

CYCLOPROPYL COMPOUNDS OF SOME
TRANSITION METALS

by

Raymond D. Houser

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in the combined option of Chemistry and Petroleum Refining.

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ABSTRACT

The preparations of σ -cyclopropyl- η -cyclopentadienyl-tricarbonyl molybdenum, σ -cyclopropyl- η -cyclopentadienyl-dicarbonyl iron, bis(η -cyclopentadienyl)dicyclopropyl-titanium(IV), and two cyclopropyl-titanium(IV) complexes with the approximate stoichiometry of $C_3H_4BrTiCl_2$ and $C_3H_4CNTiCl_2$ are described. Attempted preparations of η -cyclopentadienyl(cyclopropyl)titanium(IV) chloride, bis(η -cyclopentadienyl)cyclopropyltitanium(III), and various derivatives of iron pentacarbonyl and molybdenum hexacarbonyl are also discussed.

σ -cyclopropyl- η -cyclopentadienyltricarbonyl molybdenum and the cyclopropyl bromide-titanium(IV) chloride and cyclopropyl cyanide-titanium(IV) chloride complexes showed singlet proton magnetic resonance absorbancies for the cyclopropyl moieties at 0.40, 2.54, and 1.30 ppm(δ) respectively. These results and the infrared spectra of the above compounds is discussed in detail and molecular structures are discussed.

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INTRODUCTION

Since the discovery of ferrocene by Miller, Tebboth, and Tremaine (1) and Kealy and Paulson (2), there has been a tremendous revival of activity in the organic chemistry of the transition metals. The major portion of this vast amount of work has been centered on the olefins and arenes. However, in almost all of the known compounds, the olefins and arenes are said to act as ligands in these systems. The chemistry and theoretical basis of these systems have received considerable attention in the last few years, and are too extensive to cover in this introduction: the reader may refer to the following reviews for a complete coverage of this subject, Cotton (3), and Wilkinson and Cotton (4).

A considerable amount of work has been done on the sigma-bonded organometallics of the transition metals, although this area has had much less consideration than the so-called pi-bonded compounds. The reason for this big

difference in the amount of work being done in these two areas is probably due to the fact that the pi-systems are in general more tenaciously bonded than their sigma counterparts.

Following a suggestion by Walsh (5) that the cyclopropane ring does exhibit some double-bond character because of the delocalization of its sigma bonds, several workers (6, 7, 8) attempted to form olefin-type complexes with cyclopropane and various salts of silver(I), copper(I), mercury(II), and platinum(II and IV). These workers found that only one species, hexachloroplatinic acid (H_2PtCl_6), reacted with the cyclopropane ring system. It has been confirmed by Adams and coworkers (8) that the compound formed when cyclopropane gas is bubbled through a solution of hexachloroplatinic acid in acetic anhydride is a polymer with the empirical formula $Cl_2PtC_3H_6$. These workers have assigned the square planer structure, figure 1, with polymerization occurring through chloride bridges giving the platinum(IV) its normal coordination of six.

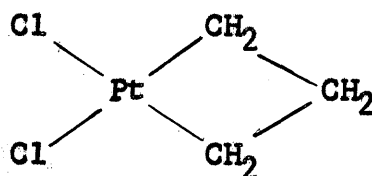


FIGURE 1: STRUCTURE OF $Cl_2PtC_3H_6$.

Since the above mentioned work, the organometallic chemistry of the cyclopropyl system has been extended only through such compounds as cyclopropyllithium by Hart and Sandri (9), cyclopropylmagnesium bromide by Roberts and Chambers (10), dicyclopropylmercury by Reynolds, Dessy, and Jaffe (11), and the more recent work of the group IV elements silicon, germanium, tin, and lead by Seyferth and Cohen (12) and Juenge and Houser (13). With the exception of dicyclopropylmercury, the bonding in the above compounds is considered to be either ionic or sigma-covalent as in the aliphatic analogues. The bonding in the dicyclopropylmercury compound hasn't as yet been fully explained. However it has been shown (14) that the cyclopropyl compound shows considerable stability over the alkyl and aryl mercury derivatives.

Since pi-bonding is believed to occur through overlap of filled metal d orbitals with vacant pi-antibonding orbitals of the hydrocarbon moieties, the pi component of a bond plays an important role in the strength and stability of the transition metal-to-carbon bond. This strengthening by the overlap of antibonding orbitals cannot operate between transition metals and the antibonding sigma orbitals of alkyl groups, since the latter are too high in energy. That is, the energy of the vacant orbitals must be relatively

low for considerable bonding to take place. This author feels that the cyclopropyl group should show some degree of stability over the saturated hydrocarbons in normal sigma-bonding to the transition metals, since the antibonding sigma orbitals which make up the ring portion of the group would be relatively low in energy in comparison with the primary and secondary alkyl groups. This reasoning comes from calculations by Wiberg (15) which requires a higher percentage of the p character from the carbon be distributed to the ring portion of the group and the s character then shifted to the external portion of the molecule. These calculated values give roughly 0.80p and 0.20s hybridization for the ring orbitals whereas the external orbitals are 0.70p and 0.30s hybrids. Also the cyclopropyl group may show a higher degree of resonance between a pure covalent and a back donation type structure as proposed by Cotton (3), figure 2.

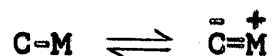


FIGURE 2: RESONANCE STRUCTURE OF CARBON-TRANSITION METAL SIGMA BOND.

