₂. The GLC analysis of the reaction showed 2-heptene and 5-decene in a 3:1 ratio.³⁶

After the reaction mixture was allowed to stand 4 h, another ESCA sample was prepared and another aliquot of the reaction mixture was examined by GLC. ESCA showed the presence of the initial species [W($4f_{7/2}$) = 36.0 eV, W($4f_{5/2}$) = 38.2 eV] plus some of the decomposition products [W($4f_{7/2}$) = 34.5 and 35.5 eV, W($4f_{5/2}$) = 36.7 and 37.7 eV] of the initial species after deconvolution of the W(4f) photoelectron peaks. The complexes were in a ca. 3:2:1 ratio [W($4f_{7/2}$) = 36.0:34.5:35.5 eV, respectively]. The GLC analysis showed the reaction had gone to completion (2-heptene:5-decene ratio of 2:1).³⁶

After another 4 h, an additional 67 μL of dry, deoxygenated 2-heptene (50 equiv) and 33 μL of dry deoxygenated undecane were added to the reaction mixture, and the mixture was swirled 2 min and then allowed to stand 3 h before preparation of another ESCA sample and removal of another aliquot for GLC analysis. At this time, ESCA showed the initial tungsten complex plus the two decomposition products in a 1:3:1.5 ratio [W($4f_{7/2}$) = 36.0:34.5:35.5 eV, respectively]. The GLC analysis indicated the system was still active but slower than before (2-heptene:5-decene ratio of 3:1).

After an additional 5 h, another set of ESCA and GLC samples were removed from the reaction mixture. At this time ESCA showed only decomposition products of the initial tungsten complex in a 2:1 ratio [W($4f_{7/2}$) = 34.5:35.5, respectively] and GLC showed the reaction had stopped short of equilibrium (2-heptene:5-decene ratio of 2.5:1).

Addition of another 67 μL of dry, deoxygenated 2-heptene and 33 μL of dry, deoxygenated undecane confirmed that the reaction had stopped because the formation of more 5-decene was not observed after an additional 5 h. ESCA showed that the tungsten species in solution did not change during this time.

ESCA on Polystyrene of the Reaction of Oxotetrachlorotungsten and 2 equiv of Ethylaluminum Dichloride with Cyclopentene. To 1.0 mL of a solution of oxotetrachlorotungsten³⁴ in dry, deoxygenated benzene (25 mg/7.0 mL) in a nitrogen-atmosphere drybox was added 14.0 μL of a

(35) The sample was mounted on the end of the rapid introductory system rod in the antechamber of the ESCA system from the drybox. The sample was evacuated for 30 min in the antechamber (10⁻⁶ mm) and then placed in the ultrahigh-vacuum system (10⁻⁸-10⁻⁹ mm) for ESCA.

(36) For the metathesis reaction of 2-heptene, 2-butene, 2-heptene, and 5-decene should be formed in a 1:2:1 ratio at equilibrium. However, 2-butene was too volatile for reliable GLC analysis so only the 2-heptene:5-decene ratio was monitored.

(34) Oxotetrachlorotungsten was purified by sublimation under vacuum (<0.01 mm) at 90 °C and handled only in a nitrogen drybox.

1.47 M solution of ethylaluminum dichloride (2 equiv) in hexane with swirling. After 2 min, a polystyrene-coated aluminum foil chip was dipped into the reaction mixture and was introduced into the ESCA system. Low-resolution ESCA showed only a trace of tungsten on the surface of the film (C:W ratio of >500:1).

Then 5.0 μL (5 equiv) of dry, deoxygenated cyclopentene³⁷ was added to the solution. After 2 min, a polystyrene-coated aluminum foil chip was dipped into the reaction mixture and inserted into the ESCA system. ESCA (low resolution) of the sample showed an increased amount of tungsten (C:W ratio of 70:1). High-resolution ESCA on the tungsten 4f photoelectron peak of another identically prepared sample³⁸ showed the same initial X-ray-sensitive species [$W(4f_{7/2}) = 36.0$ eV, $W(4f_{5/2}) = 38.2$ eV] as that found on ESCA samples prepared on polyethylene from $\text{WOC}_2\text{Cl}_4/2\text{EtAlCl}_2$ with or without 5 equiv of cyclopentene present.

After the solution was allowed to stand for 24 h in the drybox, another ESCA sample was prepared on polystyrene. ESCA showed two tungsten species [$W(4f_{7/2}) = 34.5$ and 35.5 eV, $W(4f_{5/2}) = 36.7$ and 37.7 eV in a 2:1 ratio]. These would appear by ESCA to be the decomposition products of the initially formed tungsten species, which had $W(4f_{7/2}) = 36.0$ eV and $W(4f_{5/2}) = 38.2$ eV.

