DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 9

PREPARATION AND CHARACTERIZATION OF NEW ORGANOMETALLIC COMPOUNDS SYNTHESIZED BY USING METAL VAPOURS

BY
TUULA ASUNTA

Academic Dissertation
for the Degree of
Doctor of Philosophy

Jyväskylä, Finland 1980
ISBN 951-678-408-9
ISSN 0357-346X

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 9

PREPARATION AND CHARACTERIZATION OF NEW ORGANOMETALLIC COMPOUNDS SYNTHESIZED BY USING METAL VAPOURS

BY
TUULA ASUNTA

Academic Dissertation
for the Degree of
Doctor of Philosophy

To be presented by permission of the Faculty of
Mathematics and Natural Sciences of the University
of Jyväskylä for public examination in Auditorium
S-212 of the University on November 20, 1980,
at 12 o'clock noon.

Jyväskylä, Finland 1980
ISBN 951-678-408-9
ISSN 0357-346X

URN:ISBN:978-952-86-0155-5
ISBN 978-952-86-0155-5 (PDF)
ISSN 0357-346X

University of Jyväskylä, 2024

PREFACE

This work was carried out at the Department of Chemistry, The Pennsylvania State University during the years 1976-1978 and at the Department of Chemistry, University of Jyväskylä during the years 1978-1980.

The subject was proposed by professor Philip S. Skell, Ph.D., The Pennsylvania State University, USA. I am very grateful for his help. Without his inspiring advice and critisism this work would not have materialized.

Also owe thanks to my coworkers, especially to Mr. Jerry Dobson, Ph.D., now the Research Director of Cyprus Metallurgical Processes Corporation, Tucson, Arizona, for his unselfish help and advice both in the practical and theoretical area and to Mr. Loren K. Beard Jr. B.Sc. for all his numerous helpful advice and optimism at difficult times. Mr. Beard also corrected the language of this text.

I was fortunate to have professor Jaakko Paasivirta, Ph.D., the Head of the Department of Chemistry, University of Jyväskylä as my supervisor during the interpretation of the results. I am very grateful for his experienced help.

My sincere thanks to the pre-inspectors of this work, professor Jorma Eloranta, Ph.D., Department of

Chemistry, University of Jyväskylä and professor Wolfgang Herrmann, Ph.D., University of Regensburg, FRG. Their encouraging critisim helped me to improve the manuscript.

I want to thank Mrs. Maija-Leena Kiiveri for typing the text in its final form and Mrs. Liisa Virkki for running some NMR spectra.

gratefully acknowledge the generous financial support of this research by the Air Force Office of Scientific Research, USA, Neste Oy Foundation and Eemil Aaltonen Foundation.

Last, but not least, my warm thanks to my husband for his support and help during these four years.

Jyväskylä, August 1980

Tuula Asunta

CONTENTS

ABSTRACT

A method to vapourize thorium metal, which had not been employed previously, was developed and the method of vapourizing zirconium metal was improved.

Several new organometallic compounds were synthesized using the metal atom vapourization technique. The vapour reactions of thorium, zirconium and tungsten with several different ligands were examined.

The structures of the new compounds were elucidated mainly from their ^{1}H NMR, ^{13}C NMR, IR and Mass spectra. Some of the products were investigated by elemental analysis and molecular weight determinations.

The application of thorium vapour to organometallic synthesis proved disappointing. More fruitful investigations arose from the study of zirconium vapour. The first examples of metal vapour reactions leading to oxidative addition of zirconium atoms to carbon-hydrogen and carbon-carbon bonds of alkanes at cryogenic temperatures were presented. This kind of behaviour is unique among the metal atoms studied up to this time. An investigation of an interesting organometallic compound derived from zirconium and pentamethylcyclopentadiene was carried out. Several previously unknown arene complexes of tungsten and zirconium as well as the first example of the novel zerovalent six-coordinate

complex hexakis(diethylaminodifluorophosphine)tungsten were prepared.

High vacuum and inert atmosphere methods were used for handling these air sensitive compounds.

INTRODUCTION

A gaseous atom of any element except the noble gases may be expected to be more reactive than the normal form of the element for two reasons. First, the atom can react faster because it has minimal steric requirements and generally has readily available electrons. Second, the atom has a species of higher energy than the normal state of the element.

The basic strategy in metal atom syntheses is to codeposit the metal atoms with a large excess of reactant, thereby promoting reaction between the metal atom and the substrate and suppressing recombination to the bulk metal. It is believed that only ground state atomic thorium, zirconium and tungsten were produced in the course of this work or that at least atoms would be at ground state when touching on the liquid nitrogen cooled walls of the reactor.

The role of organometallic metal derivatives in homogenous catalysis is well known and has been thoroughly investigated in recent years. Among the catalytical reactions promoted by organometallic complexes, the stereospecific polymerization of unsaturated monomers has received particular attention reaching relevant results, not only from a theoretical point of view, but also for the development of new industrially important polymerization processes. The reaction of metal atoms with organic substrates offers a useful path to complexes which are not accessible by conventional syntheses.

A large number of organometallic compounds has been synthesized in different ways using a great variety of metals and ligands. The metal atom vapourization technique offers a straightforward, one-step route to many organometallic compounds; in many cases the products do not require further purification. Moreover, the metal vapour technique uniquely permits the study of the fundamental interactions between metals and organic molecules in the absence of other supporting ligands or solvents.

1. The purpose of this study

The purpose of this study was to learn the metal atom vapourization technique, to study the low temperature chemistry of several metal atoms and to elucidate the structures of some new organo-thorium, -zirconium, and -tungsten compounds.

The study presented in this thesis was mainly carried out in the USA by using the metal atom vapourization apparatus developed by P.S. Skell et. al.[1,2,3] The main reason for selecting the metals used in this work was that they had not been used much by previous workers.

The first metal investigated was thorium. It seemed reasonable to employ those ligands which were expected to form stable complexes, like they did with some other metals such as iron, molybdenum, nickel etc. studied previously in the laboratories at The Pennsylvania State University.

The second choice was zirconium which was one of the less studied metals and then tungsten was picked mainly because it was expected to form complexes with the aminofluorophosphine. The reactivity of the latter was an object of my interest and the possible products were excellent models for structure determination by multinuclear NMR.

2. The development of the metal atom vapourization technique

A high boiling point implies strong bonding between atoms. These strong bonds must be overcome for reactions to occur in which an atom is detached from its condenced phase form. Only reagents which can engage the atom in a reaction sufficiently exothermic to overcome these forces can react. When a substance has vapourized these forces are overcome, and an atom unreactive in condenced phase becomes highly reactive. The higher the boiling point, the less will the chemical properties of the bulk material serve as a useful guide for the behaviour of the free atoms.

The development of the metal atom vapourization technique began with the development of atomic carbon chemistry in the 1960's when Wescott solved the problem of producing and reacting carbon atoms as described by Skell et al.[1] After that the method of producing atomic carbon was used in the study of the chemistry of this species in reactions with organic molecules. The method is described in several papers.[1,4,5] Carbon was vapourized either by using an arc or by resistive heating, and the hot species were then transferred to a cold zone across a vacuum which insulated the hot source from the site of the reaction.[6] The residual pressure 1.3×10^{-3} Pa (10^{-5} Torr) and the dimensions of the container were chosen such that the mean free path was much greater than the distance from the hot source to the cold reaction zone, thus avoiding gas phase reactions.

Skell and his coworkers[5] expected that the reaction of a saturated hydrocarbon with a carbon atom produced in a low intensity carbon arc would lead to a monoalkylcarbene by insertion into a carbon-hydrogen bond and they started a wide study in that area. Their first studies dealt with the reactions of atomic carbon with hydrocarbons,[4,5] but were expanded to deal with reactions of carbon with alcohols,[7] halocarbons,[8] carbonyl compounds and epoxides.[9]

The good results in the area of atomic carbon awakened a desire to study the reactions of ground state atomic metals. By using the method employed in studying carbon atoms, platinum atoms were generated under a high vacuum and deposited simultaneously with a large excess of substrate on the liquid nitrogen cooled walls of the reactor.[10] Propene, 1-butene and allyl chloride were found to react with platinum atoms. In 1972 Skell and Girard[11] succeeded in obtaining organomagnesium compounds using this same system. After that the use of high-temperature species as synthetic reagents has developed very quickly and the variety of metals used has expanded rapidly.[4,11]

3. Stability of transition metal-carbon bond

A definition of stability in the case of organometallic compounds is: A compound is stable when it resists chemical change, whether it be by heat, hydrolysis, oxidation, reduction or any other process.[12] Transition metals do not form organometallic compounds in the same way as most other metals. They differ from other metals in that the d-orbitals in their penultimate shells are in an energy level close to that of their valency s- and p-orbitals. For the formation of stable organometallic compound it is essential to have more than a certain minimum difference in energy between the highest and the lowest electronic level.[13] In most transition metal compounds this minimum is not attained. The above theory of Chatt and Shaw is widely accepted,[14] eventhough it has recently been questioned.

The range of kinetically stable organic compounds of transition metals has been found to be wider than had been expected formerly.[15] Chatt and Shaw[13] had difficulties explaining the existence and stability of transition metal-organic compounds against the common belief that metal-carbon bonds were weak.[16]

Nowadays there is no reason to expect inherently weak metal-carbon bonds. They are not in any way qualitatively different, for example, from metal-hydrogen, metal-metal, or metal-nitrogen bonds.[17] The stability of complexes depends on various factors, the influence of which is not always understood and cannot a priori be predicted and explained.[18]

Semiempirical methods of the Hückel and Extended Hückel type are widely used in transition metal chemistry to explain bonding abilities.[19] For considering the general features of organotransition metal chemistry Heck's book is well qualified.[20]

4. Bonding in actinide complexes

The actinide elements derive their unique properties from the filling of an inner electronic level, 5f shell. Up to 1940 there was little or no evidence for the use of f orbitals in covalent bond formation. Kimball[21] considered their use in a few cases. The real discussion about the possible f-shell covalency in the actinide elements started in 1950. Since then it has been widely studied and discussed in several papers.[22,23] While the formation of Π-bonds enhances the participation of the f orbitals, conversely the contribution of the f orbitals to the bonding will strengthen the Π-bonds.

5. Some general features of cyclopentadienyl and arene metal compounds

The chemistry of compounds formed between transition metals and the cyclopentadienyl group, benzene and related aromatic systems, is widely discussed in the book written by Cotton.[24] The book gives the present knowledge about this type of compounds, which is now so extensive that even a brief reference to all of the papers would require writing another book. Both Π-and σ-types of bondings have been found in these compounds. The nature of the bonding in metal sandwich compounds and theoretical studies of the nature of the metal-ring bonding have been examined. The molecular orbitals formed by combining the metal orbitals and the ring orbitals of cyclopentadiene have been of interest to many investigators and are widely studied in Cotton's book. The application of molecular orbital theory to different complexes of this type has been carried out and a lot of data is available.[25]

II EXPERIMENTAL

1. Instrumental methods

1.1. *Infrared spectrometry*

Infrared spectra were recorded on a Perkin Elmer model 621 spectrometer either as a film between KBr windows or as pellets prepared from the compound and KBr (about 1.5 mg/200 mg). The registered range was from 4000 to 400 cm^{-1}.

1.2. ^{1}H, ^{13}C, ^{31}P *and* ^{19}F *NMR spectrometry*

Proton magnetic resonance spectra were recorded with a Varian 60 A Spectrometer.

Carbon-13 magnetic resonance spectra were obtained with a JEOL Model FX-60 Spectrometer. Tetramethylsilane (TMS) was used as an internal standard and chemical shifts were reported in reference to TMS.

Phosphorus-31 magnetic resonance spectra were recorded on JEOL Models FX-60 and FX-100 Spectrometers. Chemical shifts were calculated relative to an 80% H_3PO_4 external reference solution.

Fluorine-19 magnetic resonance spectra were recorded on a JEOL Model SP-100 Spectrometer. Chemical shifts were calculated in reference to $CFCl_3$ internal reference. Fluorine resonance spectra were recorded by Miss L. Heino.

1.3. *Mass spectrometry*

Mass spectra were recorded on an AEI Model MS 902 mass spectrometer or on a Finnican 3200 GC-MS system with a Finnican 6000 data handling system, using either a direct inlet system or GC depending on the sample. The electron impact ionization voltage was 70 eV, and the ionization chamber was approximately 373 K. When measuring isotope ratios, greater accuracy was obtained by slow scanning so that the peaks had "Flat Tops".

The computer program "CAMFAC" written by W.Brugger and J. Campana [26] was used for identifying isotope patterns.

1.4. *Molecular weight determination and elemental analysis*

Molecular weight determinations were carried out cryoscopically in isobutane using a method modified from several formerly used methods[27] by Dr. Dobson[28] or by using high resolution mass spectrometry.

The method of determining the molecular weight was based on Raoults law. The apparatus used is shown in Fig. 1.

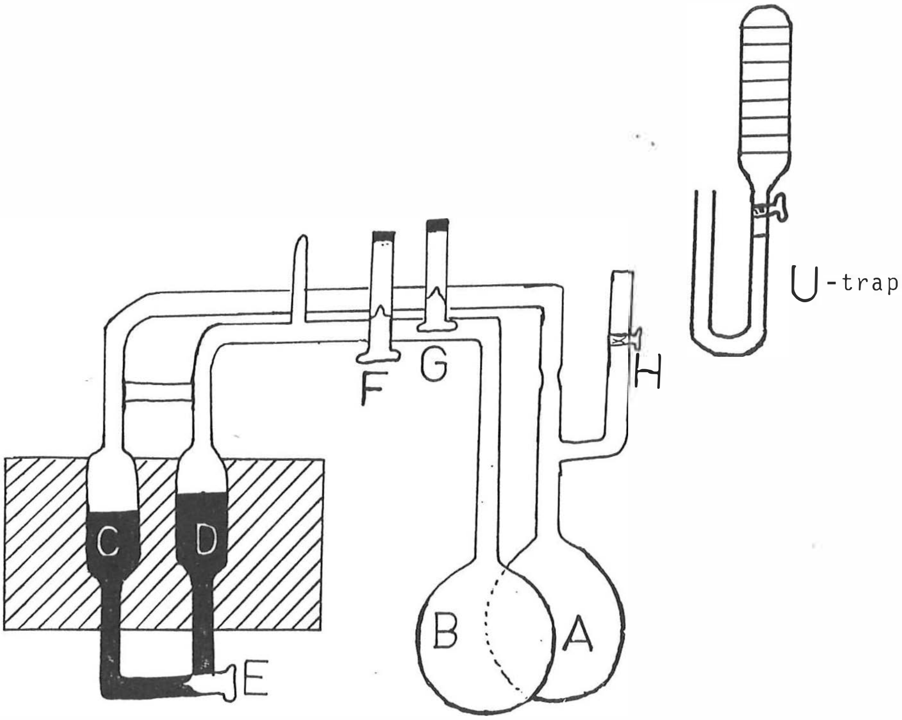


Fig. 1. The apparatus used in determining the molecular weight.