To investigate this proposal the properties of σ -cyclopropyl- π -cyclopentadienyldicarbonyl iron and σ -cyclopropyl- π -cyclopentadienyltricarbonyl molybdenum

were examined. They were prepared from the sodium salts $C_5H_5Fe(CO)_2Na$ and $C_5H_5Mo(CO)_3Na$ and cyclopropyl bromide, using tetrahydrofuran as the solvent. This procedure is similar to the one described by Piper and Wilkinson (16) for the preparation of the methyl, ethyl, isopropyl, and sigma-cyclopentadienyl derivatives. The above workers found the order of stability of this series of compounds to be in the order of decreasing stability: methyl > sigma-cyclopentadienyl > ethyl > isopropyl. These workers felt that the greater stability of the methyl derivatives may be due to some double-bond character of the carbon-metal bond. This reasoning comes from a postulate in organic chemistry (17), that the methyl group can release electron density, thus giving a partial double-bond character to the metal-to-carbon bond. Also they felt that the shielding of the methyl group by the carbonyl ligands would be greater than for the ethyl and isopropyl groups.

In contrast to this line of reasoning, these workers were faced with the problem of explaining the relatively high stability of the sigma-cyclopentadienyl system. They found that the proton magnetic resonance spectra of these compounds showed two distinct absorbancies at chemical shift values of +0.6 and +2.1 ppm relative to benzene, having area ratios of 1:1, with the latter peak being attributed

to the pi-cyclopentadienyl and the first peak to the sigma-cyclopentadienyl ring. They then proposed two possible explanations for this observation. One explanation was that the sigma ring and the remaining portion of the molecule may dissociate into ions of the type, $\eta^1\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^+$ and C_5H_5^- and $\eta^1\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3^+$ and C_5H_5^- . However this type of reasoning seemed unlikely, since the compounds failed to react with ferrous chloride in organic solvents to give ferrocene. The other explanation was that the metal atom may be executing a 1, 2-rearrangement in the sigma-bonded ring at a rate greater than the sweep frequency of 200-300 cycles per second. They then regard the sigma-cyclopentadienyl ring-to-metal bond as rotating with respect to the carbon atoms, but they do feel that the metal atom is bonded to a single carbon atom most of the time.

It has been shown by Plowman and Stone (18) and Murdock and Weiss (19) that allyltricarbonyliron iodide may be prepared by reacting allyl iodide and iron pentacarbonyl either in a solvent or in the absence of a solvent in a sealed tube. From infrared and proton magnetic resonance studies these workers have shown that in solution a complex mixture of species with both sigma-allyl and pi-allyl groups present.

Similar to, but yet quite different from the allyl

derivatives, is the n-heptafluoropropyl derivatives of iron pentacarbonyl. It has been shown by Manuel and others (20) and King and coworkers (21) that n-heptafluoropropyl iodide will react with iron pentacarbonyl either in a benzene solution or in a closed system in the absence of a solvent, to give n-heptafluoropropyltetracarbonyliron iodide. Thus the perfluoro iodide differs from the allyl iodide by replacing only one carbonyl group.

Treatment of both the allyl and perfluoro derivatives with triphenylphosphine results in quite different reactions. King (22) has shown that treatment of the allyl compound with triphenylphosphine replaces both the allyl and iodide, leaving the carbonyl groups attached to the iron. However Plowman and Stone (23) have shown that in the n-heptafluoropropyl derivative the triphenylphosphine will replace two carbonyl groups, leaving the n-heptafluoropropyl group and iodide attached. Thus it appears that the sigma-bonded perfluoro organometallics of iron are less susceptible to replacement than similar pi-bonded systems of olefins. It should then be possible to distinguish considerable pi-bonding or a true sigma-bonded system in cyclopropyl derivatives by examining the infrared and proton magnetic resonance spectra and the triphenylphosphine cleavage products.

Attempts to prepare cyclopropyl derivatives analagous

to the allyl and n-perfluoropropyl derivatives of iron pentacarbonyl from cyclopropyl bromide and iron pentacarbonyl or cyclopropyl bromide and molybdenum hexacarbonyl were unsuccessful. Also attempts to prepare cyclopropylallyl-dicarbonyl iron and cyclopropyl-n-heptafluoropropyltricarbonyl iron from the iodide derivatives and cyclopropylmagnesium bromide led to the reduction of the iron. Thus studies of the pi-character of the cyclopropyl group through this route were unsuccessful.

There have also been some attempts (16, 24) to prepare stable derivatives of sigma-bonded alkyls and aryls of titanium(IV). However the above workers found these compounds to be quite unstable under normal laboratory handling and storage techniques and decomposed autocatalytically within two to three hours.

Attempts to prepare η -cyclopentadienyl(cyclopropyl)-titanium(IV) chloride and bis(η -cyclopentadienyl)cyclopropyl-titanium(III) from η -cyclopentadienyltitanium(IV) chloride and bis(η -cyclopentadienyl)titanium(III) chloride respectively and cyclopropylmagnesium bromide led to the reduction of the titanium which was apparent from the color change during the reactions. However bis(η -cyclopentadienyl)-dicyclopropyltitanium(IV) was successfully prepared from bis(η -cyclopentadienyl)titanium(IV) chloride and cyclopropylmagnesium bromide in tetrahydrofuran.

Also it was found that titanium(IV) chloride will react with either cyclopropyl bromide or cyclopropyl cyanide in n-pentane to give a solid yellow complex with the empirical formulas of approximately $\text{Cl}_2\text{TiC}_3\text{H}_4\text{Br}$ or $\text{Cl}_2\text{TiC}_3\text{H}_4\text{CN}$, respectively. The structure and physical properties of these complexes are discussed in this thesis.

Attempts to form complexes similar to the above from cyclopropane and titanium(IV) chloride by bubbling cyclopropane gas through a n-pentane-titanium(IV) chloride solution were unsuccessful. Also no reaction was observed when equal molar quantities of cyclopropyl bromide and π -cyclopentadienyltitanium(IV) chloride were heated to 100°C in a sealed tube for periods of up to one hundred hours.

EXPERIMENTAL WORK

Reagents

Reagents which did not require laboratory preparations are listed in this section as well as the reagents which had to be prepared in order to carry out further syntheses.

