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PERMANENT ADDRESS/*RÉSIDENCE FIXE* [redacted]

THE STEREOCHEMISTRY OF ADDITION OF CYCLOPROPANES TO TETRACHLORO(DIETHYLENE)DIPLATINUM(II)

by

NICHOLAS DOMINELLI

B.Sc. Simon Fraser University, 1971

A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

in the Department

of

Chemistry

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THE STEREOCHEMISTRY OF ADDITION OF CYCLOPROPANES TO TETRACHLORO(DIETHYLENE)DIPLATINUM(II)

Author: Nicholas Dominelli

(signature)

(name)

August 5, 1976

(date)

ABSTRACT:

Two stereospecifically deuterium labelled cyclopropanes, namely trans-1-n-hexyl-cis-2,3-dideuteriocyclopropane (XII), and cis-1-n-hexyl-cis-2,3-dideuteriocyclopropane (XIII), have been synthesized. Reaction of tetrachloro(diethylene)diplatinum(II) (Zeise's dimer) with n-hexylcylopropane, XII, and XIII yielded dichloro (2-n-hexylpropane-1,3-diyl)platinum complexes. These complexes were converted to their dipyridyl adducts to give trans-dichlorobispyridine (2-n-hexylpropane-1,3-diyl)platinum (XVI), derived from n-hexylcyclopropane, and the corresponding adducts XVII, and XVIII, derived from XII, and XIII respectively. Comparison of the 220 Mhz n.m.r. spectrum of XVI, with the 220 Mhz spectra of XVII, and XVIII revealed that the insertion of Pt into the C_2-C_3 bond of the cyclopropanes proceeded with retention of configuration at both carbons. This result represents the first unequivocal evidence for a concerted cycloaddition mechanism during the oxidative addition of a transition metal complex to a strained C-C bond.

DEDICATION:

This thesis is dedicated to my wife, Carol, and my parents for their understanding and encouragement during the course of this work.

ACKNOWLEDGEMENTS:

I wish to acknowledge the financial support of the S.F.U. President's Research Fund and the National Research Council for support of this work. Thanks are also extended to Dr. Harold Pierce and Professor A.C. Oehlschlager for guidance and encouragement during the course of this research project. Finally, I wish to express gratitude to the staff and fellow graduate students of the S.F.U. Chemistry Department who made my graduate studies all that much more enjoyable.

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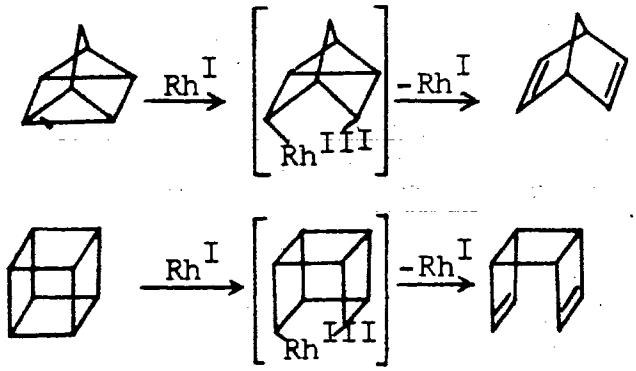
Introduction

The development of hydrogenation catalysts by Wilkinson and coworkers[1] has led to widespread interest in the field of homogeneous catalysis by transition metal complexes. To a large extent, this interest has focused on what have been loosely classified as oxidative addition reactions.[2,3,4] This includes the reactions of any transition metal complex in which an increase in the formal oxidation state of the metal is accompanied by an increase in its coordination number. Among the most interesting transition metal catalyzed organic reactions inferred to proceed by oxidative additions are[3,4] hydrogenation (1), and hydroformylation (2) of olefins, and valence isomerization (3).

$$RCH = CH_2 + H_2 \xrightarrow{RhCl(PPh_3)_3} RCH_2CH_3 \qquad (1)$$

$$RCH = CH_2 + H_2, CO \xrightarrow{Co_2(CO)_8} RCH_2CH_2-C(=O)H \qquad (2)$$



(3)

Oxidative addition reactions have been studied for a variety of metals, ligands, and substrates. Most of the transition metal complexes which undergo oxidative addition reactions are low spin, coordinatively unsaturated complexes [2,3,4] with d^7 (4), d^8 (5) or d^{10} (6) electron configurations.