It consisted of two bulbs A and B which could be closed by stopcocks. A weighed amount of the product was transferred to the bulb A in pentane solution and the solvent was removed by vacuum distillation. A bulb containing pure isobutane was connected through the vacuum line to joint G and a known amount of isobutane was introduced to the liquid nitrogen cooled bulb A. The exact amount of addition was measured by weighing the isobutane bulb. The same amount of isobutane was introduced into the bulb B using joint F. A U-trap was used to make sure that the isobutane distilled into bulbs was in liquid phase. Bulbs A and B were then cooled using a water-ice bath to zero degrees. The stopcock E between mercury bulbs C and D was opened and the difference in mercury levels in bulbs C and D was measured using cathetometer. The average of three or four measurements was registered to make sure that equilibrium had been established. After that additional isobutane was introduced into both bulbs and a second reading was taken. The procedure was repeated several times.

The molecular weight, MW, of the sample was calculated from the formula:

$$MW_{sample} = \frac{(P_o - \Delta P)W_{sample} \times (MW)_{solvent}}{\Delta P \times W_{solvent}}$$

where P_o is the vapour pressure of isobutane at 273 K. $W_{solvent}$ and W_{sample} are the weights of the solvent and sample used. $(MW)_{solvent}$ is the molecular weight of the solvent and ΔP is the difference between the mercury levels at zero degrees. The results of all measurements were averaged to give the final value of $(MW)_{sample}$.

Elemental analyses were made either by high resolution mass spectra using the computer program "CAMFAC" or using combustion analyses designed by Dr. Dobson.[28]

1.5. *Gas- and column chromatography*

Vapour phase chromatographic analyses were performed on a Varian Model 2400 Gas Chromatograph using an SE-30 column (15 m x 3 mm). Materials used in column chromatography were florisil, silica gel and aluminium oxide.

2. Illustration of the method

2.1. *The metal atom vapourization technique used in this work*

The apparatus used to run thorium, zirconium and tungsten vapour reactions was basically the same as described previously in several papers.[1,2,3,29,30] The diagram of the thermal vapourization reactor used in the course of this work is presented in broad outline in Fig. 2. It consisted of the work-up line and the reactor part. The reactor section consisted of a 40 x 15 cm diameter cylindrical pyrex reaction flask connected by means of a 5 cm pyrex pipe to an 80 dm^3/min silicone oil diffusion pump backed by a mechanical forepump. The flask was equipped with two water cooled stainless steel electrodes which led into the reactor through well degassed "O" ring seals. These electrodes served to carry the electrical current used for thermal vapourization reactions. In the middle of the flask there was an inlet tube attached to the workup line. Nichrome wire was wound around the inlet tube to make it possible to heat it using a Variac when necessary. The flow of substrate vapour from the workup vacuum line to the inlet tube was controlled by means of either one or two mercury flowmeters with teflon valves. When high boiling substrates were used, provisions were made for direct flow of the vapour through an open 6 mm stopcock into the inlet system. The perforated inlet tube was positioned so as to provide an evenly deposited matrix of substrate in the zone of vapourized metal deposition.

The metal was vapourized under high vacuum so that the vapour species could move away from the source without intermolecular collisions, which could cause aggregation. Pressures of 10^{-3}-10^{-4}Pa (10^{-5}-10^{-6} torr) were routinely achieved and were measured with an ionization gauge. The reactor was evacuated and out-gassed for several hours and cooled with liquid nitrogen before running a reaction. The metal vapour reacted with organic compounds at liquid nitrogen temperature, 77 K or during warm up, provided that thermodynamic and kinetic factors were favourable. To preclude the possibility of gas phase collisions and substrate pyrolysis the reactions were carried out at pressures between 1×10^{-4} - 4×10^{-3}Pa (1×10^{-6} - 3×10^{-5}torr).

While the metal was evaporating the vapour of organic substrate passed into the chamber and condensed on its walls so rapidly that high vacuum conditions were maintained. Even with substantial rates of addition of organic compound only a very small amount of it interacted with the metal vapour species before the moment of condensation on the walls. The internal pressure of the reactor should not be allowed to exceed 10^{-2}Pa (10^{-4}torr). At pressures above 10^{-2}Pa (10^{-4}torr) the mean free path of substrate molecules is short enough to result in pyrolysis of substrate on the wire. Pyrolysis of substrate causes a weight increase of the wire and premature burnout due to carbide formation.

The reactor was directly connected to the workup line by a 6 mm stopcock. The workup line consisted of a glass tube and U-traps in series and was equipped with (in addition of the two flowmeters already described) gas storage bulbs, a reflux condenser,

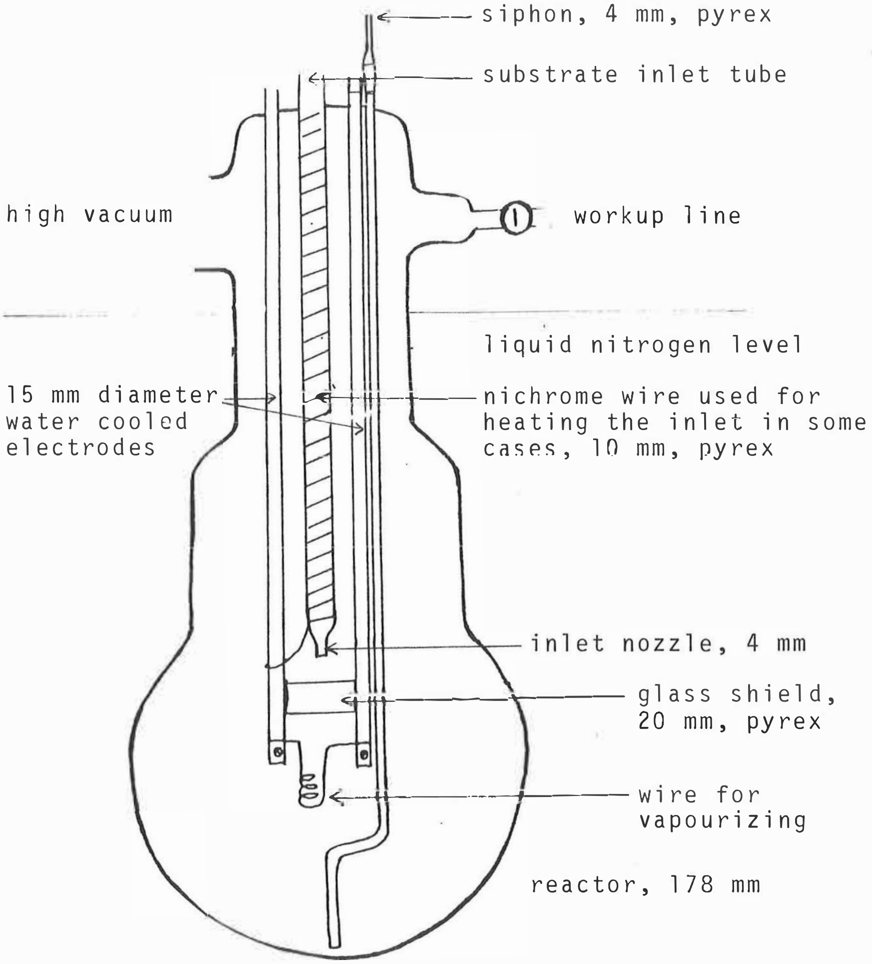


Fig. 2. The thermal vapourization apparatus.

a Toepler pump, a manometer and a thermocouple pressure gauge. It was evacuated by means of a mercury diffusion pump backed by a mechanical forepump. Pressures of 0,1 Pa (1 x 10^{-3}torr) were routinely obtained.

2.2. *Description of the method and apparatus developed to vapourize thorium metal*

The radioactivity of thorium metal puts some restrictions on its use. A good method to vapourize thorium metal has not previously been published. The method developed during the present work makes it possible to get 200 - 400 mg thorium metal on the surface of a tantalum (or tungsten) wire, from which it was possible to vapourize 100 - 300 mg of thorium during 30 - 60 minutes.

A diagram of the system developed is presented in Fig. 3. It consists of a 3 x 20 cm quartz tube equipped with a joint and a top part with a joint and a side arm with a vacuum stopcock and a joint. A smaller perforated glass tube equipped with a copper tube for carrying the cooling water and the current was connected using epox hardener. The other end of the copper tube is closed and a small piece of copper plate is joined in it. Another flat copper plate is joined on the inner glass tube and the wire which to be coated will be fitted between these two copper electrodes.

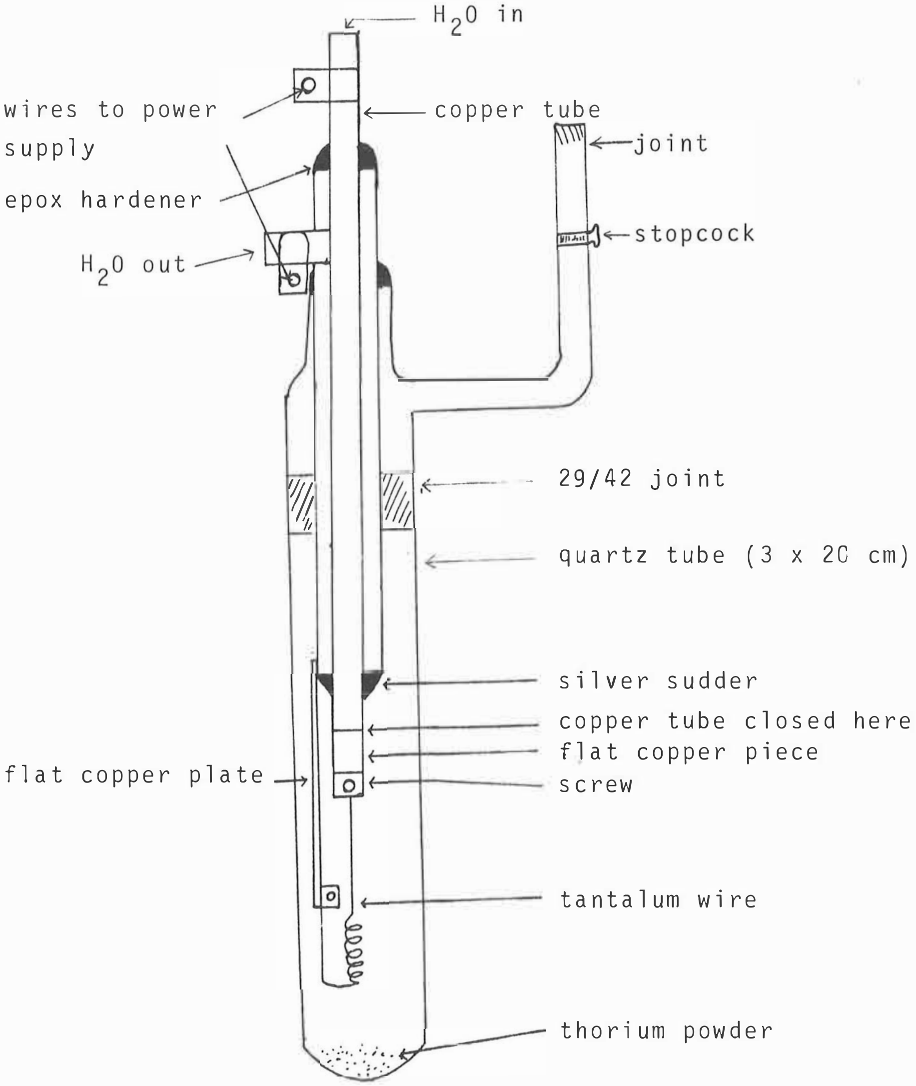


Fig. 3. The system used in coating wires with thorium metal.

When starting to make a wire for a reaction the tube was connected to the vacuum line and evacuated. After about 10^{-3}Pa (10^{-5}torr) vacuum was achieved, the apparatus was connected to the power supply and by using a small current first (10 - 20 A) the wire was cleaned and weighed. Thorium powder was then placed in the bottom of the quartz tube in the dry box and the tube was evacuated. Using a current of about 34 A (~ 55 V) thorium powder was shaken several times inside the tube in order to get it in contact with the hot wire. When the wire was coated with thorium powder a current of 45 A (~ 80 V) was used to melt the metal on the wire. After cooling the wire could be removed from the chamber and loaded into the reactor without fear of oxidation. A good water flow through the electrodes during the operation is necessary.

3. Composition and purity of the reactants

All ligands and solvents were degassed and dried before use. The solvents used were mostly dried by refluxing them over Na/K (1:3) alloy for 6-12 hours. THF was dried by distillation over Mg-chips. The purity of the compounds was tested using ^{1}H NMR and IR spectra.

1,3-cyclopentadiene (98 %) from Aldrich Chemical co.

was dried over molecular sieves, which were heated beforehand to eliminate impurities, and distilled at 315 K just before use to be sure that it had the monomeric structure.

Cyclooctatetraene (97 %) from Aldrich Chemical co. was distilled at 414 K using an oil bath and dried over molecular sieves before use.

trans-2-butene from Matheson Gas products, California, was dried without further purification.

Bromine (99,8 %) from Baker analyzed reagent.

n-butyllithium solution in hexane from Merck for synthesis.

n-butylbromide from Fischer Scientific company.

Silica gel Davidson chromatographic grade H, 60 - 200 mesh.

Alumina (Al_2O_3) adsorbtion from Fischer Scientific company for chromatographic analysis, 80 - 200 mesh.

Florisil from Fischer Scientific company.

Benzylchloride (99,6 %) from J.T. Baker Chemical co.

Methylbenzoate from J.. Baker Chemical co, for chemical purposes.

Chlorobenzene from Eastman Organic Chemicals for chemical purposes.

Neopentane research grade 99,9 %, dried by distilling through a 195 K trap.

Isobutane, research grade, dried by distilling through a 195 K trap.

Tert-butylbenzene (99 %) from Aldrich Chemical co.

Diethylphosphoroamidous difluoride was obtained from Dr. J. Dobson.[28] Its structure and purity were confirmed by GC and NMR.

Cu(*I*)I from Fischer Scientific co.

Tantalum wire, 0,5 mm diameter, from General Electric.

Thorium powder (99,9 %) 100 mesh, from Ventron alpha products.

Zirconium powder (99,9 %) GMS from Pfaltz and Bauer Inc.

Tungsten wire, double strand of 0,75 mm type 3D - 218 from General Electric.

4. Preparation of two ligands used in the reactions

4.1. *Preparation of 1,2,3,4,5-pentamethylcyclopentadiene*

Synthesis of 1,2,3,4,5-pentamethylcyclopentadiene was carried out in four steps starting from *trans*-2-butene. The reaction of *trans*-2-butene with bromine gave *meso*-2,3-dibromobutane in 76 % yield.[31] Treatment of dibromobutane with KOH solution in ethylene glycol gave *cis*-2-bromo-2-butene[31] in 64 % yield, which in a reaction with lithium wire gave 3,4,5-trimethyl-2,5-heptadien-4-oli.[32,33] The concentrate of the latter in a reaction with *p*-toluenesulfonic acid in dry diethylether gave 1,2,3,4,5-pentamethylcyclopentadiene[33] in 30-51 % yield. The product was purified by fractional distillation and identified using ^{1}H [34] and ^{13}C NMR[35] (Table 1).