Solvents: All solvents were purchased from the Matheson Company, Inc., East Rutherford, New Jersey and treated in the following manner before use. Tetrahydrofuran and ether solvents were distilled over lithiumaluminum hydride. Hexane and pentane were distilled over calcium oxide. All other solvents were distilled using a twelve-inch Vigreux column.

Cyclopropyl Bromide: Cyclopropyl bromide was prepared according to the procedure described by Meek and Osuga (25) then stored over calcium chloride and freshly distilled prior to use.

Titanium(IV) Chloride: Technical-grade titanium(IV) chloride was distilled under an argon atmosphere prior to use.

Bis(η -cyclopentadienyl)titanium(IV) Chloride: Bis(η -cyclo-

pentadienyl)titanium(IV) chloride was used as purchased from Eastman Organic Chemicals, Rochester, New York.

η^5 -Cyclopentadienyltitanium(IV) Chloride: η^5 -Cyclopentadienyltitanium(IV) chloride was prepared according to the procedure described by Gorisch (26) and was purified by sublimation prior to use.

Cyclopentadienyltricarbonylmolybdenum Dimer and Cyclopentadienyldicarbonyliron Dimer: These two reagents were used as purchased from Alfa Inorganics, Inc., 8 Congress Street, Beverly, Massachusetts.

Dicyclopentadiene: Dicyclopentadiene was purchased from Eastman Organic Chemicals, Rochester, New York and distilled to the monomer before use.

Allyltricarbonyliron Iodide: Allyltricarbonyliron iodide was prepared according to the procedure described by King (27).

n-Heptafluoropropyltetracarbonyliron Iodide: n-heptafluoropropyltetracarbonyliron iodide was prepared to the procedure described by King and coworkers (21).

Allyl Iodide and n-Heptafluoropropyl Iodide: These two reagents were used as purchased from K & K Laboratories, Inc., Plainview, New York.

Triphenylphosphine: Triphenylphosphine was used as purchased from the Matheson Company, Inc., East Rutheford,

New Jersey.

1-Bromo-3-chloropropane: 1-Bromo-3-chloropropane was used as purchased from Eastman Organic Chemicals, Rochester 3, New York.

δ -Chlorobutyronitrile: δ -Chlorobutyronitrile was prepared according to the procedure described by Allen (28).

Cyclopropane: Cyclopropane was used as purchased from the Matheson Company, Inc., East Rutherford, New Jersey.

Cyclopropyl Cyanide: Cyclopropyl Cyanide was prepared according to the procedure described by McCloskey and Cloeman (29) with the exception that sodium amide was used in the place of sodium hydroxide.

Instrumentation

Infrared: Infrared studies were made on a Perkin-Elmer 521 Grating Infrared Spectrophotometer. All analyses were made on potassium bromide plates, using a mineral oil or perfluorokerosene mull or a potassium bromide pellet.

Proton Magnetic Resonance Studies: NMR studies were made on a Varian A-60 instrument, using chloroform as the solvent and tetramethylsilane as the internal standard.

Gas Chromatography: Chromatographic analysis were made on a Perkin-Elmer Vapor Fractometer, Model 154 using a Perkin-Elmer 154-0013A column.

Analysis

Analyses were made by Drs. G. Weiler and F. B. Strauss, Microanalytical Laboratories, 164 Banbury Road, Oxford, England and Huffman Laboratories, Wheatridge, Colorado.

Preparations

Cyclopropyl Bromide-Titanium(IV) Chloride Complex: This entire reaction and isolation was carried out in a "glove bag" under nitrogen atmosphere.

1.7 g (1 ml) of freshly distilled titanium(IV) chloride in 15 ml n-pentane was placed in a 50-ml vacuum flask. To the titanium(IV) chloride-pentane solution was added slowly with constant stirring freshly prepared cyclopropyl bromide until no further precipitation was observed (about 2 ml total). The reaction mixture was then stirred for an additional ten minutes, and the bright yellow solid allowed to settle out. The solvent and soluble materials were decanted off and the solid washed three times with 10 ml portions of n-pentane, and then dried for thirty minutes at room temperature under a vacuum of 1-2 mm.

Anal. calcd. for $\text{Cl}_2\text{TiC}_3\text{H}_5\text{Br}$: C, 15.13%; H, 2.10%; total halogen as Cl, 42.55%. Found: C, 14.81%; H, 2.88%; total halogen as Cl, 43.39%.

Hydrolysis of Cyclopropyl Bromide-Titanium(IV) Chloride Complex and Identification of the Products: A few milligrams of the complex was placed in a small test tube, to this was added 3-5 ml of wet benzene or chloroform (saturated with water). After hydrolysis was complete and the titanium(IV) oxide had precipitated out of solution chromatographic analysis and proton magnetic resonance studies were made on the resulting solutions.

The benzene solution showed three definite constituents on a Perkin-Elmer 154-0013A column at 80°C, two of the peaks were due to water and benzene, and the third peak was confirmed to have the same retention time as acetone by adding small portions of acetone to the hydrolysis solution and observing an increase in the concentration of the third constituent.

The chloroform solution was then used for proton magnetic resonance studies and the hydrolysis product confirmed to be acetone as above. Thus the hydrolysis of the complex was confirmed to give only a single identifiable product, acetone.

Cyclopropyl Cyanide-Titanium(IV) Chloride Complex: This entire reaction and isolation was carried out in "glove bag" under nitrogen atmosphere.

To 3.4 g (2 ml) of freshly distilled titanium(IV) chloride in 20 ml n-pentane in a 50-ml flask was added slowly with constant stirring 2.4 ml of freshly prepared cyclopropyl cyanide; a very exothermic reaction occurred, giving a bright yellow solid. The reaction mixture was then stirred for an additional five minutes, the solvent and volatile materials removed under vacuum and the yellow solid dried for an additional six hours at 55°C and 10-12 mm.

Anal. calcd. for $\text{Cl}_2\text{TiC}_3\text{H}_4\text{CN}$: C, 25.91%; H, 2.16%; Cl, 38.32%. Found: C, 29.30%; H, 3.23%; Cl, 42.43%.