ESCA of the Oxotungsten-Alkylidene Complex 10. A solution of 20 mg of **10**²¹ in 5.0 mL of dry, deoxygenated benzene was prepared in a drybox. An ESCA sample was prepared by dipping a polyethylene-coated aluminum foil chip into the solution. The sample was introduced into the ESCA system without exposure to air. ESCA of **10** gave the following binding energies: $W(4f_{7/2}) = 34.1$ eV, $W(4f_{5/2}) = 36.3$ eV.

ESCA of the Reaction of Oxotetrachlorotungsten-Ethylaluminum Dichloride (2 equiv) and Trimethylphosphine (4 equiv). To 1.0 mL of a solution of oxotetrachlorotungsten³⁴ in dry, deoxygenated benzene (25 mg/7.0 mL) in a nitrogen-atmosphere drybox was added 14.0 μL of a 1.47 M solution of ethylaluminum dichloride (2 equiv) in hexane with swirling. Then 6 μL of trimethylphosphine²¹ was added. The dark red-brown solution turned to a golden yellow solution.

An ESCA sample was prepared by dipping a polyethylene-coated aluminum foil chip into the reaction. The sample was introduced immediately in the ESCA antechamber for evacuation without exposure to air. ESCA showed one X-ray-stable tungsten species having the following binding energies: $W(4f_{7/2}) = 34.0$ eV, $W(4f_{5/2}) = 36.2$ eV. These values were in good agreement with those found for the oxotungsten-alkylidene complex **10**.

After the original solution stood for 96 h, an ESCA sample showed that the initial species had decomposed to a new, lower binding energy tungsten species [$W(4f_{7/2}) = 33.5$ eV, $W(4f_{5/2}) = 35.7$ eV].

Treatment of 10 with Bis(benzonitrile)palladium Dichloride. The reaction of **10** with bis(benzonitrile)palladium dichloride was carried out in benzene according to the method of Schrock and co-workers.²⁰ Sampling of the product on a polyethylene-coated aluminum foil chip gave binding energies of $W(4f_{7/2}) = 34.4$ eV and $W(4f_{5/2}) = 36.5$ eV.

Treatment of 10 with Ethylaluminum Dichloride. The reaction of **10** with 1 equiv of ethylaluminum dichloride was carried out in benzene according to the literature procedure.²⁰ Sampling of the product on a polyethylene-coated aluminum foil chip followed by ESCA gave binding energies of $W(4f_{7/2}) = 34.7$ eV and $W(4f_{5/2}) = 36.8$ eV.

Addition of olefins to this solution showed it to be a slow metathesis catalyst. Addition of cyclopentene followed by probing of the reaction mixture with a polystyrene-coated aluminum foil chip and ESCA gave $W(4f_{7/2}) = 34.9$ eV and $W(4f_{5/2}) = 37.0$ eV.

1-Bromocyclooctene. The procedure of Gream³⁸ was modified. To 50 g of cyclooctene in 100 mL of methylene chloride cooled to <0 °C by an ice/salt bath was added dropwise 72 g of bromine at such a rate to maintain the reaction temperature at 0 °C. The solvent was removed in vacuo to give 122 g of crude 1,2-dibromocyclooctene.

The crude 1,2-dibromocyclooctane (122 g) was mixed with 200 mL of piperidine, and the solution was refluxed for 18 h. The precipitated piperidine hydrobromide was filtered off, and the salt was washed with 200 mL of benzene. The combined filtrates were washed with 200 mL of 5% sulfuric acid. The aqueous layer was extracted with two 100-mL portions of benzene. The organic layers were combined, washed with 50 mL of 5% sulfuric acid, 100 mL of water, 50 mL of saturated sodium bicarbonate, 100 mL of water, and 100 mL of brine, and dried over anhydrous sodium sulfate. After filtration, the solvent was removed in vacuo and the resulting oil was vacuum-distilled to give 60 g (70%) of 1-bromocyclooctene: 82–84 °C (10 mm) [lit.³⁸ 83–85 °C (10 mm)]; ¹H

NMR (CDCl_3) δ 6.0 (1 H, t), 2.6 (2 H, m), 2.1 (2 H, m), 1.6 (8 H, m) [lit.³⁹ ¹H NMR (CCl_4) δ 5.96 (1 H, t, $J = 8.5$ Hz), 2.56 (2 H, m), 2.11 (2 H, m), 1.53 (8 H, m)].