4.2. *Preparation of n-butylcyclooctatetraene*

N-butylcyclooctatetraene was prepared in several steps starting from cyclooctatetraene. *N*-bromocyclooctatetraene was prepared according to Cope and Burg[36] or using a modified method.[37] The purity of *n*-bromocyclooctatetraene was checked before further use by IR[36] and ^{1}H NMR.[37,38] The reaction of *n*-butyllithium in hexane solution with a catalytic amount of Cu(*I*)I gave *n*-butylcyclooctatetraene.[37,38,39] The *n*-butyllithium used was either prepared as described formerly[40,41] or obtained from Foote Mineral Co. *N*-butylcyclooctatetraene was identified using IR[40] and ^{1}H NMR spectra[37] and refractory index.[41]

5. NMR and IR spectroscopy procedures

Samples for infrared spectra were made in the following way: About 1,5 mg of dry purified sample was finely ground in a mortar and pestle with 150 mg of KBr in the nitrogen filled dry box. The mixture was introduced to a pellet-maker and quickly pressed under a good vacuum. Higher speed was used while running the spectra to eliminate the possibility of the sample contact with air.

Samples for NMR spectra were also prepared inside the dry box. Dry, degassed solvent and dry purified sample were transferred into the dry box and put inside an NMR-tube equipped with a side arm with stopcock (Fig. 4). Then the tube was taken out and frozen using liquid nitrogen. Using a nitrogen stream through the side arm the tube was connected to the vacuum line and sealed under vacuum by melting.

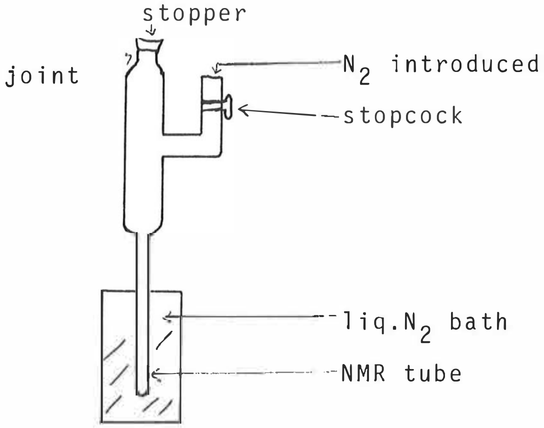


Fig. 4. The apparatus for making NMR samples.

6. Optimized conditions for the vapourization of metals used in this work

Optimum circumstances to vapourize sufficient amounts of metals were first tested without using any ligands. Thorium does not reach an appreciable vapour pressure in the molten state until heated well above 1 800 K and it was vapourized from the wire at approximately 2 400 K. A 0,75 mm double strand tungsten wire covered with thorium, made as explained previously was easily heated with currents of 40 - 44 A (15 - 17 V) to temperatures suitable for vapourization of thorium in the 10^{-3} Pa (10^{-5} torr) vacuum at rates of 0,5 - 1 mmol/h. When tantalum wire was used instead of tungsten wire, corresponding currents were 50 - 54 A (18 - 20 V). The currents used depended somewhat on the length of the wire. Wires about 20 cm long were usually used. Temperatures corresponding to certain currents were measured using an optical pyrometer.

A double strand of 0,75 mm tungsten wire was coated with zirconium powder by making a water slurry of the metal powder, dipping the wire in the slurry and then heating it under high vacuum until the metal powder melted. Electric current of 35 A (13 V) for 1 - 2 seconds was enough to melt zirconium metal on a wire. This procedure made it possible to get 100 - 200 mg of zirconium metal on the tungsten wire. A current of 30 - 40 A (13 - 15 V) was enough to vapourize zirconium atoms during cocondensation at the rate of 1 - 2 mmol/30 minutes. The vapourization temperature was approximately 2 000 K.

A 0,75 mm tungsten wire of 20 cm length was easily heated with currents of 45 - 50 A (14 - 20 V) to temperatures suitable for vapourization in 10^{-3} Pa (10^{-5} torr) vacuum at the rates of 1 - 2 mmol/30 minutes. The vapourization temperature was approximately 3 200 K.

7. Preparation of organometallic compounds by using the metal atom vapourization technique

All compounds were prepared several times and the yields varied considerably between preparations. Different column chromatographs were used for purification. Gas chromatograph was found useless in most cases. Recrystallization proved to be a good method for purification of the compounds. Oily products were many times found too difficult to identify. They seemed to be polymeric (mass spectrometry, molecular weight). Most of the compounds were very air sensitive which limited the available purification methods.

7.1. *The reaction of thorium atoms with cyclopentadiene*

Over a period of 30 to 60 minutes thorium vapour (80 mg, 0,35 mmol to 175 mg, 0,75 mmol) and cyclopentadiene (4,0 g, 60,5 mmol to 8,0 g, 121,0 mmol) were continuously deposited on the liquid nitrogen cooled walls of an evacuated (3×10^{-4} - 5×10^{-3} Pa) reaction flask. A small amount of a yellow product was formed on the walls of the reactor during vapourization. After completion of the codeposition the reaction flask was allowed to warm up to room temperature. The excess cyclopentadiene was pumped off. The reactor was cooled to 77 K and 10 - 30 ml of dry degassed solvent was added through the inlet system to dissolve the black reaction product formed. The product was not soluble in pentane, chloroform, dimethylchloride, acetone, ether or alcohol, but some of it was removed from the reactor by suspending it in various solvents. The solvents and the solid part were investigated separately though it seemed apparent there was nothing soluble. Because of the insolubility of the product the exact amount of the product was not determined.

7.2. *The reaction of thorium atoms with cyclooctatetraene (COT)*

Over a period of 40 to 100 minutes thorium vapour (100 - 300 mg, 0,43 - 1,30 mmol) and cyclooctatetraene (4,0 - 8,0 g, 38,5 - 77,0 mmol) were continuously deposited on the liquid nitrogen cooled walls of an evacuated (3×10^{-4} - 3×10^{-3} Pa) reaction flask. The flask containing COT was heated to 353 K with an oil bath or a heating mantle and the inlet heating system was warmed sufficiently to prevent condensation of the substrate in the inlet. When the reaction was over, the light yellow matrix was melted and the excess cyclooctatetraene was pumped off. After recooling the reactor some solvent was added. Pentane, chloroform, benzene, diethylether and dimethylsulfoxide were the solvents used. There were two differently coloured parts in the reactor: the black part and the yellow part. Neither of them was soluble. Some solvent could be used for washing the reactor and as a carrier liquid to get the products out of the reactor. The yellow part was somewhat soluble in an acetone-pentane mixture.

7.3. *The reaction of toluene-solvated thorium atoms with n-butylcyclooctatetraene (n-BuCOT)*

Toluene solvated thorium atoms were tried to use as intermediates in the preparation of organometallic compounds.[42] Two different synthetic techniques were used: a) treatment of metal-toluene matrices at 77 K with ligand followed by slow warming to room temperature or b) warming of the metal-toluene matrices to the desired temperature followed by addition of the ligand.

During a period of 25 minutes 1,50 mmol of thorium was vapourized from a tungsten wire and codeposited with 5 ml of toluene on the liquid nitrogen cooled walls of an evacuated ($6 - 9 \times 10^{-3}$ Pa) reaction flask. After completion of the codeposition vapourization was stopped and 3 mmol of BuCOT, heated to 321 K using an oil bath, were introduced into the reactor using the inlet heating system (30 V). Then the reactor was allowed to warm up to room temperature. During melting the colour of the matrix changed from green to brown, showing that some kind of reaction happened. After the warm up the reactor was cooled again and more toluene (20 ml) was introduced to dissolve the yellow-brown product formed. It was not soluble in toluene but it could be siphoned out with it. The product was not soluble in pentane, hexane, heptane, ether, acetone, ethanol, toluene, benzene or tetrahydrofuran. All solvents were removed by vacuum distillation and the dry insoluble solid was investigated.

7.4. *The reaction of zirconium atoms with cyclooctatetraene*

Over a period of 20 minutes zirconium vapour was codeposited with fifty fold excess of cyclooctatetraene on the liquid nitrogen cooled surface of the reactor. Each time vacuum problems occurred,caused, presumably, by pyrolysis and because of that the yields were very poor.

7.5. *The reaction of toluene-solvated zirconium atoms with n-butylcyclooctatetraene*

Toluene-solvated zirconium atoms were tried as intermediates as in the case of thorium (7.1). In a typical run 1 - 2 mmol of zirconium was cocondensed with 100 - 200 mmol of toluene and right after that 10 - 20 mmol of BuCOT was vapourized on the liquid nitrogen cooled walls of the reactor. An inlet heating system was used to prevent the condensation of the substrate in the inlet. When the reaction was complete a brown-yellow matrix formed on the walls of the reactor. The system was allowed to warm up to room temperature and the excess toluene and BuCOT were pumped away. The product was removed using 20 ml of pure toluene and siphoned into a schlenk tube through a frit. A small amount of black solid was left in the reactor and was identified as bulk metal. About 50 mg of orange powder was left in the schlenk tube when toluene was removed.

7.6. *The reaction of zirconium atoms with 1,2,3,4,5-pentamethylcyclopentadiene*

In a typical run 150 mg (1,6 mmol) of zirconium was cocondensed with approximately 20 ml of 1,2,3,4,5-pentamethylcyclopentadiene freshly made as described formerly (4.1). The reactor was evacuated and outgassed for several hours at 10^{-4}Pa before running the reaction. Pentamethylcyclopentadiene was warmed with an oil bath or a heating mantle up to 343 K and a mechanical stirrer was used to help fluent vapourization during the reaction. The orange condensate formed was filtered through a fritted-glass filter of medium porosity into a schlenk tube. The removal of the extra ligand in vacuo was carried out using the apparatus shown in Fig. 5. The orange reaction product was soluble in benzene, hexane, pentane and toluene. Toluene and pentane were used as eluents in column chromatography (silica gel columns). Finally the product was dried in a vacuo. The yield was 65 % based on vapourized zirconium.

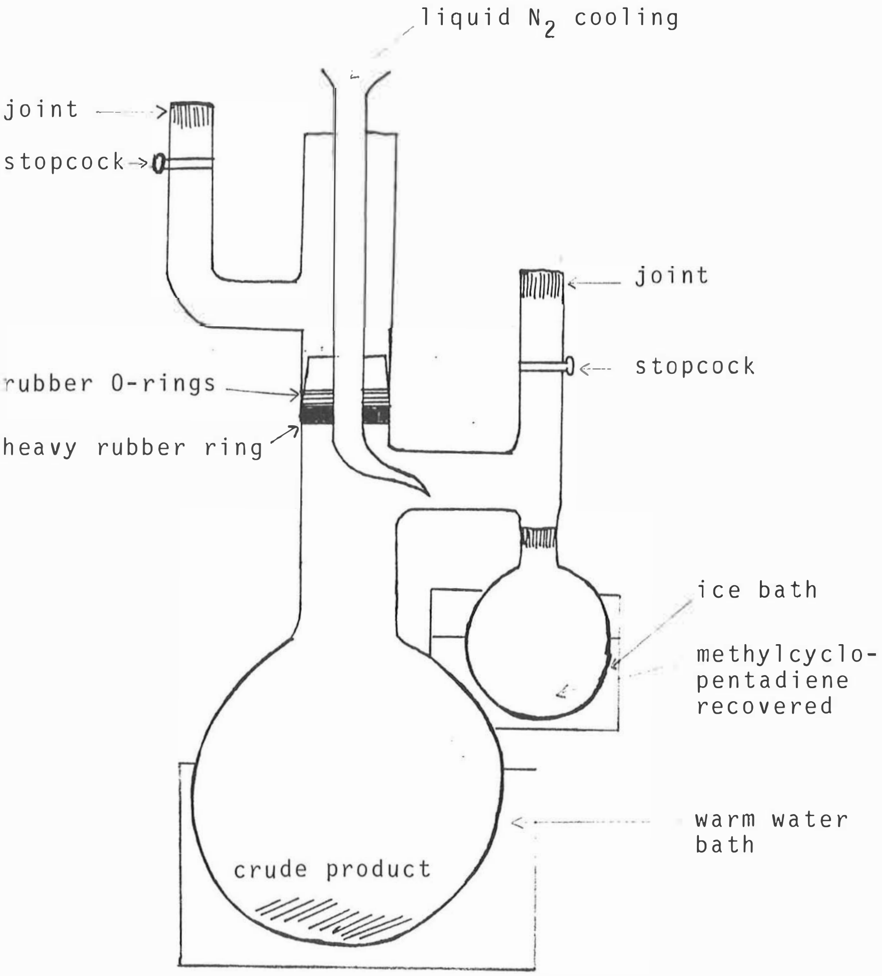


Fig. 5. The distillation apparatus used in purifying the products.

7.7. *The reaction of zirconium atoms with benzylchloride*

Over a period of 25 minutes an average of 0,5 mmol of zirconium was vapourized from the tungsten wire and cocondensed with 20 ml of benzylchloride. Beforehand it was checked by IR and GC to be sure that no water or alcohol was present in the benzylchloride used. During codeposition the colour of the matrix was orange. When the reaction was complete and the reactor was allowed to warm up, the colour of the product turned yellow. A small amount of HCl gas was found to develop during vapourization and warm up. It was collected by using the Toepler pump and measured by manometer. The product formed was siphoned to a schlenk tube with extra benzylchloride, which was then removed by vacuum distillation using water bath and 0,1 Pa vacuum. All of the benzylchloride was very difficult to remove because of the problem of thermal decomposition.[43] The product was dried under vacuum during a period of 24 hours using a 318 K water bath. The product was soluble in toluene, benzene, and CCl_4. It was dissolved in toluene, filtered and dried again. It was purified using column chromatography.

7.8. *The reaction of zirconium atoms with neopentane*

The vapourization of zirconium (1 - 2 mmol) and cocondensation of the metal atoms with neopentane (100 - 200 mmol) was carried out during a period of 25 minutes. The pressure varied from 1×10^{-4} to 4×10^{-3} Pa. A light brown matrix formed on the walls of the reactor during cocondensation. During warm up to room temperature it turned black. The excess neopentane was removed during the melting process. The recovered neopentane was found to contain only small amounts of impurities, which were present in the starting material. The black solid was hydrolyzed and the volatile products identified by gas chromatography and mass spectrometry as described in the paper published previously.[44]

7.9. *The reaction of zirconium atoms with isobutane*

At a pressure of 1×10^{-4} Pa isobutane (200 mmol) was codeposited with zirconium atoms during 20 minutes forming a colourless matrix. The final product was a black solid which was vacuum dried and hydrolyzed using D_2O. The products of the hydrolysis were identified using mass spectrometry and gas chromatography as described in the paper published previously.[44]

7.10. *The reaction of tungsten atoms with methyl benzoate*

Over a period of 45 minutes 20 ml methyl benzoate was cocondensed with an average of 300 mg of tungsten vapour on the liquid nitrogen cooled walls of the reactor. The inlet heating system was warmed using a 20 V potential (about 353 K) to prevent condensation of the substrate in the inlet. For this reaction the end of the inlet tube was changed to make it easier for the substrate to vapourize (Fig. 6.).

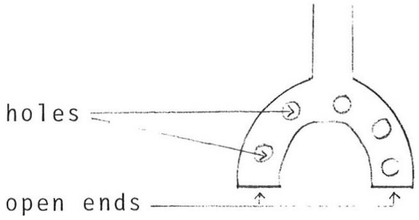


Fig. 6. The shape of the inlet used in this reaction.

The condensate formed was light orange. It was soluble in toluene and was siphoned out through the filter which stopped the bulk metal. Toluene and excess methyl benzoate were distilled away under high vacuum. The residue, a red powder, was slowly sublimed to a cold finger using a 423 K oil bath. The sublimed product was soluble in benzene and toluene. It was air sensitive. The yield was 10 % based on tungsten vapourized.