Mol. wt. calcd. for $\text{Cl}_2\text{TiC}_3\text{H}_4\text{CN}$: 185. Found: 80.

Hydrolysis of Cyclopropyl Cyanide-Titanium(IV) Chloride

Complex and Chromatographic Analysis of the Products:

Hydrolysis of the above complex was carried out in wet benzene according to the procedure described previously for the cyclopropyl bromide-titanium(IV) chloride complex.

On a Perkin-Elmer 154-0013A column at 95°C the hydrolysis solution showed only one foreign constituent. This peak was confirmed to have the same retention time as cyclopropyl cyanide by adding a small portion of cyclopropyl cyanide to the hydrolysis solution and observing an increase in the concentration of the third constituent with no change in retention time.

Bis(π -cyclopentadienyl)dicyclopropyltitanium(IV): In a 100-ml three-neck flask fitted with a stirrer, water condenser, nitrogen inlet, and additional funnel was prepared 0.02 mole cyclopropylmagnesium bromide in 25 ml tetrahydrofuran. The Grignard solution was then allowed to come to room temperature and 0.01 mole (2.60 g) bis(π -cyclopentadienyl)titanium(IV) chloride in 10 ml tetrahydrofuran was slowly added through the dropping funnel. The reaction mixture immediately came to reflux temperature and turned dark brown to black in color. After the addition was complete, the mixture was then refluxed for an additional hour, allowed to come to room temperature and the solvent and volatile materials removed under vacuum, leaving a dark red viscous oil. The residue was then extracted with 50 ml anhydrous ethyl ether and the insoluble materials filtered off. Normal pentane was slowly added to the reddish ether solution until further addition yielded no more oil. The very thick caramel-colored oil changed to a dark red solid within two to three hours, the change appeared to be autocatalytic.

The compound was identified by the cyclopropyl absorbance in the infrared at 1045 cm^{-1} (30).

σ -Cyclopropyl- π -cyclopentadienyldicarbonyl Iron: A three-neck 250-ml flask fitted with a stirrer, water

condenser, nitrogen inlet, and dropping funnel was flushed several times with anhydrous nitrogen and charged with 4.0 g sodium (as a three per cent amalgam), 14.0 g η -cyclopentadienyldicarbonyl iron dimer, and 100 ml tetrahydrofuran. The reaction was then stirred rapidly at room temperature for fifteen hours, at which time 14.0 g cyclopropyl bromide was slowly added through the additional funnel. The mixture was stirred for an additional five hours, solvent and volatile materials removed with the aid of a water aspirator vacuuo, and the residue extracted with 150 ml anhydrous ether. The red ether solution was then evaporated to dryness under vacuum, leaving a caramel-colored oil from which the product could be sublimed at 50°C and 1-2 mm onto a water cooled probe. The σ -cyclopropyl- η -cyclopentadienyldicarbonyl iron (a very viscous caramel-colored oil) decomposed within an hour or so when exposed to air but was fairly stable when kept in a closed system at reduced temperatures.

The compound was identified by its infrared absorbancies at 1022 and 870 cm^{-1} .

σ -Cyclopropyl- η -cyclopentadienyltricarbonyl Molybdenum:

The preparation was carried out in a 500-ml three-neck flask with a stopcock fused to the bottom and fitted with a nitrogen inlet, efficient motor stirrer, pressure-equalizing dropping funnel, and reflux condenser. After being flushed

with nitrogen, the flask was charged with 150 g sodium amalgam containing 0.7 g sodium. To the amalgam was slowly added 4.9 g η^5 -cyclopentadienyltricarbonylmolybdenum dimer in 250 ml anhydrous tetrahydrofuran. After the addition was complete, the mixture was stirred vigorously for about one hour; at which time the dark red color of the molybdenum dimer had completely disappeared and the solution changed to the yellow color of $C_5H_5Mo(CO)_3Na$.

After the formation of the $C_5H_5Mo(CO)_3Na$ was complete, the excess amalgam was removed through the stopcock at the bottom. To the remaining solution was then added dropwise 5.0 g cyclopropyl bromide; a slight exothermic reaction occurred. The reaction mixture was then stirred for an additional five hours, the stirrer replaced with a stopper, and the solvent removed under vacuum. When only a dry residue remained, the flask was fitted with a water-cooled probe, connected to a vacuum line maintained at 1-2 mm, and submerged in a warm water bath at 80-90°C. After about two hours a nice crop of bright yellow crystals had collected on the probe. Melting point 136-138°C.

Cyclopropyl-n-heptafluoropropyltricarbonyl Iron and Cyclopropylallyldicarbonyl Iron: Attempts to prepare the above compounds from n-heptafluoropropyltetracarbonyl iron iodide and allyltricarbonyl iron iodide and cyclopropyl-

magnesium bromide using tetrahydrofuran as the solvent led to the reduction of the iodide compounds to the dimers $[\text{C}_3\text{F}_7\text{Fe}(\text{CO})_3\text{I}]_2$ and $[\text{C}_3\text{H}_5\text{Fe}(\text{CO})_2\text{I}]_2$ respectively, which were identified by infrared spectra and melting points as found by Plowman and Stone (23).

EXPERIMENTAL RESULTSProton Magnetic Resonance Studies σ -Cyclopropyl- η^5 -cyclopentadienyltricarbonyl Molybdenum:

Proton magnetic resonance studies of σ -cyclopropyl- η^5 -cyclopentadienyltricarbonyl molybdenum were made in chloroform at a temperature of approximately 40°C and a radio frequency (R. F.) field of 0.08 mG. At a sweep frequency of 500 cps, two distinct singlets at 0.40 and 5.36 ppm(δ) with the area ratios of 1:1 (area measured by cutting out peaks and weighing paper) were observed. The singlet at 5.36 ppm(δ) was assigned to the pi-cyclopentadienyl ring by comparison with the methyl derivative which shows two singlets at 5.45 and 0.44 ppm(δ) with the area ratios of 5:3 respectively. The singlet at 0.40 ppm(δ) has been assigned to the cyclopropyl ring system. Various sweep frequencies were studied, however the 0.40 ppm(δ) peak always showed up as a singlet, figure 3.