1-Tritiocyclooctene. The method of Seebach³⁹ was modified. A solution of 6 g of 1-bromocyclooctene in 15 mL of dry, deoxygenated diethyl ether was added dropwise over a 2-min period to a stirred solution of 15 mL of dry, deoxygenated diethyl ether and 41 mL of a 1.55 M solution of *tert*-butyllithium in pentane. The solution was stirred for an additional 5 min and then 350 μL of tritium oxide (50 mCi/mL) was added. The reaction mixture was allowed to warm to room temperature. A vigorous evolution of gas was observed just below room temperature. The precipitated lithium hydroxide was removed by filtration through anhydrous magnesium sulfate. The solvent was removed by distillation at atmospheric pressure, and the resulting residue was distilled to give 1.8 g (51%) of 1-tritiocyclooctene.

If the tritium oxide was replaced with deuterium oxide (99% pure), 2.0 g (57%) of 1-deuteriocyclooctene was obtained. The mass spectrum of the 1-deuteriocyclooctene indicated 90% deuterium incorporation; ¹H NMR (CDCl_3) showed a 1-H triplet at δ 5.6, indicating only one olefinic proton was present.

On standing, the 1-tritiocyclooctene slowly turned yellow. It was purified just prior to use by a freeze-thaw degassing under vacuum (0.01 mm) and vacuum transferring of the 1-tritiocyclooctene away from a colored, high molecular weight contaminant.

The radioactivity of the 1-tritiocyclooctene was determined by scintillation counting. Counting was conducted in a Beckman LS-230 liquid scintillation system. A 0.4- μL sample of this material gave 553 890 counts/min, which corresponds to an activity of 0.6 $\mu\text{Ci/mL}$.

Radioisotope Study of Oxotetrachlorotungsten with 2 equiv of Ethylaluminum Dichloride. To 1.0 mL of a solution of oxotetrachlorotungsten³⁴ in dry, deoxygenated benzene (26 mg/7.0 mL) in a nitrogen-atmosphere drybox was added 14.0 μL (2 equiv) of a 1.47 M solution of ethylaluminum dichloride in hexane with swirling. Then a polyethylene-coated aluminum foil chip was dipped into the solution and the ESCA antechamber was evacuated for 15 min. The sample was taken back into the drybox and treated with 50 μL of dry, deoxygenated 1-tritiocyclooctene and then placed immediately back in the ESCA antechamber for evacuation. After 15 min the sample was examined by ESCA, which showed only one tungsten species with the following binding energies: $W(4f_{7/2}) = 36.0$ eV and $W(4f_{5/2}) = 38.2$ eV, which are in agreement with those observed previously for material from an active metathesis solution. Again, this species was X-ray sensitive. Scintillation counting showed the sample contained a considerable amount of radioactivity (64 390 counts/min).

Another ESCA sample was prepared in a similar manner except the sample was exposed to air before treatment with 1-tritiocyclooctene. ESCA of this sample showed an X-ray-stable species having binding energies of $W(4f_{7/2}) = 36.2$ eV and $W(4f_{5/2}) = 38.4$ eV. Scintillation counting showed the sample contained only 8047 counts/min. This was much lower than that observed for the active metathesis sample.

A third ESCA sample was prepared after allowing the solution to stand 24 h. After treatment with 1-tritiocyclooctene, ESCA showed two tungsten species [$W(4f_{7/2}) = 34.5$ and 35.5 eV, $W(4f_{5/2}) = 36.7$ and 37.7 eV] that corresponded to the decomposition products from the active metathesis solution. Scintillation counting showed the sample contained only 13 208 counts/min.

Two other control samples were prepared. The first was 1-tritiocyclooctene on a polyethylene-coated aluminum foil chip. This was prepared by treating a polyethylene-coated aluminum foil chip with 50 μL of 1-tritiocyclooctene in a drybox, followed by evacuation of the sample in the ESCA antechamber for 0.5 h. ESCA of the sample showed only carbon on the sample. Scintillation counting showed only 2940 counts/min.

The second control sample was prepared by dipping a polyethylene-coated aluminum foil chip into a benzene solution (1.0 mL) containing 14.0 μL of a 1.47 M solution of ethylaluminum dichloride in hexane. The sample was evacuated in the ESCA antechamber for 15 min. Then 50 μL of 1-tritiocyclooctene was added. The sample was again evacuated in the ESCA antechamber. ESCA showed a very small amount of aluminum, chlorine, and oxygen on the sample. Scintillation counting showed only 2885 counts/min.