7.11. *The reaction of tungsten atoms with tert -butylbenzene*

Tungsten (2.5 mmol) was cocondensed with 20 ml of *tert* -butylbenzene during 20 minutes in a 9 x 10^{-3} Pa vacuum. A light brown matrix formed on the walls of the reactor. After the reaction was complete and the liquid nitrogen removed, the matrix on the walls turned darker. It was allowed to melt down and stay for a while at room temperature. Then 20 ml of toluene was rapidly introduced through the inlet to dissolve the product. The dark brown solution was siphoned from the reactor directly to the distillation apparatus shown in figure 5 through a fritted-glass filter. The black residue on the filter was unreacted bulk metal. Toluene and extra *tert* -butylbenzene were distilled away and the product was dried in a vacuo for four hours. Sublimation of the dry reaction product using a 393 K oil bath gave a green product. The yield was 10 % based on the amount of vapourized tungsten.

7.12. *The reaction of tungsten atoms with diethylaminodifluorophosphine*

Vapourization of an average of 400 mg tungsten was carried out during 20 minutes at an average pressure of ca 10^{-3} Pa and the metal vapour was condensed with

20 ml of pure diethylaminodifluorophosphine. When the reaction was over the reactor was allowed to warm up to room temperature and the extra ligand was pumped away using high vacuum. Then 20 ml of hexane was used to dissolve the product. The dark solution was siphoned to the schlenk tube through a thin filter and the solvent removed by vacuum distillation. Recrystallization from a hexane-toluene mixture (3:1) gave 160 mg of colourless crystals. The yield was 40 % based on vapourized tungsten. The other materials recovered were bulk metal and unreacted ligand.

III RESULTS AND DISCUSSION

1. Thorium vapour reactions

The first attempt made after developing a method of vapourizing reasonable amounts of thorium using short enough times and vacuums good enough to minimize the gas phase collisions of the metal atoms and pyrolysis of the substrate, was to allow thorium atoms react with cyclopentadiene. Several attempts proved that the product mainly constituted unreacted thorium metal which was confirmed by determining the exact quantity of thorium in the black part of the reaction product. Only a very minor part of the product was soluble in pentane, but no evidence of thorium being present in that part was found in spite of numerous attempts. Mass spectra showed no isotope patterns of thorium, and infrared spectra gave no further information. It was not possible to obtain an NMR spectrum because of the extremely low solubility of the product in any solvent. The soluble part was most likely a polymeric product and was not tried to identify more exactly because the quantities obtained in each experiment were insignificantly small.

Attempts to prepare cyclopentadienyl derivatives of thorium by using ordinary synthetic methods have also been only partially successful. Several derivatives have been prepared and analyzed. Fischer and Treiber[45] synthesized a product whose approximate composition was indicated to be $(C_5H_5)_4Th$. ^1H NMR of that compound showed only one signal.[46] The mass spectroscopic fragmentation pattern for this compound was presented later.[47] *Tris*(cyclopentadienyl)thorium (IV) borohydride has been prepared and was characterized by ^1H NMR.[48] Haar and Dubeck[49] also synthesized several thorium cyclopentadienyl derivatives in 1964. Ten years later *tris*(cyclopentadienyl)thorium was synthesized and characterized by elemental analysis, molecular weight determination, IR- and ^1H NMR spectroscopy.[50,51] A number of other cyclopentadienyl derivatives of thorium has been reported in the literature.[52,53] Many thorium cyclopentadienyl derivatives have turned out to be highly reactive.[52,53]

In order to see if thorium would react better with other ligands, cyclooctatetraene was used next. This compound has a nonplanar "tub" structure[54] with alternate single and double bonds. The experimental data concerning the complexation of actinides with cyclooctatetraene dianion $C_8H_8^{2-}$ are highly limited. The relative stability of *bis*(Π-cyclooctatetraene)-uranium, synthesized from cyclooctatetraene (COT) dianion and uranium tetrachloride by Streitwieser and Müller-Westerhoff[23] in 1968, made other investigators interested in the chemistry of complexes of same type.

The reaction of COT with thorium vapour yielded a black solid which was the main product, and also a light yellow material. The black part was identified to be unreacted thorium metal according to elemental analysis. The yellow material was soluble in an acetone-pentane mixture. For purification column chromatography and sublimation were tried. Florisil and silica gel columns were used. Sublimation at 443 K under vacuum (6×10^{-3} Pa) proved to be unfruitful. It only revealed that the product was not identical with the known *bis*(Π-cyclooctatetraene)thorium[55] because the latter was found to sublime at 433 K. Hydrolysis of the yellow product with ethanol proved that the amount of compound containing cyclooctatetraene ligands was extremely small. Gas chromatography column SE-30 was used to find out the hydrolysis products (standard: toluene).Because of the tiny amounts of the hydrolysis products they were not identified.

The spectral data were compared with those formerly presented in the literature for cyclooctatetraene thorium complexes. The IR spectrum of the yellow product showed no similarity to the spectrum reported for the well known complex $Th(COT)_2$.[56-58] The ^1H NMR spectrum reported for *bis* (Π- cyclooctatetraene)-

thorium[55] was also not the same as that obtained from the reaction product.

Various combinations of this reaction were carried out without any significant results. For example, the reactions of thorium with cyclooctatetraene in the presence of heptane, tetrahydrofuran, or toluene all gave very small amounts of an unidentified, insoluble, yellow-brown solid and bulk metal.

The main problems with the products of the thorium reactions seemed to be the small yields and the insolubility of the products in organic solvents. Several investigators had found that substituted compounds were more soluble in organic solvent than non-substituted[44,59,60] and therefore *n*-butylcyclooctatetraene (n-BuCOT) was used in several reactions. Reaction conditions were varied but none of them led to the expected results. No compounds similar to those of uranium, for example, 1,1'-diphenyluranocene or 1,1'-dibutyluranocene[59,61] were obtained. A series of substituted thorocenes prepared from substituted cyclooctatetraenes by using standard synthetic methods has just recently been communicated by LeVanda and Streitwieser.[62]

Toluene-solvated thorium atoms[42] had been found to be successful intermediates for the preparation of a variety of organothorium compounds. The method was applied to the reaction of thorium and *n*-butylcyclooctatetraene. The following complexes were expected to result: (toluene)Th(n-BuCOT), $(arene)_nTh(n-BuCOT)$ or $(n-BuCOT)_nTh$. The amounts of products obtained from these reactions proved to be so small that the reactions would have little importance either from a catalytic or synthetic point of view. The solubility of the product was not better either, as was expected. Based on the mass spectra it seemed obvious that the reaction product decomposed in the conditions where the spectra were run. The infrared spectrum of the yellow-brown solid was compared to those given in the literature for $(COT)_2Th$ and $(COT)_2Th(THF)$ complexes[57,58] but it did not resemble either of them at all. Unfortunately, while it was not possible to run solid state NMR spectra during our experiments, the indication of the compound obtained in this reaction was not completed. If it were possible to run solid state NMR spectra under an inert atmosphere, it could open a new area for investigation of these thorium compounds.

Because one of the main requirements of the atom vapour technique to be of interest to a synthetic chemist is that it should be possible to form species in a fairly pure state at the rate of at least a few millimoles per hour and since the case of the thorium reactions this requirement was not met, it was not worth while putting more effort in studying these.

According to the literature all organometallic compounds of thorium known so far have been made by using standard synthetic methods. Obviously in the case of thorium vapour reactions, either one or both thermodynamic and kinetic factors do not favour the reactions.[63]

2. Zirconium vapour reactions

2.1. *Characterization of zirconium vapour reactions with cyclooctatetraene*

The reactions of zirconium with cyclooctatetraene did not prove to be more fruitful than those of thorium. In spite of many attempts no reasonable amounts of reaction products were obtained and their insolubility in any organic solvents made their exact identification impossible.

When toluene was present while running the reaction, a very finely divided orange reaction product was obtained, which was insoluble in organic solvents, very air sensitive and somewhat sensitive to nitrogen. When exposed to nitrogen the colour of the product changed from orange to white over a few hours. Sublimation of the product (403 K; 1 h) was unsuccessful. No product sublimed to the cold finger. Even when the sublimation was attempted over a longer period of time at higher temperatures no sublimation took place.

Because of the insolubility of the product, no NMR spectra were obtained. The mass spectrum showed decomposition of the product. The observed infrared values did not agree with those reported for Zr(COT)-complexes.[64]

In spite of variations in the substrate-to-metal ratio the yields were found to be unsatisfactory for making organometallic compounds for catalytical purposes by using this technique and it was therefore no longer applied to this specific project.

2.2. *Structure determination of (toluene)(n-butylcyclooctatetraene)zirconium*

Toluene solvated zirconium atoms were tried to use as intermediates for the preparation of organometallic compounds, as it was done with thorium atoms[41] (see chapt. II.1).

The structural assignment of proposed (toluene)-(*n*-butylcyclooctatetraene)zirconium(1) structure in Fig. 7 comes primarily from the mass spectrum which shows a molecular ion at m/e 342. This corresponds the structure $(C_4H_9\text{-COT})(C_6H_5CH_3)Zr = M(1)$. The fragment corresponding to loss of the *n*-butyl group is also observed at m/e 282. A peak corresponding to free cyclooctatetraene at m/e 104 can be observed as well as the peaks corresponding toluene at m/e 92 and fragment $C_6H_5CH_2^+$ at m/e 91. The mass spectrum is presented in Fig. 8.

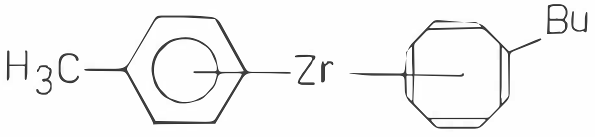


Fig. 7. The structure of (toluene)(*n*-butylcyclooctatetraene)zirconium complex 1.

Because of the low solubility of the product (~0,05 weight % in toluene) no NMR spectra were recorded. Vitulli and co-workers[65] obtained similar results with ruthenium metal.

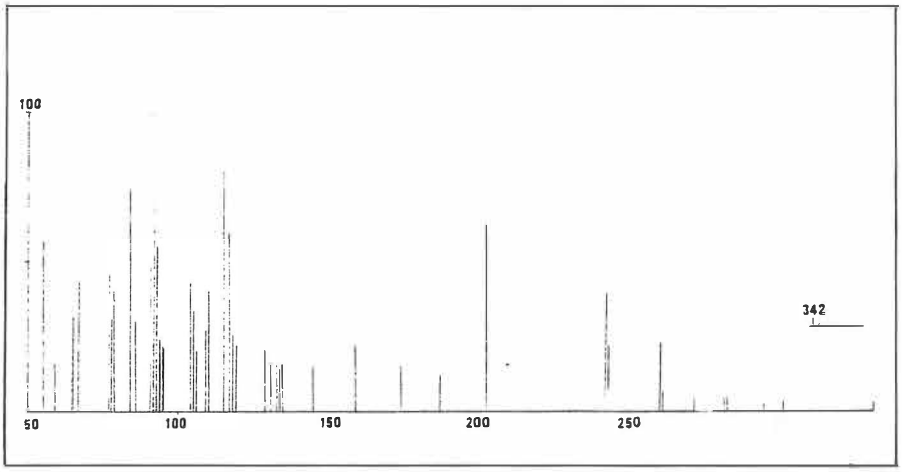


Fig. 8. The mass spectrum of 1 taken at 75 eV with an ionization chamber temperature of about 373 K with direct sample inlet.

The infrared spectrum confirms the interpretation of the mass spectrum. It shows a C=C stretching band at 1 630 cm^{-1} which is very characteristic of the cyclooctatetraene ligand.[64]

2.3. *Structure determination of bis(η^5-pentamethylcyclopentadienyl)(η^4-1,2,3,4,5-pentamethylcyclopentadiene)zirconium*

In 1976, Bercaw[44,66] and his co-workers reported the preparation of a dinitrogen complex of *bis*(pentamethylcyclopentadienyl)zirconium. His work made us interested to learn whether the metal vapourization technique would give the same results with fever steps and better yield.

The product was identified as *bis*(η^5-pentamethylcyclopentadienyl)(η^4-1,2,3,4,5-pentamethylcyclopentadiene)zirconium, $(Me_5C_5)_2Zr(Me_5C_5H)$, fig. 9.

Measurements of the product formed and zirconium evaporated are in good agreement with 3:1 $C_5(CH_3)_5$:Zr formulation as well as the elemental analysis. Elemental analysis of the product gave following results: Found. Zr 20.6; C 72.1. Calculated for $(Me_5C_5)_2Zr(Me_5C_5H)$, Zr 18.4; C 72.6 %. Molecular weight determination gave the result 500 + 5. Based on the high solubility and the molecular weight determination, the possibility of the structure of the complex 3 not being monomeric can be eliminated.

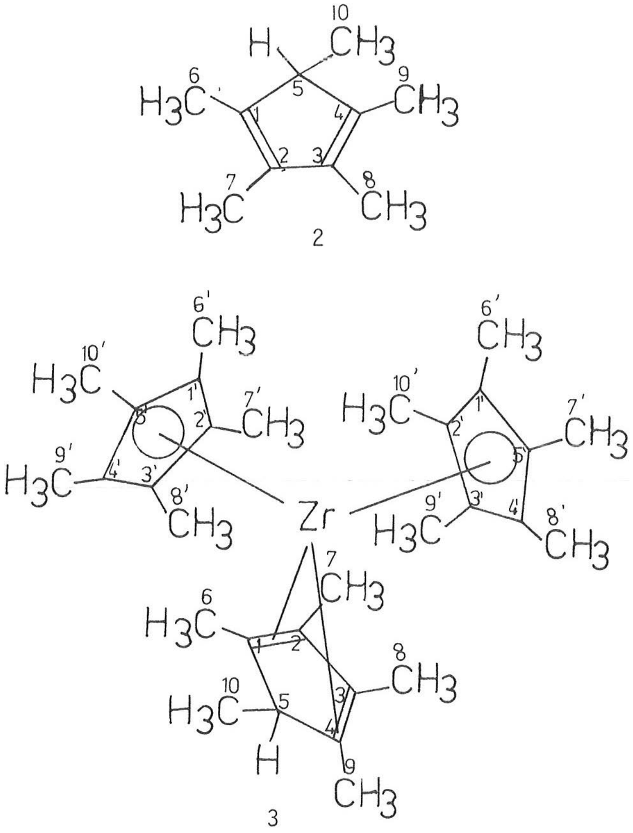


Fig.9. The structure of pentamethylcyclopentadiene (2) and *bis*(η^5-pentamethylcyclopentadienyl) (η^4-1,2,3,4,5-pentamethylcyclopentadiene)-zirconium (3)

The compound appears as an orange, thick, oily liquid. It turned out to be a very air sensitive but thermally quite stable compound. It was soluble in pentane, hexane, benzene and toluene. The solutions were studied at room temperature in the absence of air.