Cyclopropyl Bromide-Titanium(IV) Chloride Complex: Proton

magnetic resonance studies of the above complex were made in chloroform at a temperature of approximately 40°C and an R. F. Field of 0.06 mG. At a sweep frequency of 500 cps a singlet was observed at 2.54 ppm(δ) while chloroform showed the normal singlet at 7.25 ppm(δ). Upon the addition of water to the chloroform solution of the complex the 2.54 ppm(δ) peak disappeared and a new singlet at 2.09 ppm(δ) appeared. The latter peak was found to be due to acetone from comparison studies. In figure 4 peak "a" represents the complex before hydrolysis, "b" represents the solution after hydrolysis, and "c" is the hydrolyzed solution after the addition of a drop of acetone to the mixture.

Cyclopropyl Cyanide-Titanium(IV) Chloride Complex: Proton magnetic resonance studies of the complex were made in chloroform solvent at a temperature of approximately 60°C and an R. F. Field of 0.20 mG. At a sweep frequency of 500 cps a singlet was observed at 1.30 ppm(δ). A complete investigation of the proton region showed no other constituents present.

Infrared Studies

σ -Cyclopropyl- η -cyclopentadienyltricarbonyl Molybdenum: Infrared studies of the above compound were made using a potassium bromide pellet of 0.582-per cent sample.

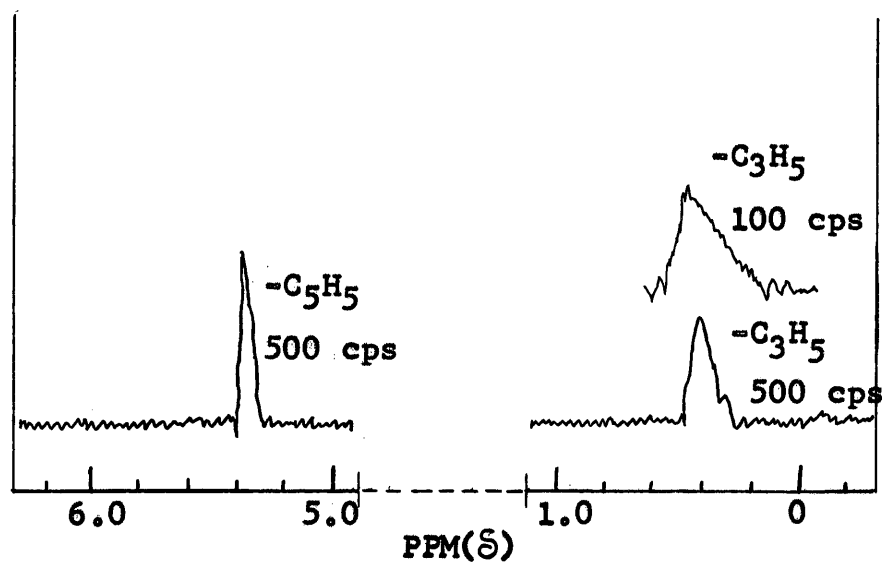


FIGURE 3: PMR OF
 σ -CYCLOPROPYL- η^5 -CYCLOPENTADIENYLTRICARBONYL MOLYBDENUM

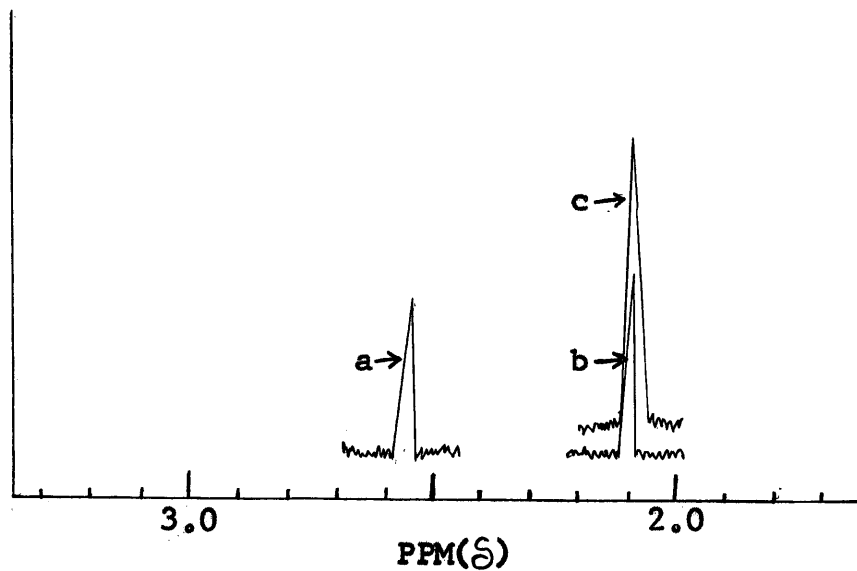


FIGURE 4: PMR OF
CYCLOPROPYL BROMIDE-TITANIUM(IV) CHLORIDE COMPLEX

In the carbon-hydrogen stretching region three peaks are observed, 2976(s), 2900(s), and 2814(m) cm^{-1} . These three peaks are generally observed at a slightly higher frequency by about 20-to-50 cm^{-1} for most cyclopropyl organometallics, however the spread of the three peaks is somewhat less than that normally observed for the cyclopropyl system.

Three other characteristic cyclopropyl peaks are present, 1060(s), 1006-1012(s), and 765(m) cm^{-1} which have been assigned to ring deformation and/or CH_2 -twist. The 1060 cm^{-1} peak is present in almost all cyclopropyl compounds thus far reported (30). The strong peak at 1006-1012 usually appears around 10-to-20 cm^{-1} higher and in some cases (30) never shows up at all. Some authors (31) have attributed this absorbancy to a CH_2 -twisting motion rather than ring deformation. The 765(m) absorbancy is common to most cyclopropyl derivatives and is almost always assigned to a deformation mode.