Reaction of Inactive Olefin Metathesis Catalyst ($\text{WOC}_2\text{Cl}_4/2\text{EtAlCl}_2$) with 2-Heptene. A 1.0-mL solution of oxotetrachlorotungsten in dry, deoxygenated benzene (20 mg/7.0 mL) in a nitrogen-atmosphere drybox to which 14.0 μL (2 equiv) of a 1.47 M solution of ethylaluminum dichloride in hexane had been added was allowed to stand for 24 h. An ESCA sample prepared on a polyethylene-coated aluminum foil chip showed the expected decomposition complexes [$W(4f_{7/2}) = 34.5$ and 35.5

(37) Cyclopentene was distilled from lithium aluminum hydride and deoxygenated by three freeze-thaw cycles under vacuum (<0.01 mm). It was then passed through a 5-g plug of alumina [EM Reagents, basic type E, activity I, 70–230 mesh; previously heated to 150 °C under vacuum (0.01 mm) for 24 h] in the drybox.

(38) Gream, G. E.; Mular, M. *Aust. J. Chem.* **1975**, *28*, 2227.

(39) Seebach, D.; Neuman, H. *Chem. Ber.* **1978**, *111*, 2785.

eV, $W(4f_{5/2}) = 36.7$ and 37.7 eV in a 2:1 ratio].

To this solution was added 0.5 mL of dry, deoxygenated 2-heptene. The solution was allowed to stand 24 h at room temperature. Analysis of the reaction by GLC (10 ft \times $1/8$ in. diameter, 10% Carbowax, 20M, 5% potassium hydroxide on 80-100-mesh Chromosorb P) showed no detectable amount of 5-decene, thus confirming the inactivity of the solution for the olefin metathesis reaction.

The reaction was quenched by addition of 1.0 mL of deoxygenated water. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was removed in vacuo to leave 100 mg of a yellow oily residue: $^1\text{H NMR}$ (CDCl_3) δ 7.2-6.7 (1 H, m), 1.5 (4 H, m), 1.25 (17 H, m), 0.9 (11 H, m). The structure of this high molecular weight material is unknown, but it appears to be formed by a nonmetathesis oligomerization of 2-heptene or alkylation of the solvent. This indicated that the spent metathesis catalyst was able to convert simple olefins into higher molecular weight species by some type of oligomerization process.

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Registry No. 1, 14694-95-2; 2a, 52393-94-9; 2b, 52393-93-8; 2c, 94859-66-2; 2d, 94859-67-3; 3a, 52438-22-9; 3b, 52478-79-2; 3c, 94859-68-4; 3d, 94859-69-5; 4a, 94859-70-8; 4b, 94859-71-9; 4c, 94859-72-0; 4d, 94859-73-1; 6, 15318-33-9; 7, 94859-75-3; 8, 52244-84-5; 10, 74666-77-6; RhCl_3 , 10049-07-7; WOCl_4 , 13520-78-0; EtAlCl_2 , 563-43-9; $[(\text{PPh}_3)_2\text{RhCl}]_2$, 14653-50-0; WO_2Cl_2 , 13520-76-8; WCl_6 , 13283-01-7; WO_3 , 1314-35-8; $\text{WO}(\text{O}-t\text{-Bu})_4$, 58832-09-0; WCl_5 , 13470-14-9; $\text{WCl}_3(\text{OC}_2\text{H}_5)_2$, 10382-47-5; $\text{WOCl}_3(\text{PEt}_3)_2$, 94942-78-6; WCl_4 , 13470-13-8; $\text{WCl}_4[\text{P}(\text{C}_6\text{H}_5)_3]_2$, 36216-20-3; WO_2 , 12036-22-5; $\text{WO}[\text{CHC}(\text{CH}_3)_3]_2\text{Cl}_2(\text{PEt}_3)$, 74658-29-0; $\text{WO}[\text{CHC}(\text{CH}_3)_3]_2\text{Cl}(\text{PEt}_3)_2$, 94859-74-2; bis(benzonitrile)palladium dichloride, 14220-64-5; 4-bromobenzyl bromide, 589-15-1; 4-bromotoluene, 106-38-7; 1-(4-bromophenyl)pentadecane, 94859-76-4; 1-bromotetradecane, 112-71-0; 4-*n*-pentadecylbenzoic acid, 62443-08-7; 4-(*n*-tetradecyloxy)benzoic acid, 15872-46-5; 4-hydroxybenzoic acid, 99-96-7; benzoyl chloride, 98-88-4; anisoyl chloride, 100-07-2; 2-heptene, 592-77-8; 5-decene, 19689-19-1; cyclopentene, 142-29-0; 1-bromocyclooctene, 4103-11-1; cyclooctene, 931-88-4; 1,2-dibromocyclooctane, 29974-69-4; 1-tritiumcyclooctene, 94859-77-5; tritium oxide, 14940-65-9; 1-deuteriocyclooctene, 87922-00-7; deuterium oxide, 7789-20-0; polystyrene, 9003-53-6; polyethylene, 9002-88-4.