The ^1H NMR spectrum of 3 recorded in toluene-d_8 displays a multiplet at $\delta = 3.89$ (1H), a broad singlet at $\delta = 2.10$ (30H) arising from two pentahapto pentamethylcyclopentadienyl rings, a sharp singlet at $\delta = 1.78$ (12 H) due to the methyl groups of cyclopentadiene ring and a doublet at $\delta = 0.98$ (3 H) representing the methyl group attached to the unique ring carbon of cyclopentadiene ring. A total of 16 protons arises from the tetrahapto diene-bonded ring. The spectrum of compound 3 was compared with the spectrum of the free ligand 2 run in CCl_4. It shows a multiplet at $\delta = 2.40$ (1 H), abroad singlet at $\delta = 1.80$ (12 H) and a doublet at $\delta = 0.92$ (3 H). The spectrum of the ligand 2 recorded in $CDCl_3$ has been reported in the literature.[34]

The ^{13}C NMR spectrum of 3 in toluene-d_8 is presented in Table 1 and compared with the spectrum of the free ligand recorded formerly by Grishin, Solkan, Ustynuyk and Mironbo.[35] They had used CS_2 as a solvent and reference. In this work the spectrum of compound 2 was taken with neat samples (external TMS/D_2O as standard). The solvent effect seemed to be rather large with the chemical shift variations being presented in Table 1. The C-H couplings ($^{1}J_{C-H}$(Hz)) in the methyl groups of the two cyclopentadienyl ligands measured from ^{13}C NMR spectrum are 125 Hz. The C-H coupling of carbon 5 of the cyclopentadiene ring and proton is 125 Hz.

Table 1. Chemical shifts (δ,ppm) of the carbons of 1,2,3,4,5-pentamethylcyclopentadiene (2) and *bis*(η^5-pentamethylcyclopentadienyl)(η^4-1,2,3,4,5-pentamethylcyclopentadiene)zirconium (3) in CS_2 and in toluene-d_8. Notation indicated in formulae 2 and 3.

Reference	35	This work	This work
Compound	2	2	3
Solvent	CS_2	–	Toluene-d_8
Carbons and 4	143.5	134.1	117.4
Carbons 2 and 3	150.7	137.1	126.6
Carbon 5	55.5	51.8	51.8
Carbons 6 and 9	26.5	14.2	14.3
Carbons 7 and 8	25.8	11.4	11.7
Carbon 10	26.2	11.0	11.2
Carbons 1',2',3',4',5'	–	–	119.1
Carbons 6',7',8',9',10'	–	–	12.5;12.5;12.1; 11.7;11.2

The infrared spectrum of compound 3 in nujol is presented in Table 2 together with i.r. spectrum of the free ligand (2).

Table 2. I.r. spectra (cm^{-1}) of 2 and 3.[67]

Compound 2		Compound 3		
710	1250	710	1160	1600
790	1370	770	1260	1620
1005	1440	960	1360	2860
1050	1650	1000	1450	2910
1100		1050	1510	2950

The mass spectra do not give any further information because 1,2,3,4,5-pentamethylcyclopentadiene isomerizes upon heating yielding a number of substituted cyclopentadienes.[68,69]

Reactions of *bis*-(η^5-pentamethylcyclopentadienyl)(η^4-1,2,3,4,5-pentamethylcyclopentadiene)zirconium(3)

(a) with bromine

Treatment of compound 3 in pentane with an excess of bromine at room temperature produced a colour change from yellow to black. The mass spectrum of the product with expected isotope patterns gave evidence that the main product was $(C_5Me_5)_2ZrBr_2$ (Table 3).

(b) with iodine

Treatment of compound 3 in benzene with an excess of iodine at room temperature gave an analogous result as the treatment with bromine (Table 3).

(c) with hydrogen bromide and hydrogen chloride

The reaction was carried out similarly to the bromine and iodine reactions. The results are presented in Table 3.

(d) with PF_3, $P(C_6H_5)_3$, CO and NEt_3

It was found that PF_3, $P(C_6H_5)_3$, CO and NEt_3 were inert towards compound 3. The attempted oxidative addition by CH_3I also resulted only in unaltered starting material. This shows that the compound cannot be a very electron poor but highly suggests an eighteen electrons structure.

The structures of *bis*(η^5-pentamethylcyclopentadienyl)(η^4-1,2,3,4,5-pentamethylcyclopentadiene)-zirconium(3) and 1,2,3,4,5-pentamethylcyclopentadiene(2) were verified from their solubility, analytical, molecular weight, infrared, NMR and mass spectroscopic data as well as from their chemical reactions.

The proposed structure of 3 contains a diene-bonded pentamethylcyclopentadiene ligand as well as two pentahapto pentamethylcyclopentadienyl ligands. King and Bisnette[70] have studied pentamethylcyclopentadienyl complexes of various transition metals including titanium.

Table 3. Intensities and assignments of fragments in the mass spectra of *bis*(η^5-pentamethylcyclopentadienyl)(η^4-1,2,3,4,5-pentamethylcyclopentadiene)zirconium(3) after treatment with different halogens and hydrohalogens (electron energy 70 eV, 463 K); CH_3 = Me.

(a)	$(Me_5C_5)_2Zr(Me_5C_5H)$ + Br		(b)	$(Me_5C_5)_2Zr(Me_5C_5H)$ + I_2	
m/e	Ion$^+$	I(%)	m/e	Ion$^+$	I(%)
119	$(C_5Me_5)CH_2$	100	91		96
120	$C_5(Me)_4$	32	135	C_5Me_5	16
121	$C_5(Me)_4H$	32	254		100
135	C_5Me_5	72	394		7
151		64	614	$(C_5Me_5)_2ZrI_2$	1 M$^+$
384	$(C_5Me_5)ZrBr_2H$	59			
466	$(C_5Me_5)ZrBr_3$				
520	$(C_5Me_5)_2ZrBr_2$	18 M$^+$			

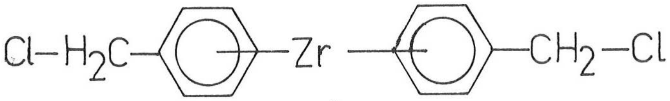
(c)	$(Me_5C_5)_2Zr(Me_5C_5H)$ + HBr			$(Me_5C_5)_2Zr(Me_5C_5H)$ + HCl	
m/e	Ion$^+$	I(%)	m/e	Ion$^+$	I(%)
135	C_5Me_5	88	119		46
271	C_5Me_5- H$^+$	52	135	C_5Me_5	34
384	$(C_5Me_5)ZrBr_2H$	100	294	$(C_5Me_5)ZrCl_2H$	100
466	$(C_5Me_5)ZrBr_3$	80	330	$(C_5Me_5)ZrCl_3$	25
520	$(C_5Me_5)ZrBr_2$	22 M$^+$	430	$(C_5Me_5)_2ZrCl_2$	3 M$^+$

The difference between three rings of the complex 3 can be deduced from NMR spectra of compound 2 and 3. Observed carbon shifts of 2 and 3 are listed in Table 1. In the nondecoupled ^{13}C NMR spectrum there are quartets caused by the carbons due to methyl groups of the cyclopentadienyl and cyclopentadiene rings. Because of overlapping it is difficult to distinquish the origin of each quartet.

The mass spectra of the halogenation and hydrohalogenation products of compound 3 showed a molecular peak M^+ having the formula $(C_5Me_5)_2ZrX_2$, where X was the halogen used (Table 3). The byproduct of this compound complicated the attempted use of NMR spectroscopy. It was not tried to analyze more specific.

2.4. *Bis(benzylchloride)zirconium*

The orange product was found to react quickly with toluene and benzene at room temperature. The orange colour disappeared in these solvents within a few minutes. The reaction product was determined to have the structure 5 (Fig. 10).



5

Fig. 10. The structure of *bis*(benzylchloride)zirconium complex.

The proton magnetic resonance spectrum in CCl_4 using TMS as a standard were run at 273 K. The spectrum of complex 5 shows absorptions at δ = 3.72 ppm (2H, multiplet) due to the CH_2-group and at δ 7.00 ppm (5H, multiplet) due to the ring protons. When toluene was used as a solvent and the spectrum was run very quickly the chemical shifts were δ = 3.82 ppm (multiplet) and δ = 7.18 ppm (multiplet). A comparison of these values with those of the free ligand is presented in Table 4. It shows that the chemical shifts of the complex are somewhat higher than those of the free ligand. This is typical of Π-sandwich complexes.[71] A multiplet at δ = 7.00 ppm includes ortho, meta and para protons of the benzene ring. In the case of $Zr(PhCH_2)_3Cl$ the shifts of ortho protons have been announced to be slightly different from those of meta and para.[43]

	Ring protons	$-CH_2$
benzylchloride	7.28	4.42
$(benzylchloride)_2Zr$	7.00	3.72

Table 4. The chemical shifts (δ, ppm) of protons of *bis*(benzylchloride)zirconium 5 and pure benzylchloride.

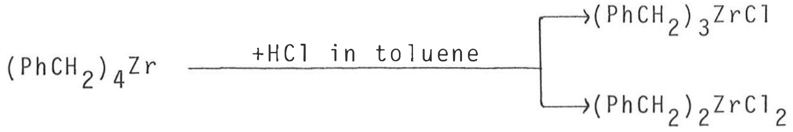
The infrared spectrum shows aromatic C-H stretching absorption peaks at 3 100 - 2 800 cm^{-1}.

Peaks at 1 860 - 1 660 cm^{-1} are typical for mono substituted benzene and C = C ring stretches at the area 1 580 - 1 420 cm^{-1} support the assumed sandwich structure.

The mass spectrum confirms the structure to be a bis arene complex of zirconium. It shows a molecular ion M^+ at m/e 342,344,346 with the typical chlorine isotope pattern 9:6:1 expected for $(C_6H_5CH_2Cl)_2Zr$. Loss of HCl gives a peak at m/e 306,308 (3:1). The fragment $(C_6H_5CH_2Cl)Zr$ at m/e 216,218 (3:1) is very typical of sandwich compounds of different types.[23,55,72] The other peaks observed are at m/e 181 due to zirconium-tropylium ion (B^+), m/e 91 ($C_6H_5CH_2$ or Zr) and m/e 77 due to phenylic cation.

Previously it has been found that the compound having the formula $Zr(CH_2Ph)_2Cl_2$ is orange-yellow and decomposes at 333 K.[43] The compound prepared in this work proved to behave similarly. It was also soluble in the same solvents.[73] HCl gas that developed during vapourization in the preparation of this compound was due to carbide formation.

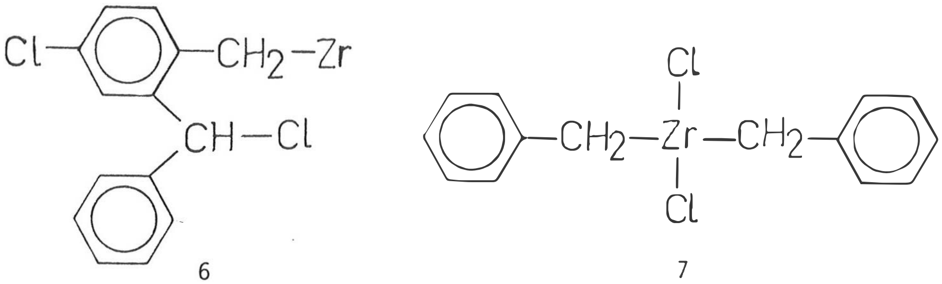
All results support strongly *bis*(benzylchloride)-zirconium which has been prepared previously using a different method.[43,73] If some amounts of $(PhCH_2)_4Zr$ compound had formed during the reaction they probably reacted further with free HCl gas present in the following way:[73]



$$(\mathrm{PhCH_2})_4\mathrm{Zr} \xrightarrow{+\mathrm{HCl\ in\ toluene}} \begin{cases} (\mathrm{PhCH_2})_3\mathrm{ZrCl} \\ (\mathrm{PhCH_2})_2\mathrm{ZrCl_2} \end{cases}$$

The mass spectrum strongly supports the structure $(PhCH_2)_2ZrCl_2$ in this case.

The molecular peak M^+ in the mass spectrum could also be explained in several different ways. Possible structures having M^+ peak at m/e 342 could also be of the types presented in Fig. 11.



6 7

Fig. 11. Other possible reaction products in zirconium vapour reaction with benzylchloride.

These were, however, rejected because the proton magnetic resonance strongly supported the *bis*(benzylchloride)zirconium structure and because the mass spectrum showed cleavages typical of sandwich compounds.

All the benzyl compounds of zirconium are found to behave as catalysts in the polymerization of ethylene and olefins.[73,74] That knowledge gives more importance to the preparation of this compound.

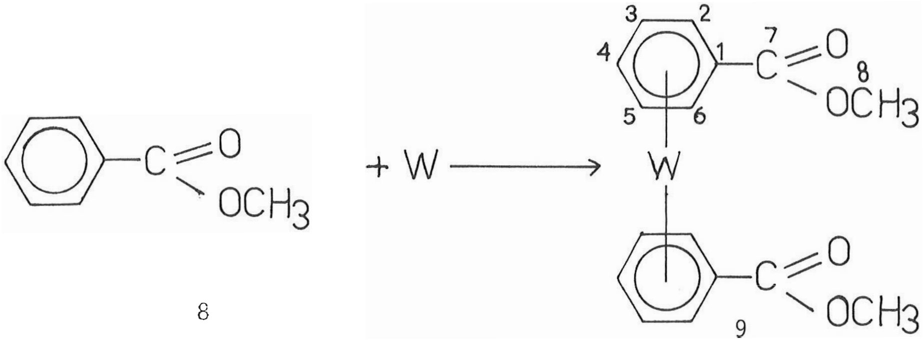
2.5. *Structures of the products formed in zirconium vapour reactions with neopentane and isobutane*

The results of these reactions are given in the Appendix.

3. Tungsten vapour reactions

3.1. *Bisarene sandwich compound of methylbenzoate with tungsten*

The reaction of tungsten atoms with methylbenzoate(8) was expected to give a sandwich compound of tungsten 9 (Fig. 12).



8

9

Fig. 12. The structure of *bis*(methylbenzoate)tungsten (9) and free ligand methylbenzoate (8).

Several sandwich compounds of this type had formerly been made using the same technique.[71]

The proton magnetic resonance spectrum of compound 9 shows a sharp singlet at δ = 3.71 ppm which is assigned to the CH_3 group of methylbenzoate and two multiplets at δ = 5.86 ppm and δ = 5.06 ppm due to the ring protons of benzene Fig. 13. Compared to the ^1H NMR spectrum of the free ligand 8 (Table 5) the signals of complex 9 appear upfield. This supports a sandwich compound.[75]

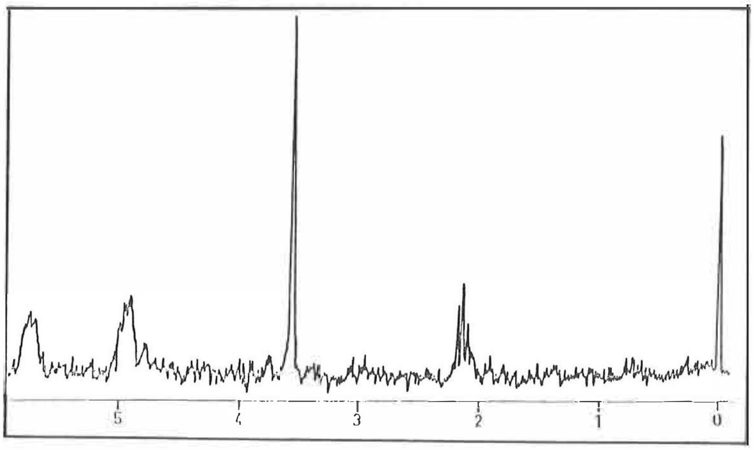


Fig. 13. The ^1H NMR spectrum of compound 9.