A comparison of $\sigma\text{-C}_3\text{H}_5\text{-}\eta\text{-C}_5\text{H}_5\text{Mo(CO)}_3$ with cyclopropane and $[\eta\text{-C}_5\text{H}_5\text{Mo(CO)}_3]_2$ is made in figure 5.

Cyclopropyl Bromide-Titanium(IV) Chloride Complex:

Infrared studies of the complex were made using a 0.276-per cent potassium bromide pellet. Listed in figure 6 are the

$\sigma\text{-C}_3\text{H}_5\text{-}\eta\text{-C}_5\text{H}_5\text{Mo(CO)}_3$ cm ⁻¹	C_3H_6 cm ⁻¹	$[\eta\text{-C}_5\text{H}_5\text{Mo(CO)}_3]_2$ cm ⁻¹
3115(s)		3115(s)
2976(s)	3103	
2900(s)	3028	
2814(m)		
2022(vs)		1952(vs)
1935(vs)		1926(vs)
1905(m)		1885-1900(vs) (doublet)
1422(s)	1441	1418-1428(vs) (doublet)
1264(w)		1266(w)
1353(w)		1350-1358(m) (doublet)
1160(s)		
1110(w)		
1060(m)		1068(w)
1006-1012(s) (doublet)	1028	1007-1014(m) (doublet)
913-924(w) (doublet)		912-920(w) (doublet)
849(w)	868	
838(m)		850(w)
823(s)		838(m)
		824(s)
765(m)		

FIGURE 5: INFRARED COMPARISON OF CYCLOPROPYLMOLYBDENUM COMPOUND WITH CYCLOPROPANE AND A CYCLO-PENTADIENYLMOLYBDENUM COMPOUND.

assignable absorbancies which are evaluated below.

Absorbancy (cm^{-1})

1090(m)
1242(m)
1360(s)
1416(m)
1614(vs)
1676(s)

FIGURE 6: INFRARED ABSORBANCIES OF
CYCLOPROPYL BROMIDE-TITANIUM(IV)
CHLORIDE COMPLEX.

The absorbancies at 1614 and 1676 cm^{-1} are very characteristic of a conjugated and halogen substituted olefin system. Although the C=C stretching frequency for olefins usually occurs around 1660-1640 cm^{-1} and is weak, it is well known that conjugation such as in a diene system, without a center of symmetry, shows two strong bands at around 1600 and 1660 cm^{-1} and that the frequency is increased slightly with the addition of an electron withdrawing group such as a halogen near the center of conjugation (32). Thus the two absorbancies in the 1600 cm^{-1} region can be assigned to a conjugated, halogen substituted olefinic system. Also the absorbancies at 1360 and 1416 cm^{-1} are characteristic of conjugated olefins (31), however these absorbancies are also characteristic CH_2 -wag and deformation bands respectfully. Thus it may appear to be ambiguous to

assign a definite origin to these peaks. The 1242 cm^{-1} absorbancy may also have a double explanation as to its origin, CH_2 -wag and/or ring deformation, which is observed in many small ring systems such as cyclobutenes. The 1090 cm^{-1} absorbancy is very characteristic of conjugated olefins (32) and shows very little frequency shift upon substitution in the system.

Although it may appear to be quite presumptuous to assign infrared absorbancies to organic moieties which may be coordinated to a transition metal, it has been shown by Powell and Sheppard (33) that the vibrational frequency of olefins show little shift in going from a free olefin to a coordinated olefin.

Cyclopropyl Cyanide-Titanium(IV) Chloride Complex:

Infrared studies of this complex were made using a 0.150 per cent potassium bromide pellet in the 600 to 2500 cm^{-1} region and a perfluorokerosine mull for the 2500 to 4000 cm^{-1} region. Listed in figure 7 are the major absorbancies of the complex as well as those for cyclopropyl cyanide.

The medium absorption at 3092 cm^{-1} is very indicative of an asymmetric stretching band of a terminal methylene ($=\text{CH}_2$) group (34). Also, the 3035 cm^{-1} peak is significantly strong for interpretative purposes and very characteristic of a $=\text{C-H}$ stretching band. The strong

absorbancy at 935 cm^{-1} is very indicative of molecules having a $=\text{CH}_2$ group and is usually attributed to a carbon-hydrogen out-of-plane bending vibration (34).

Absorbancy (cm^{-1})	
Cl ₂ TiC ₃ H ₄ CN	C ₃ H ₅ CN
3092(m)	3170(m)
3056(m)	3055(s)
3035(s)	3025(s)
2285-2265(s) (doublet)	2280(w) 2235(vs)
1610(s)	1510(w)
1450(m)	1460(m)
1430(m)	1342(w)
1385(m)	1260(w)
1340(w)	1190(m)
1125(m)	1120(m)
1065(m)	1065-1040(s) (doublet)
1040(m)	
935(s)	935(s)
	820(m)
	735(m)

FIGURE 7: INFRARED ABSORBANCIES OF CYCLOPROPYL CYANIDE AND CYCLOPROPYL CYANIDE-TITANIUM(IV) CHLORIDE COMPLEX.