Synthesis and Electrophilic Reactivity of Dicarboxylnitrosyl(cyclohexadienyl)manganese Cations: Double Nucleophilic Addition to Coordinated Arenes

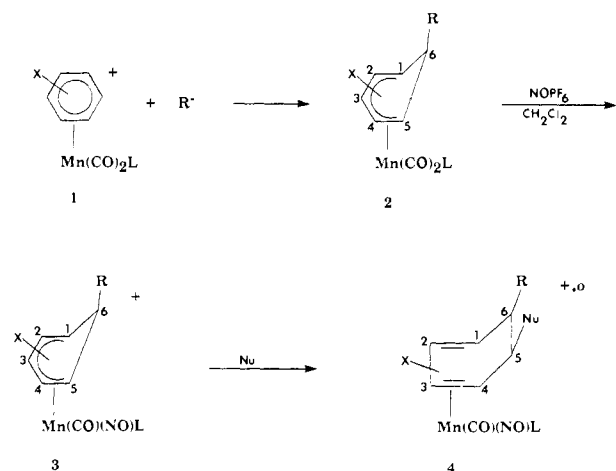
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Abstract: Treatment of (cyclohexadienyl) $\text{Mn}(\text{CO})_2\text{L}$ ($\text{L} = \text{CO}, \text{PBU}_3$) with NOPF_6 provides a convenient synthesis of (cyclohexadienyl) $\text{Mn}(\text{CO})(\text{NO})\text{L}^+$ cations (**3**; $\text{X} = \text{Me}, \text{OMe}$; $\text{R} = \text{H}, \text{Me}, \text{Ph}, \text{CN}, \text{CH}_2\text{COCMe}_3$; $\text{L} = \text{CO}, \text{PBU}_3$). Reaction of **3** with nucleophilic reagents gives attack at the ring to yield (cyclohexadiene) $\text{Mn}(\text{CO})(\text{NO})\text{L}$ complexes (**4**). Phosphorus and nitrogen nucleophiles add to **3** in a regio- and stereospecific manner (exo at C-5). Hydride donors add to **3** stereospecifically endo to the metal; **3** is the first class of coordinated cyclic π -hydrocarbon complexes that reacts with hydride in this manner. While $\text{NaCH}(\text{CO}_2\text{Me})_2$ reacts with **3** in the normal way to give exo addition, many other carbon donor nucleophiles react by what appears to be a single electron-transfer pathway that ultimately gives a variety of products, including (cyclohexadienyl) $\text{Mn}(\text{CO})_2\text{L}$. Ways to eliminate the undesirable side reactions with carbon donors are discussed. Overall, this report describes a simple procedure for the manganese-mediated conversion of coordinated arenes to difunctionalized coordinated cyclohexadienes by the addition of a nucleophile to (arene) $\text{Mn}(\text{CO})_2\text{L}^+$ to give **2**, reaction with NOPF_6 to give **3**, and finally addition of a second nucleophile.

The electrophilic activation of π -hydrocarbons by coordination to a transition-metal moiety represents a fundamental process in organometallic chemistry. Studies of nucleophilic addition to π -hydrocarbons activated in this manner have led to significant synthetic and mechanistic applications.¹ With cyclic π -hydrocarbons the best known reactions involve the addition of a single nucleophile to a coordinated arene or cyclohexadienyl ring to give monofunctionalized products. The addition of two nucleophiles to coordinated rings would be a synthetically useful reaction, particularly if the two nucleophiles could be varied independently. Not surprisingly, such double additions are rare because the electrophilicity of the π -hydrocarbon is weakened or lost after the first nucleophile adds. However, we recently discovered² what appears to be a general procedure for the addition of two nucleophiles to coordinated arenes to yield difunctionalized coordinated cyclohexadienes. Scheme I illustrates the process. To effect double addition to the arene in **1**, the complex obtained after the first addition must be reactivated. NOPF_6 performs this function cleanly by converting **2** to **3**, which then reacts with a

Scheme I



second nucleophile (Nu) to give the diene. In this paper we report details of the chemistry in Scheme I.

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