The mass spectrum supports the Π-sandwich formulation. It shows an M^+ peak at m/e 454 with the expected isotope pattern for tungsten due to $(C_6H_5COOCH_3)_2W$. Fragment $(C_6H_5COOCH_3)$ at m/e 136, $(C_6H_5CO^+)$ (B^+) at m/e 105 and phenylic cation at m/e 77 are identified. The mass spectrum is presented in Fig. 14.

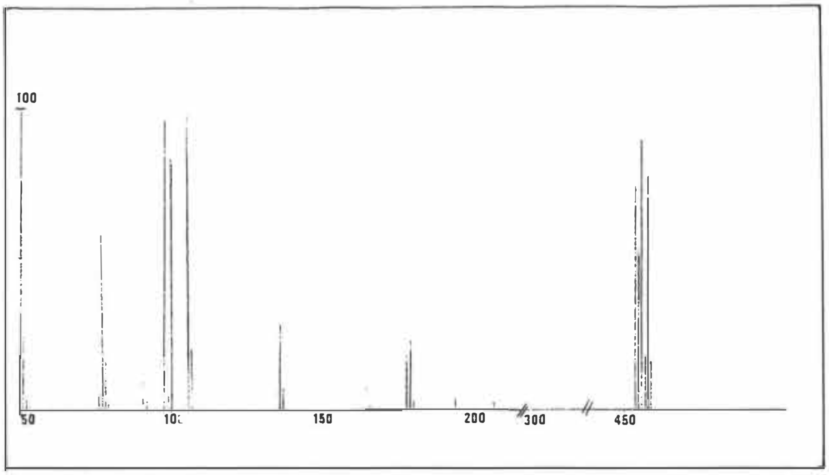
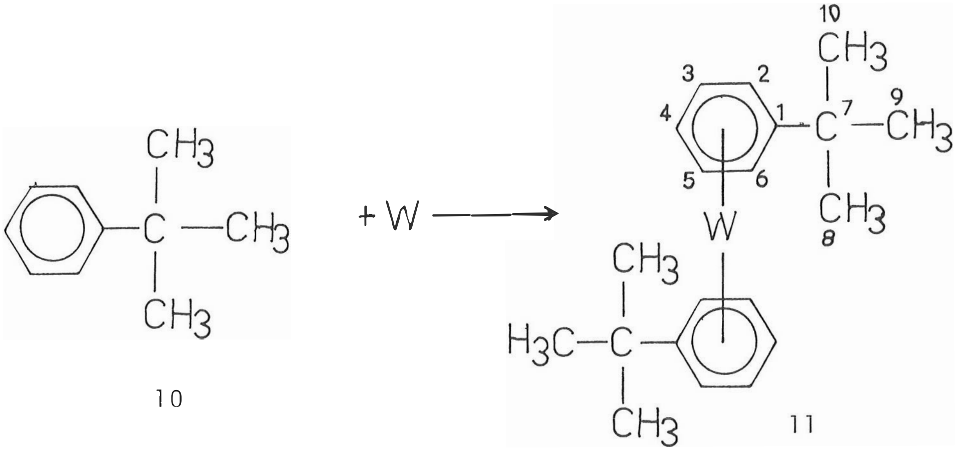


Fig. 14. The mass spectrum of compound 9.

The carbon-13 nuclear magnetic resonance spectrum of complex 9 was compared with the spectrum of free ligand 8 (Table 6). The ^{13}C NMR spectrum of methylbenzoate has been presented previously in the literature recorded in CS$_2$ [76] and CCl$_4$.[77] The chemical shifts when toluene is used as a solvent differ only a little from those recorded (Table 6). A comparison of the chemical shifts of C(1)- C(4) nuclei in the free aromatic ligand 8 and in the complex 9 shows a general upfield shift of all signals assigned to the ring carbons when the ring is coordinated to tungsten. Some correlations have been found between observed chemical shifts due to different carbon nuclei in Π-arene complexes and in free aromatic ligands.[77] In this case the aromatic ring carbons of complex 9 absorb at about 2-4 ppm higher field than those of the free ligand 8. The shift differences indicate that not all carbon atoms are equally involved in the coordination with tungsten, Some are more strongly coordinated than the others. That causes variation in the chemical shifts. The same phenomenon has previously been noticed in the case of the sandwich complex of benzene with palladium.[78] Carbon-7 in complex 9 aborbs at about 30 ppm lower field compared to that of free ligand 8. This agrees with the results of Bodner and Todd.[79] The unexpectedly large difference in chemical shifts of carbon-8 and carbonyl carbon-7 in free ligand and in complex may result from many factors. For example the carbonyl group may turn toward the metal center causing changes in electronic conditions and consequently in the magnetic shielding in the ligand. Similar changes in chemical shifts have been found in the case of a chromium complex by Fedorov et. al.[80] Different substitution patterns have been found to cause different degrees of bending. Chemical shifts can also vary depending on which part of the benzyl ligand the metal is complexed to. The dependence of chemical shifts on solvents has been found to vary a lot. The isotopic abundance of ^{183}W is 14.4 %. Thus the sidebands rising from $^{1}J(^{183}W-{}^{13}C)$ should be detectable but they were not detected. It may be that they were superimposed with the spectra of other tungsten isotope complexes. The above information shows the structure 9 to be correct for the reaction product in question.

3.2. *Bisarene sandwich compound of tert- butylbenzene with tungsten*

The atom vapour reaction of tungsten and tertiary butylbenzene was expected to give a sandwich compound of tungsten (Fig. 15) analogous to *bis*-Π- methylbenzoate tungsten compound.[71]



10

11

Fig. 15. The structure of *bis*(*tert* -butylbenzene)-tungsten (11) and free ligand (10).

The proton magnetic resonance spectrum shows a sharp singlet at δ = 1.17 ppm due to the methyl groups of *tert* -butylbenzene and two multiplets between δ = 4.74 - 5.06 ppm due to the ring protons of the ligand (Fig. 16).

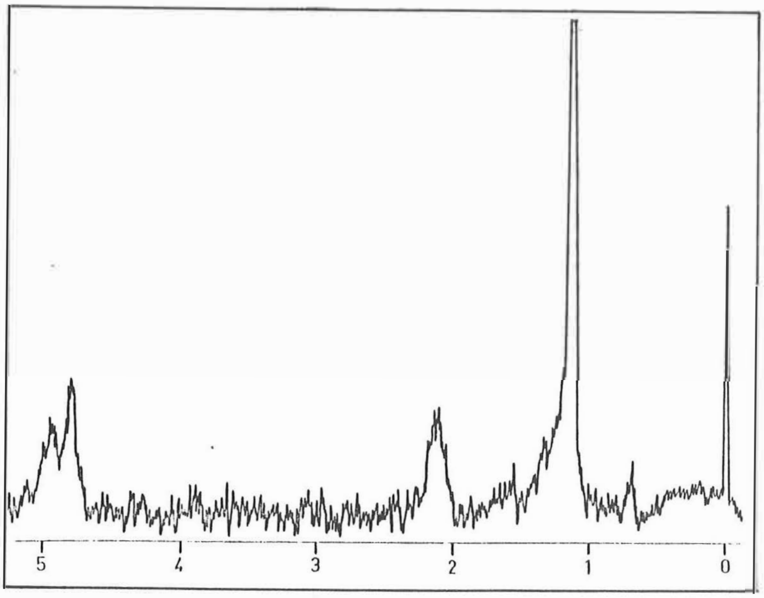


Fig. 16. The ^{1}H NMR spectrum of the compound 11.

When these shifts are compared to the shifts of the free ligand 10 (Table 5) they are found to be 1-3 ppm upfield from those of the uncomplexed ligand. Previous investigators have found this to be typical of arene sandwich compounds.[75]

The mass spectrum presented in Fig. 17 supports a Π-sandwich compound. It shows an M^+ peak at m/e 454 with the expected isotope pattern of tungsten due to $(C_6H_5\text{-}C(CH_3)_3W)$. Peaks corresponding the free ligand

$(C_6H_5-C(CH_3)_3)$ at m/e 134 are also present. The cleavage of CH_3 group from this causes a peak at m/e 119 (B^+).

Table 5. Proton chemical shifts (δ, ppm from internal TMS) of *bis*(methylbenzoate)tungsten (9) and *bis*(*tert*-butylbenzene)tungsten (11) and free ligands 8 and 10.

Compound	proton 2,6	 3,5	 4	 7	 8	 9,10
8	7.97	7.38	7.38	-	3.82	-
9	5.86	5.06	5.06	-	3.71	-
10	7.00	———	7.35	-	1.32	1.32
11	4.74	———	5.06	-	1.17	1.17

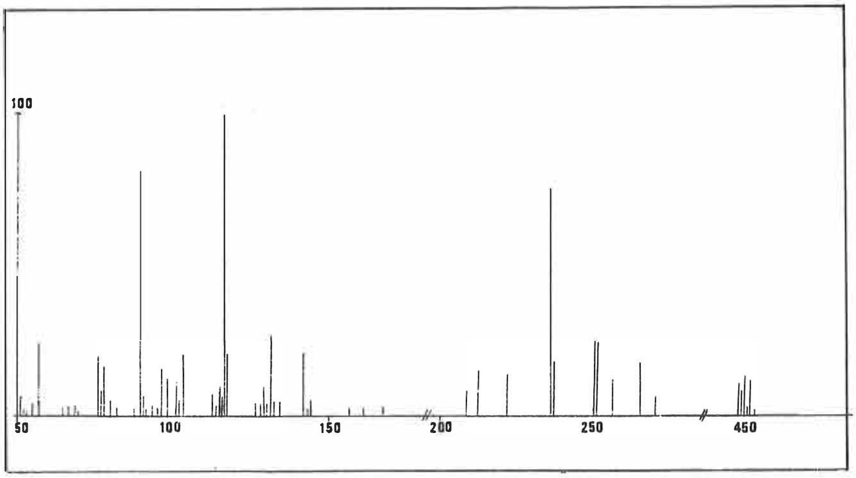


Fig. 17. The mass spectrum of compound 11.

The carbon-13 nuclear magnetic resonance spectrum of the compound was compared with the spectrum of the free ligand (Table 6).

Table 6. Chemical shifts (δ, ppm in reference to TMS) of carbons in Π-arene complexes 9 and 11 and in free aromatic ligands 8 and 10. Deuterated toluene was used as a solvent.

Compound	Carbons							
		2,6	3,5	4	7	8	9	10
8	130.6	129.6	128.3	132.6	166.4	51.4		
9	126.7	127.9	126.4	130.5	196.7	76.5		
10	150.9	128.3	126.4	125.3	34.5	31.4	31.4	31.4
11		128.8	127.1	126.2		70.3	70.3	70.3

The ^{13}C NMR spectrum of *tert*-butylbenzene (10) recorded in reference to CS_2 has been reported previously by Friedel and Retcofsky.[81] Corresponding shifts in reference to TMS were calculated and these values were found to differ only a little from the values obtained in this work. The high field signals in the ^{13}C NMR spectrum of the free ligand 10 and the complex 11 are presented in Fig. 18.

There is no former knowledge about the effect of the *tert*-butyl group in this type of complexes and

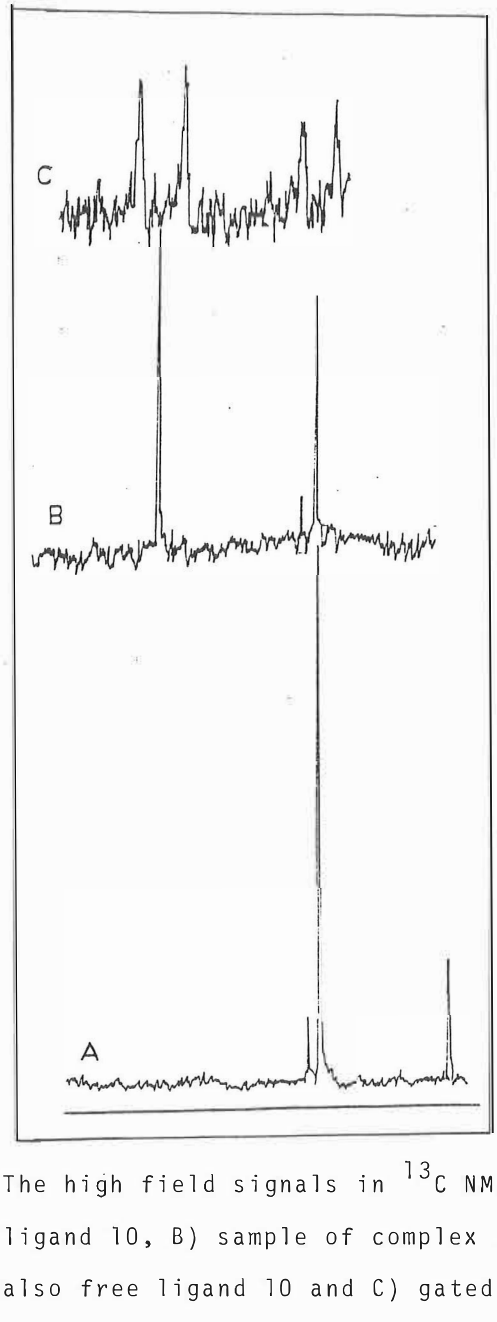


Fig. 18. The high field signals in ^{13}C NMR of A) free ligand 10, B) sample of complex 11 containing also free ligand 10 and C) gated 1 spectrum of the sample.

it is impossible to make any overall conclusions based on the knowledge obtained in the case of this compound. It is quite obvious that there can be rather big differences in chemical shifts between complexes 9 and 11 because the substituent groups are so different and can cause a different degree of bending and vary complexation to the metal atom. The distortions in complex 11 can be caused by steric interactions of the substituent methyl groups among themselves.

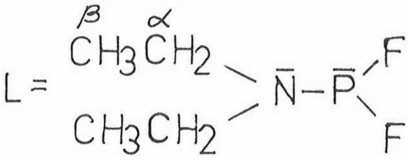
The above information supports structure 11 to be the correct one for the compound in question.

3.3. *Structure determination of hexakis (diethylaminodifluorophosphine)tungsten*

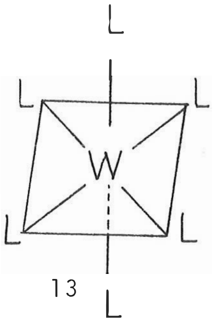
Various complexes are known in which aminofluorophosphines have served as ligands in coordination compounds with different metals.[82,83,84] Several papers have dealt with the preparation and coordination ability of dialkylaminofluorophosphines.[85]

The present product turned out to be colourless and very air sensitive. It is stable at room temperature under nitrogen but rapidly decomposes in the air releasing free ligand. It is diamagnetic, slightly soluble in hexane and toluene and could be sublimed at 353 K in a high vacuum. Sublimation gave a small amount of colourless crystals but most of the product decomposed during sublimation and the unchanged ligand was identified from the decomposition. The complex was identified as hexakis(diethylaminodifluorophosphine)-tungsten 13 presented in Fig. 19.

Elemental analysis as well as the spectral data supported the octahedral structure. (Found H 5.5; C 28.2; W 18.3 %; $C_{24}H_{60}F_{12}N_6P_6W$ requires it 5.8: C 28.0: W 17.9 %).



12



13

Fig. 19. Structures of diethylaminodifluorophosphine (12)and hexakis(diethylaminodifluorophosphine)-tungsten (13).