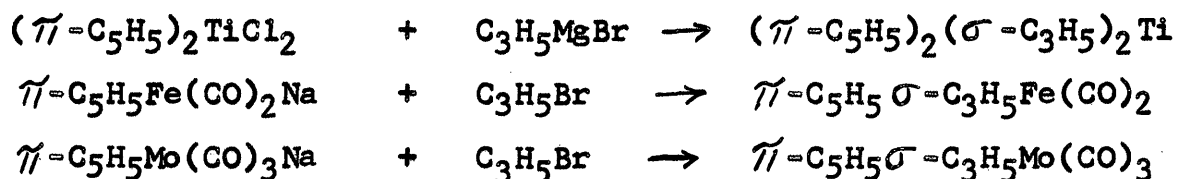
The nitrile ($-\text{C}\equiv\text{N}$) stretching band in the 2200 to 2300 cm^{-1} region deserves considerable attention in this analysis. In cyclopropyl cyanide this band is a strong singlet at 2235 cm^{-1} which is common for a non-conjugated nitrile (34). However in the complex this band is split into a doublet at the higher frequencies of $2285\text{-}2265\text{ cm}^{-1}$.

This splitting and shifting to higher frequencies of the nitrile stretching band is very indicative of a conjugated system such as the $C=C-C\equiv N$ and $O=C-C\equiv N$ linkages (32). Thus it appears that the nitrile group in the complex is conjugated with a methylene such as that observed in the above analysis.

The strong and broad band of the complex at 1610 cm^{-1} (which is observed as a doublet in the cyclopropylbromide-titanium(IV) chloride complex) is very characteristic of a highly conjugated $C=C$ stretching vibration which is usually a very strong and broad band in the $1600-1620\text{ cm}^{-1}$ region (34). The absorbancies at 1385 and 1340 cm^{-1} are usually characteristic for conjugated olefins (31).

DISCUSSION

It has been shown in this thesis that the sigma bonded cyclopropyl derivatives of the transition metals, bis(η -cyclopentadienyl)dicyclopropyltitanium(IV), σ -cyclopropyl- η -cyclopentadienyldicarbonyl iron, and σ -cyclopropyl- η -cyclopentadienyltricarbonyl molybdenum can be prepared according to the following reactions:



using tetrahydrofuran as the solvent. The cyclopropyl group was confirmed to be sigma bonded to the transition metal by comparison of the cyclopropyl absorbancies in the infrared which are similar to those described for the cyclopropyl derivatives of the main group elements (11, 12, 13). The stability of the transition metal-to-cyclopropyl bond decreases in the order molybdenum > iron > titanium, with the overall stability of these compounds being similar to that

of the analogous methyl derivatives previously described (16).

Due to the high sensitivity of the above sigma bonded cyclopropyl derivatives to ambient conditions, proton magnetic resonance studies were made only on the relatively stable molybdenum derivative which showed two distinct singlets at 0.40 and 5.36 ppm(δ). Although it is normally found that cyclopropyl derivatives give rise to quite complex proton magnetic resonance spectra it has been shown that in highly charged species such as the tricyclopropyl carbonium ion that the cyclopropyl group can give rise to a singlet (35). Also in this recent work it has been shown that both the alpha and beta protons of the cyclopropyl group are shifted downfield about three ppm when the group is bonded to a highly positive charged ion.

Since it is possible to consider that a high percentage of the electron density in the cyclopropyl molybdenum compound is shifted into the cyclopentadienyl and carbonyl groups leaving the molybdenum atom with considerable positive character, a relatively low (δ)-value for the cyclopropyl moiety can be explained. Although it would be rather highly speculative on the part of this author to assume that the alpha proton be shifted to the same chemical shift value as that of the beta proton or vice versa, it is almost certain

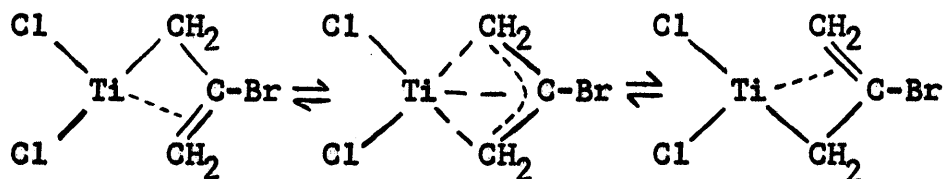
That the magnetic interactions of the carbonyl groups and the molybdenum atom would be more influential on the alpha proton than the beta protons of the group and thus give rise to an unfamiliar proton magnetic resonance spectra for the cyclopropyl group.

Until a further investigation into compounds analogous to those above has been undertaken, a direct correlation between molecular structure and possible origin of the singlet proton magnetic resonance absorbancy for the cyclopropyl group should not be attempted.

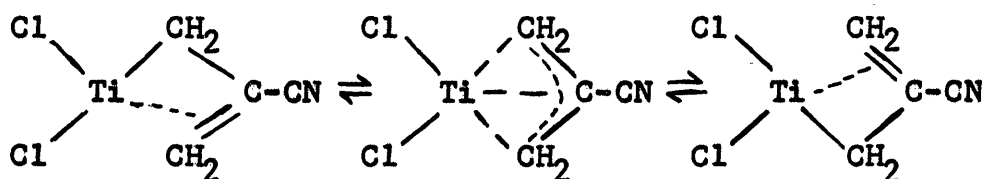
Although numerous complexes of titanium(IV) halides have been described (36), the complexes described in this thesis are the first examples of a system not containing donor atoms in groups VA and VIA of the periodic table. In previous work it has been assumed that the complexes formed involve a coordination of the highly electron donor elements of the VA and VIA elements with the titanium(IV) halides to give complexes with the stoichiometry $TiX_4(Y)$, $TiX_4(Y)_2$, and $TiX_4(Y)_4$, where X represents a halogen and Y may be a group such as esters, amines, azo-compounds, oximes, imines, acid halides, cyanides, and phosphorus and arsenic compounds. However in all the previously described complexes there is no data available which indicates that the organic portion of the molecule is involved in the complex formation.

In contrast to the above work it has been shown in this thesis that cyclopropyl bromide and cyclopropyl cyanide form complexes with titanium(IV) chloride involving the cyclopropane ring system. Unlike the normal sigma bonded alkyl derivatives of titanium(IV) chloride, which are dark red-to-maroon the cyclopropyl-titanium(IV) chloride complexes are a bright yellow color. Also the cyclopropyl-titanium(IV) chloride complexes differ in solubility from the sigma alkyl derivatives of titanium(IV) chloride which are highly soluble in normal hydrocarbons whereas the cyclopropyl complexes are insoluble. Because of these differences the cyclopropyl cyanide and cyclopropyl bromide complexes have been assigned the resonance structures in figure 8, with possible polymerization occurring through a chloride bridge mechanism. These structures are consistent with the observed infrared and proton magnetic resonance spectra and hydrolysis products of the complexes which were discussed previously in the Experimental Results section and in more detail below. Although the analytical and molecular weight values found are not in desirable agreement with the calculated values, several experimental factors may contribute to these observed values. For example, small quantities of solvent and reaction products such as hydrogen chloride or chlorine may be trapped in the solid as it is being formed during the reaction. Impurities such as these

would be essentially impossible to remove with the purification procedures used.



(a.)



(b.)

FIGURE 8: PROPOSED STRUCTURES FOR CYCLOPROPYL BROMIDE-TITANIUM(IV) CHLORIDE AND CYCLOPROPYL CYANIDE-TITANIUM(IV) CHLORIDE COMPLEXES.

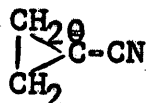
When a hydrocarbon is attached as an uncharged ligand to a metal atom, as in Zeise's salt, $K[\text{PtCl}_3(\text{C}_2\text{H}_4)] \cdot \text{H}_2\text{O}$ (33) and dibenzenechromium (37), the infrared spectra of the ligand is similar to that of the free ligand. If, therefore the cyclopropyl group were bonded to the titanium(IV) chloride moiety as a ring its local symmetry would be largely preserved and its infrared and proton magnetic resonance spectra should exhibit bands similar in number and position to those of other cyclopropyl systems (30). That this is

not the case must mean that the cyclopropane ring has opened and one or two carbon-titanium pi or sigma bonds formed, giving a compound somewhat analogous to the cyclopropane-hexachloroplatinic acid complex previously described (8). If only one sigma-type bond were formed, the C₃ chain would probably end with a CH₃, CH₂Cl, or =CH₂ group. The first two possibilities are ruled out since the easily detectable C-H stretching frequency for these groups are absent. However a strong indication of the =CH₂ C-H stretching bands are present from the peaks at 3092(m), 3056(m), and 3035(s) cm⁻¹ in the case of the cyclopropyl cyanide-titanium(IV) chloride complex. A detailed study of this region was not made on the cyclopropyl bromide-titanium(IV) chloride complex. The strong bands 1610(s) cm⁻¹ for the cyclopropyl cyanide-titanium(IV) chloride complex and 1614(vs) and 1676(s) cm⁻¹ for the cyclopropyl bromide-titanium(IV) chloride complex are very indicative of a C=C stretching frequency. The bands at 1360(s) and 1416(m) cm⁻¹ for the cyclopropyl bromide-titanium(IV) chloride complex and 1340(w), 1385(m), and 1430(m) cm⁻¹ for the cyclopropyl cyanide-titanium(IV) chloride complex are also strongly favored for a conjugated olefin system. These observations are consistent with the resonance structures proposed in figures 8a and 8b for the cyclopropyl bromide-titanium(IV) chloride

and cyclopropyl cyanide-titanium(IV) chloride complexes, respectively.

Since only a singlet proton magnetic resonance spectrum in solution is observed for both the cyclopropyl bromide-titanium(IV) chloride and the cyclopropyl cyanide-titanium(IV) chloride complexes it must be assumed that all four protons in structures "a" and "b" of figure 8 are equivalent. This may be the case if the designated equilibria represented in figure 8 are occurring faster than 500 cycles per second, which is similar to that observed for the sigma-cyclopentadienyl derivatives of iron, chromium, and molybdenum (16). Thus the observed proton magnetic resonance spectra of the cyclopropyl bromide-titanium(IV) chloride and cyclopropyl cyanide-titanium(IV) chloride complexes are also in agreement with the structures represented in figure 8. The hydrolysis products are also in agreement with the structures proposed in figure 8 for the cyclopropyl bromide-titanium(IV) chloride and cyclopropyl cyanide-titanium(IV) chloride complexes. The cyclopropyl bromide complex as proposed in figure 8a would give rise to 2-bromo-2propanol in accordance with both Markovnikov's rule (38) and the hydrolysis of titanium(IV) alkyls which yields the corresponding alkanes (36). The 2-bromo-2-propanol could then rapidly disproportionate to give hydrogen bromide and acetone. Acetone was confirmed to

be the only detectable product from hydrolysis of the cyclopropyl bromide complex by chromatographic analysis and proton magnetic resonance spectrum. Although the hydrolysis of the cyclopropyl cyanide complex appears to give only cyclopropyl cyanide by chromatographic analysis, this does not rule out structure "b" of figure 8, for it is known that the degree of ring closure in similar trimethylene organometallics is a function of both the substrate and the attaching specie(s) (8, 39). Thus it is conceivable that the hydrolysis of the cyclopropyl cyanide complex would give rise to a cyclopropyl cyanide carbanion,



which could then rapidly abstract a proton from either the water or the hydrogen chloride formed in the hydrolysis, giving rise to the observed cyclopropyl cyanide.

CONCLUSION

The synthesis of σ -cyclopropyl- η -cyclopentadienyldi-carbonyl iron, σ -cyclopropyl- η -cyclopentadienyltricarbonyl molybdenum, bis- η -cyclopentadienyl(dicyclopropyl)titanium(IV), and two complexes of titanium(IV) chloride with cyclopropyl-bromide and cyclopropyl cyanide has been described. The infrared and proton magnetic resonance spectra of the above compounds has been extensively studied and a molecular structure for the titanium(IV) chloride-cyclopropyl complexes is proposed. The sigma bonded cyclopropyl derivatives of titanium, iron, and molybdenum were found to have similar stability and chemical properties as that of the analogous methyl derivatives previously described (16).

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