The infrared spectrum of complex 13 was compared with the spectrum of the free ligand 12 reported previously.[86] The C-H stretching region in the spectrum of uncoordinated ligand 12 and its metal complex 13 gave nearly equal absorptions. It indicates that donation in the complex is through phosphorus rather than through nitrogen (Fig. 20).[86]

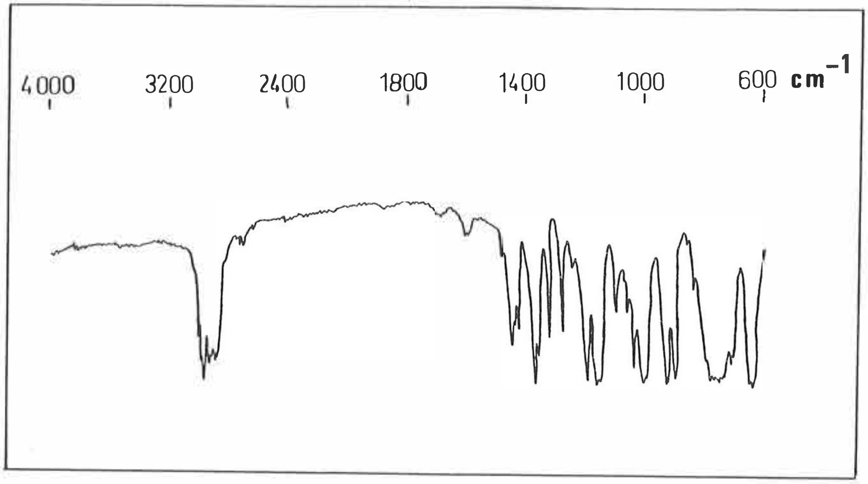


Fig. 20. The i.r. spectrum of $(Et_2NPF_2)_6W$ (KBr pellet).

The free ligand 12 has P-F stretching frequences at 738 (vs)and 792 (vs) whereas the complex 13 has a slightly higher frequencies:

(P-F) ligand (cm^{-1})^a	(P-F)WL$_6$ complex (cm^{-1})^b
792, 738 (vs)	820, 720 (vs)

vs = very strong

In the ^{1}H NMR spectrum the signal assigned to the α-protons of aminodifluorodiethylphosphine coordinated to tungsten is a broad multiplet at δ = 3.52 ppm while the β-proton resonance is a 1:2:1 triplet at δ = 1.15 ppm arising from spin coupling with the adjacent α-protons (Table 7). Both signals have some fine structure which arises from couplings with tungsten, phosphorus, fluorine or nitrogen nuclei (Fig. 21).

The signal at δ = 38.8 ppm in the carbon-13-nuclear magnetic resonance spectrum is attributed to the α-carbons and the signal at δ = 13.2 ppm to the β-carbons. These could easily be characterized by using nondecoupled spectra. Couplings with other nuclei caused only a slight line broadening of ^{13}C NMR signals. Carbon chemical shifts are shown in Table 7.

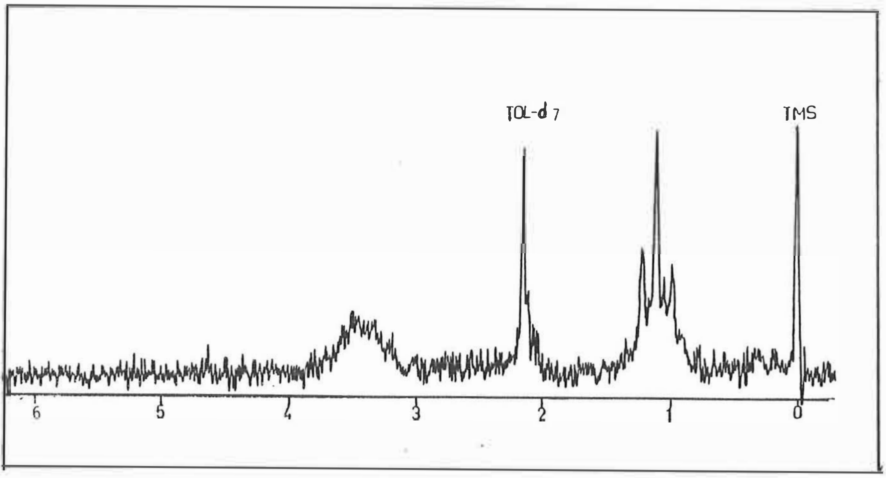


Fig. 21. The ^{1}H NMR spectrum of the compound 13.

The chemical shifts of phosphorus and fluorine and their direct couplings were obtained from ^{31}P (Fig. 22) and ^{19}F NMR spectra of the complex 13. Phosphorus and fluorine chemical shifts are shown in Table 7.

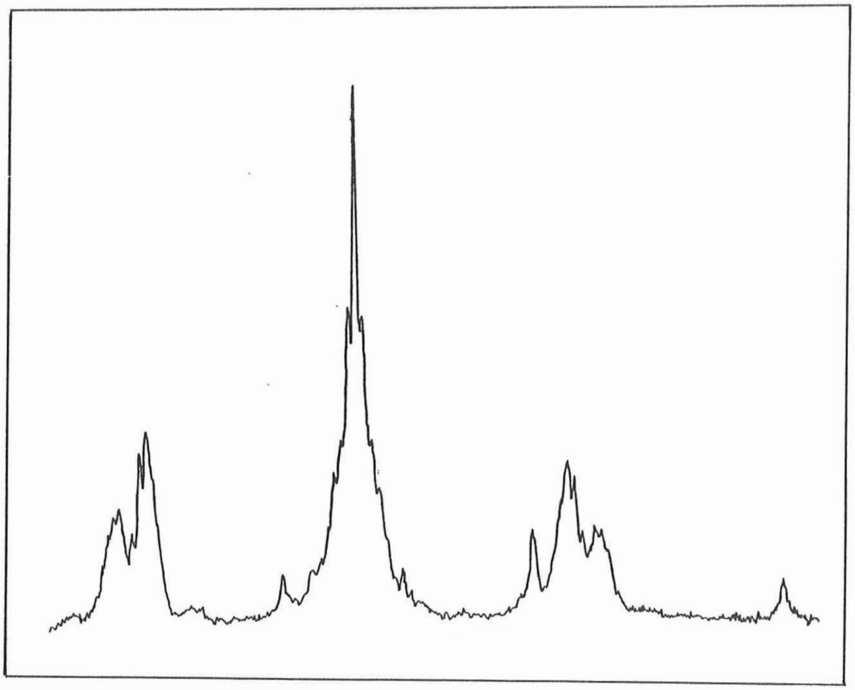


Fig. 22. The ^{31}P NMR spectrum of compound 13. L=free ligand present as an impurity.

All PF_2-groups give a basic 1:2:1 triplet structure in the phosphorus resonance arising from spin coupling with two equivalent fluorine nuclei and a doublet 1:1 in the fluorine resonance.[87]

The ^{31}P NMR spectral data may be interpreted in terms of an octahedral model, in which two axial and four equatorial positions are occupied by phosphorus atoms to which the rest part of the ligand is bound. Two triplets in ratio 2:1 having the same chemical shifts but different P-F coupling constants due to

Table 7. Chemical shifts and coupling constants of the free ligand Et_2NPF_2 (12) and its tungsten complex $(Et_2NPF_2)_6W$ (13).

Compound	^{31}P		^{19}F	^{1}H	^{13}C		Ref
	δ(ppm)[1]	J_{P-F}(Hz)	δ(ppm)[2]	δ(ppm)[3]	δ(ppm)[3]	$^{1}J_{C-H}$(Hz)	
Et_2NPF_2	144.0[4]	1197[4]	-64.8[4]				92
	147.2[4]	1204[4]	-64.8[4]	3.15(α)[4]			91
				1.10(β)			
	139.0	1196					
$(Et_2NPF_2)_6W$	159.5	1156(ax)	-36.4(ax)	3.47(α)	38.8(α)	135.7(α)	90,96
		1007(eq)	9.8(eq)	1.15(β)	13.2(β)	109.4(β)	

[1] In parts per million from 85 % H_3PO_4 external reference, positive to higher frequencies.

[2] In parts per million from $CFCl_3$ external reference.

[3] In parts per million from $Si(CH_3)_4$ internal reference.

[4] Reported values; see references.

The indices ax and eq refer to phosphorus atoms in axial and equatorial positions in the octahedron.

For indices α and β see the structure 12.

different positions of phosphorus atoms in the octahedron are characterized from the ^{31}P NMR spectrum. Axial phosphorus atoms (P_{ax}) have coupling constant $^{1}J(P_{ax}-F)$ 1156 Hz and equatorial phosphorus atoms (Peq) $^{1}J(P_{eq}-F)$ 1000 Hz. This measurement of spin -spin coupling involving nitrogen is hampered because the major isotope of nitrogen has a spin of and most coupling is either partially or completely washed out by quadrupole relaxation.[88] The line broadening can be due to a low abundance of the metal isotope of suitable spin or quadrupole relaxation. A small quantity of unremoved and unreacted ligand is also observable in the spectrum having a phosphorus chemical shift of 139.0 ppm and a coupling constant $^{1}J(P-F)$ of 1196 Hz.[85,87,89] The fine structure can be due to couplings between phosphorus and hydrogen. Magnetic equivalency of the ligand nuclei can be ascribed to a rapid intramolecular rearrangement.

Tungsten 183 (nuclear spin 1/2, natural abundance 14.4 %) causes splitting of phosphorus signal for those molecules containing ^{183}W and the total NMR signal consists of a large main peak due to those molecules containing tungsten with zero spin, flanked equidistance by small satellites. The coupling of 14.4 % abundant ^{183}W with 100 % abundant ^{31}P results in a 1:11.5:1 system of equally spaced peaks. The separation of the satellites in this case is 210 Hz[90] (Fig. 22). The magnitude of the $^{183}W-^{31}P$ spin-spin coupling constants increases linearly with the electronegativity of the substituents of phosphorus. The satellites were not observed in the present spectrum due to the limited solubility of the compound 13 and consequent lack of sensitivity.

The spectrum of the compound 13 is temperature independent. No observable changes in phosphorus spectra were found when the temperature was varied from 313 K to 193 K. The only change was line broadening below 223 K as might be expected from increased viscosity of the solution at that temperature.

The resonance of fluorine atoms directly bonded to phosphorus occurs as a basic doublet at δ = -36.4(ax) and δ = +9.8 (eq) ppm. The area ratio of these two doublets is approximately 1:2. The significant low field chemical shift of fluorine atoms directly bonded to phosphorus in the complex compared with the shifts of the uncoordinated ligand has previously been examined by Nixon.[91] The difference he observed in the case of nickel complexes is of about the same magnitude as is observed now in the case of the six coordinate tungsten complex. The coupling constant $J_{F_{ax}-F_{eq}}$ is 63.5 Hz.[84] This confirms the octahedral structure of the complex. The fine structure which can be seen in the fluorine resonance arises from fluorine coupling with other parts of the ligand. Fluorine coupling with ethyl group causes some fine structure observed in the spectrum.

An alternative explanation for the structure of this compound is that it would have full octahedral symmetry. ^{31}P NMR spectrum is an obvious 1:2:1 triplet as a result of the strong J_{P-F} primary coupling with further unresolvable fine structure. It is apparent from the methylene resonance in the proton spectrum that these protons are coupled in a complex fashion with other than the methyl group, perhaps indicating a significant J_{P-N-CH} value. A further consideration is virtual coupling giving rise to the effect that the other ligands in the system appear coupled via a J_{P-W-P} interaction. These couplings may yield a considerable complex spectrum.

Chemical shifts and coupling constants measured from the spectra are shown in Table 7 for the free ligand 12 and complex 13. Based on the above information an octahedral structure is proposed for the complex.

This present method is currently the only synthetic route to complex 13. The relevance of the preparation of it by the atom vapourization technique is thereby incontestable. Coordination number of six is quite common for tungsten metal but no hexakis complex of this type has been reported previously.

The coordination complexes of dialkylaminofluorophosphines with transition metals which have been studied so far are those with copper,[92] nickel[91,86] and molybdenum.[86,93] Studying the coordination ability of different phosphines and the character of metal-ligand bond by using NMR- method has grown lately and many papers have been published in that area.[94] Unambiquous evidence for phosphorus-metal coordination has been obtained from a detailed study of the ^{19}F and ^{31}P NMR spectra.[95] However in spite of numerous physical and chemical methods employed in attempts to elucidate the nature of the metal-ligand bond in these compounds, there still seems to be a lot of work to do to have a full understanding of the bonding in different cases. The importance of this new zerovalent six coordinated metal phosphine complex in coordination chemistry is evident.

The coordination ability of dialkylamino-halogenphosphines and the character of the metal-to-ligand bond has been videly studied and discussed in several papers.[12,96] In previous studies the nature of the bonding between the metal and phosphorus was believed to involve both σ- and Π-character. Later the concept of Π-bonding between phosphorus and transition metals was accepted and was utilized to explain various phenomena. Among others Schmutzler[82,86,97] has dealt with the problem of the character of the bond between metals and phosphine ligands in several papers and was convinced about the Π-character of the metal-ligand bond in phosphorus complexes.

In these days there has been considerable interest in the coordination ability of phosphorus ligands and their reactions with transition metals.[98]

REFERENCES

1. Skell, P.S., Wescott, L.D., Goldstein, J.-P. and Engel, R.R., *J.Amer.Chem.Soc.* 87 (1965) 2829.
2. Dobson, J.E., Remick, R.J., Wilburn, B.E. and Skell, P.S., *Inorg. Synth.* 19 (1978) 80.
3. Klabunde, K., Timms, P., Skell, P.S. and Ittel,D., *Inorg.Synth.* 19 (1979) 59.
4. Skell, P.S. and Engel, R,R., *J.Amer.Chem.Soc.* 87 (1965) 1135.
5. Skell, P.S. and Engel,R,R., *J.Amer.Chem.Soc.* 88 (1966) 3749, 4883.
6. Skell, P.S. and Glinchey, M.J., *New Synth.Methods* 3 (1975) 7.
7. Skell, P.S. and Harris, R.F., *J.Amer.Chem.Soc.* 91 (1969) 4440.
8. Skell, P.S. and Harris, R.F., *J.Amer.Chem.Soc.* 87 (1965) 5807.
9. Skell, P.S., Plonka, J.H. and Engel, R.R., *J.Amer.Chem.Soc.* 89 (1967) 1748.
10. Skell, P.S. and Havel, J.J., *J.Amer.Chem.Soc.* 89 (1967) 3933.
11. (a) Skell, P.S. and Girard, J.E., *J.Amer.Chem.Soc.* 94 (1972) 5518.
    (b) Skell, P.S., Williams-Smith, D.L. and Mc Glinchey, M.J., *J.Amer.Chem.Soc.* 95 (1973) 3337.
    (c) Benfield, F.W.S., Green, M.L.H., Ogden,J.S. and Young, D., *J.Chem.Soc.Chem.Comm.* (1973) 866.
    (d) Skell, P.S., VanDam, E,M, and Silvon, M.P., *J.Amer.Chem.Soc.* 96 (1974) 626.
    (e) Skell, P.S. and Mc Glinchey, M.J., *Angew. Chem.* 87 (1975) 215.
    (f) Kolesnikov, S.P., Dobson, J.E. and Skell, P.S., *J.Amer.Chem.Soc.* 100 (1978) 999.

12. Chatt, J., *J.Inorg.Nucl.Chem.* 8 (1958) 515.

13. (a) Chatt, J. and Shaw, B.L., *J.Chem.Soc.* (1959) 705.
    (b) Chatt, J. and Shaw, B.L., *J.Chem.Soc.* (1960) 1718.
    (c) Chatt, J., *Record.Chem.Progr.* 21 (1960) 147.

14. Green, M.L.H., *"Organometallic Compounds"*, Methuen, London, 1968, vol II, p. 220.

15. (a) Yagybsky, G., Mowat, W., Shortland, A. and Wilkinson, G., *J.Chem.Soc.Chem.Comm.* (1970) 1369.
    (b) Collier, M.R., Lappert, M.F. and Truelock, M.M., *J.Organometallic Chem.* 25 (1970) C36.

16. Cotton, F.A., *Chem.Rev.* 51 (1955) 551.

17. Braterman, P.S. and Cross, R.J., *J.Chem.Soc. Dalton Trans.* 5 (1972) 657.

18. Kriskaya, I.I., *Russian Chem.Reviews* 35 (1966) 167.

19. Mingos, D.M., *Adv.Organometallic Chem.* 15 (1977)1.

20. Heck, R.F., *"Organotransition Metal Chemistry"*, Academic Press, New York 1974.

21. Kimball, G.E., *J.Chem.Phys.* 8 (1940) 188.

22. (a) Glueckauf,E. and McKay, H.A.C., *Nature* 165 (1950) 594.
    (b) Katzin, L.I., *Nature* 166 (1950) 605.
    (c) Diamond, R.M., Street, K. and Seaborg, G.T., *J.Amer.Chem.Soc.* 76 (1954) 1461.
    (d) Connick, R.E. and Hugus, Z.Z., *J.Amer.Chem. Soc.* 74 (1952) 6012.
    (e) Eisenstein, J.C., *J.Chem.Phys.* 25 (1956) 142.
    (f) Moffitt, W., *J.Inorg.Nucl.Chem.* 2 (1956) 246.
    (g) Coulson, C.A. and Lester, G.R., *J.Chem.Soc.* (1956) 3650.
    (h) Seaborg, G.T., *"The Actinide elements"*, National Nuclear Energy Series, Mc Graw-Hill Book Company, Inc., New York, 1954, vol IV, 14a, p. 733.

(i) Streitwieser, A., Müller-Westerhoff, U., Sonnichsen, F.M., Mares, F., Morrell, D,G., Hodgson, K.O. and Harmon, C.A., *J.Amer.Chem.Soc.* 95 (1973) 8644.

(j) Fragala, I., Cordonelli, G., Zanella, P., and Tondello, E., *J.Organometallic Chem.* 122 (1976) 357.

(k) Baker, E.C., Halstead, G.W. and Raymond, K.N. *Struct.Bonding* 25 (1976) 23.

23. Streitwieser, A., Müller-Westerhoff, U., *J.Amer.Chem.Soc.* 90 (1968) 7364.

24. Cotton, F.A.,"*Progress in Inorganic Chemistry*", Interscience Pub., Inc., New York, 1959, vol I, p.1.

25. (a) Evans, S., Green, M.L.H., Jewitt, B., Orchard, A.F. and Pygall, C.F., *J.Chem.Soc. London, Faraday II,* (1972) 1847.

(b) Brown, D.A., *J.Inorg.Nucl.Chem.* 10 (1959) 39, 49.

(c) Brown, D.A., *J.Chem.Soc.* (1963) 4389.

(d) Brown, D.A. and Carroll, D.G., *J.Chem.Soc.* (1965) 2822.

(e) Brown, D.A. and Raju, J.R., *J.Chem.Soc.* (A), *Inorg.Phys.Theor.* (1966) 40.

(f) Brown, D.A. and Fitzpatric, N.J., *J.Chem.Soc.* (A), *Inorg.Phys.Theor.* 7 (1966) 941.

26. Brugger, W. and Campana, J., *Department of Chemistry,* University Park, Pa 16802, USA, 1976.

27. (a) Clark, E.P., *Anal.Chem.*, 13 (1941) 820.

(b) White, L.M. and Morris, R.T., *Anal.Chem.* 24 (1952) 1063.

(c) Johnson, L.F. and Shodery, J.N., *Anal.Chem.* 34 (1962) 1136.

28. Dobson, J.E., Cyprus Metallurgical Processes Corporation, Tucson, Arizona 85725, USA.
29. Skell, P.S., Havel, J.J. and McGlinchey, M.J., *Accounts Chem.Res.* 6 (1973) 97.
30. Skell, P.S. (Dep.Chem.Pennsylvania State University, Univ.Park, Pa) U.S.N.T.I.S., AD/A Rep. 1975, No 004810/8GA, 14pp.(eng). Avail, NTIS. From. *Gov.Rep.Announce Index* (U.S.) 1975, 75(7), 68.
31. Bordwell, F.G. and Landis, P.S., *J.Amer.Chem.Soc.* 79 (1957) 1593.
32. Campbell, P.H., Chiw, N.W.K., Deugau, K., Miller, I.J. and Sorensen, T.S., *J.Amer.Chem.Soc.* 91 (1969) 6404.
33. Threlkel, R.S., Nayes, A.A. and Bercaw, J.E., Laboratory of Chemical Physics, Institute of Technology, California 91125, USA, private communication.
34. Feitler, D. and Whitesides, G.M., *Inorg.Chem.* 15 (1976) 466.
35. Grishin, Yu.K., Solkan, U.N., Ustynuyk, Yu.A. and Mironbo, V.A., *Vestnik Moskovskogo Universiteta, ser.2. Himija* 12(6) (1971) 734.
36. Cope, A.C. and Burg, M., *J.Amer.Chem.Soc.* 74 (1952) 168.
37. The method got privately from P.S. Skell and Carol Lavonda, The Pennsylvania State University, University Park, Pa 16802, USA.
38. Gasteiger, J., Gream, G.E., Huisgen, R., Konz, W.E. and Schnegg, U., *Chem.Ber.* 104 (1971) 2412.
39. Corey, E.J. and Posner, G.H., *J.Amer.Chem.Soc.* 90 (1968) 5615.

40. Gilman, H., Beel, J.A., Brannen, C.G., Bullock, M.W., Dunn, G.E. and Miller, L.S., *J.Amer.Chem. Soc.* 71 (1949) 1499.
41. Cope,A.C. and Van Orden, H.O., *J.Amer.Chem.Soc.* 74 (1952) 175.
42. Klabunde, K.J., Efner, H.F., Murdock, T.O. and Ropple, R., *J.Amer.Chem.Soc.* 98 (1976) 1021.
43. Zucchini, U., Albizzati, E. and Giannini, U., *J. Organometallic Chem.* 26 (1971) 357.
44. Manriquez, J.M., McAlister, D.R., Sanner, R.D. and Bercaw, J.E., *J.Amer.Chem.Soc.* 98 (1976) 6733.
45. Fischer, E.O. and Treiber, A., *Naturforsch.* 17b (1962) 275.
46. Fischer, R.D., *Chem.Phys.Letters* 2 (1968) 513.
47. Hayes, R.G. and Thomas, J.L., *J.Organometallic Chem.* Rev. 7A (1971-2) 16.
48. Spedding, F.H. and Daane, A.M., *"The Rare Earths"*, Wiley, New York, 1953.
49. Haar, G.L.T. and Dubeck, M., *Inorg.Chem.* 3 (1964) 1648.
50. Kanellakopulos, B., Dornberger, E. and Baumgärtner, F., *Inorg.Nucl.Chem.Letters* 10 (1974) 155.
51. Kalina, D.G., Marks, T.J. and Wachter, W.A., *J.Amer.Chem.Soc., Chem.Comm.* 99 (1977) 3877.
52. Marks, T.J. and Wachter, W.A., *J.Amer.Chem.Soc.* 98 (1976) 703.
53. (a) Baker, E.C., Raymond, K.N., Marks, T.J. and Wachter, W.A., *J.Amer.Chem.Soc.* 96 (1974) 7586.
(b) Marks, T.J., *Lecture, VIIIth International Conference on Organometallic Chemistry*, Kyoto, Japan, Sept. 1977, Abstract 3B 07.
54. Streitwieser, A., *"Molecular Orbital Theory for Organic Chemists"*, J.Wiley and Sons., New York, 1961.

55. Streitwieser, A. and Yoshida, N., *J.Amer.Chem. Soc.* 91 (1969) 7528.
56. Goffart, J., Fuger, J., Gilbert, B., Kanellakopulos, B. and Duyckaerts, G., *Inorg.Nucl.Chem.* 8 (1972) 403.
57. Goffart, J., Fuger, J., Brown, D. and Duyckaerts, G., *Inorg. Nucl. Chem. Letters* 10 (1974) 413.
58. Hocks, L., Goffart, J., Duyckaerts, G. and Teyssie, P., *Spectrochim.Acta 30A* (1974) 907.
59. Streitwieser, A. and Harmon, C.A., *Inorg.Chem.* 12 (1973) 1102.
60. Karraker, D.G., *Inorg.Chem.* 12 (1973) 1105.
61. Miller, J.T. and DeKock, C.W., *Inorg.Chem.* 18 (1979) 1305.
62. LeVanda, C. and Streitwieser, A., Lecture VIIIth International Conference on Organometallic Chemistry, Kyoto, Japan, September 1977, Abstract 3 A27.
63. Timms, P.L., *Adv.Inorg. and Radiochem.* 14 (1972) 121.
64. Kablitz, H.J. and Wilke, G., *J.Organometallic Chem.* 51 (1973) 241.
65. Vitulli, G., Pertici, P., Lazzaroni, R. and Salvadori, P., An Abstract presented at 1st National Conference on Catalysis, Bologna, Italy, June 1979; got privately.
66. Manriquez, J.M. and Bercaw, J.E., *J.Amer.Chem.Soc. Chem.Comm.* 96 (1974) 6229.
67. Canty, A.J., Coutts, R.S.P. and Wailes, P.C., *Aust.J.Chem.* 21 (3) (1968) 807.
68. Cesarotti, E. and Kagan, H.B., *J.Organometallic Chem.* 162 (1978) 297.
69. Müller, J., *Chem.Ber.* 102 (1969) 152.

70. King, R.B. and Bisnette, M.B., *J.Organometallic Chem.* 8 (1967) 278.
71. Silvon, M.P., VanDam, E.M. and Skell, P.S., *J.Amer.Chem.Soc.* 96 (1974) 1945.
72. Streitwieser, A. and Yoshida, N., *J.Inorg.Chem.* 5 (1966) 1213.
73. Zucchini, U., Giannini, U., Albizzati, E. and D'Angelo, R., *J.Chem.Soc.Chem.Comm.* (1966) 1174.
74. Giannini, U., Zucchini, U. and Albizzati, E., *J.Polym.Sci., Part B,* 8 (1970) 405.
75. Gastinger, R.G. and Klabunde, K.J., *Trans.Met. Chem.* 4 (1) (1979) 1.
76. Dhami, K.S. and Stothers, J.E., *Can.J.Chem.* 45 (1967) 233.
77. Fedorov, L.A., Petrovskii, P.V., Fedin, E.I., Panosyan, G.A., Tsoi, A.A., Baranetskaya, N.K. and Setkina, V.N., *J.Organometallic* Chem. 182 (1979) 499.
78. Allegra, G., Tettamanti Casagrande, G., Immirzi, A., Porri, L. and Vitulli, G., *J.Amer.Chem.Soc.* 92 (1970) 289.
79. Bodner, G.M. and Todd, L.J., *Inorg.Chem.* 13 (1974) 360, 1335.
80. Fedorov, L.A. et al., *Dokl.Akad.Nauk.SSSR* 209 (1973) 404.
81. Friedel, R.A. and Retcofsky, H.L., *J.Amer.Chem. Soc.* 85 (1963) 1300.
82. Reddy, G.S. and Schmutzler, R., *Inorg.Chem.* 6 (1967) 823.
83. Johnson, T.R. and Nixon, J.F., *J.Chem.Soc.* A (1969) 2518.
84. Schmutzler, R., *J.Chem.Soc.* (1965) 5630.
85. Barlow, C.G. and Nixon, J.F., *J.Chem.Soc., Inorg.Phys.Theoret.* 2 (1966) 228.

86. Schmutzler, R., *Inorg.Chem.* 3 (1964) 415.
87. Reddy, G.S. and Schmutzler, R., *Z.Naturforsch.* *20b* (1965) 104.
88. Weigert, F.J. and Roberts, J.D., *Inorg.Chem.* 2 (1973) 313.
89. Mooney, E.F., "*Annual Revue of NMR Spectroscopy*", Academic Press, London 1969 vol 2, p. 383.
90. (a) Grim, S.O., McFarlane, W. and Wheatland, D.A., *Inorg.Nucl.Chem.Letters* 2 (2) (1966) 49.
(b) Bertrand, R.D., Ogilvie, F.B. and Verkade, J.G., *J.Amer.Chem.Soc.*, 92 (1970) 1908.
(c) Braterman, P.S., Milne, D.W., Randall, E.W. and Rosenberg, E., *J.Chem.Soc. Dalton* (1973) 1027.
91. Nixon, J.F., *J.Chem.Soc.* A (1967) 1136.
92. Cohn, K. and Parry, R.W., *Inorg.Chem.* 7 (1968) 46.
93. Barlow, C.G., Nixon, J.F. and Webster, M., *J.Chem.Soc.* A (1968) 2216.
94. (a) Meakin, P., Guggenberger, L.J., Peet,W.G., Muetterties,E.L. and Jesson, J.P., *J.Amer.Chem. Soc.* 95 (1973) 1467.
(b) Muetterties, E.L., Hirsekorn, F.J., *J.Amer. Chem.Soc.* 95 (1973) 5419.
(c) Choi, H.W., Gavin, R.M. and Muetterties, E.L., *J.Chem.Soc.Chem.Comm.* (1979) 1085.
(d) Rathke, J.W. and Muetterties, E.L., *J.Amer. Chem.Soc.* 97 (1975) 3272.
(e) Nixon, J.F., *J.Chem.Soc.* (1965) 777.
(f) Nixon, J.F., *Endeavour* 32 (1973) 19.
95. Barlow, C.G., Jefferson, R. and Nixon, J.F., *J.Chem.Soc.* A (1968) 2692.
96. (a) Chatt, J. and Watson, H.R., *J.Chem.Soc.* (1962) 2545.

(b) Chatt, J. and Watson, H.R., *Nature* 189 (1961) 1003.

(c) Chatt, J. and Williams, A.A., *J.Chem.Soc.* (1951) 3061.

(d) Packer, K.J., *J.Chem.Soc.* (1963) 960.

(e) Nöth, H. and Vetter, H-J., *Chem.Ber.* 96 (1963) 1109, 1298.

(f) Kodama, G. and Parry, R.W., *Inorg.Chem.* 4 (1965) 410.

(g) Grim, S.O. and Wheatland, D.A., *Inorg.Chem.* 8 (1969) 1716.

97. Nixon, J.F. and Schmutzler, R., *Spectrochim. Acta* 20 (1964) 1835.

98. Harris, T.V., Rathke, J.W. and Muetterties, E.L., *J.Amer.Chem.Soc.* 100 (1978) 6966.

APPENDIX

Robert J. Remick, Tuula A. Asunta, and Philip S. Skell

Reactions of zirconium atoms with alkanes: oxidative additions to carbon-hydrogen and carbon-carbon bonds

https://doi.org/10.1021/ja00499a065