$$2[Co^{II}(CN)_5]^{3-} + X\text{-}Y \rightarrow [Co^{III}(CN)_5X]^{3-} + [Co^{III}(CN)_5Y]^{3-} \quad (4)$$

X-Y = H_2, Br_2, H-OH, H-OOH, CH_3-I, I-CN, etc.

$$Ir^{I}(CO)Cl(PPh_3)_2 + X\text{-}Y \rightarrow Ir^{III}(X)(Y)(CO)Cl(PPh_3)_2 \quad (5)$$

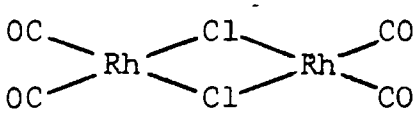
X-Y = H_2, Cl_2, HCl, CH_3-I, RSO_2-Cl, RHg-Cl, R_2Si-H, etc.

$$Pt^{O}(PPh_3)_2 + X\text{-}Y \rightarrow Pt^{II}(PPh_3)_2(X)(Y) \quad (6)$$

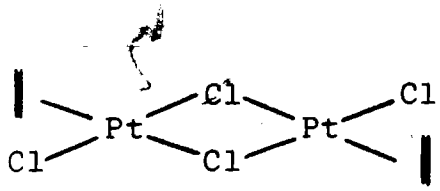
X-Y = CH_3-I, $C_6H_5CH_2$-Br, $(C_6H_5)_3Sn$-Cl, etc.

Owing to the stability of many square planar d^8 complexes of Ir^I, Rh^I and Pt^{II}, a considerable amount of research has been directed at these complexes.

Oxidative addition reactions usually proceed by insertion of the metal into an X-Y substrate single bond (e.g., X-Y = -C-Hal (Hal=I,Br,Cl), C-H, H-H, O-H). Only a few additions involving insertion into C-C single bonds have been reported to date. Such processes have been observed for two dimeric d^8 complexes of Rh^I (I) and Pt^{II} (II).

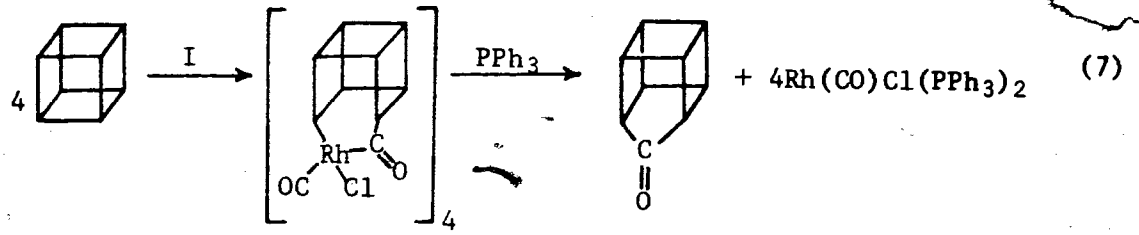


I



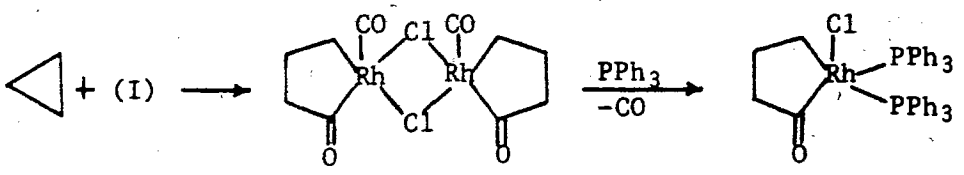
II

These reactions are particularly interesting since they are potentially useful in catalytic and synthetic organic transformations. The latter utility of these reactions has been demonstrated for the addition of cubane[5] to I which leads to the insertion of CO into a C-C single bond (7).



(7)

Insertion of Rh^{I} into strained C-C single bonds has also been reported to occur with cyclopropanes and cyclobutanes. Wilkinson, et al.[6] first reported the reaction of I with cyclopropane to yield an insoluble complex, which on the basis of i.r., n.m.r. and chemical reactions was formulated as the dimer III (8).



(8)

III

More recently Powell and McQuillin[7,8] have studied the reaction of I with substituted cyclopropanes. From the structure of the $NaBH_4$ reduction products obtained from the adducts, they deduced the structures of the addition products. The reaction scheme proposed by these authors to account for both addition and isomerization products isolated, involves a common intermediate (IV), which may be trapped by carbonyl insertion or isomerized by hydrogen transfer (Figure 1).

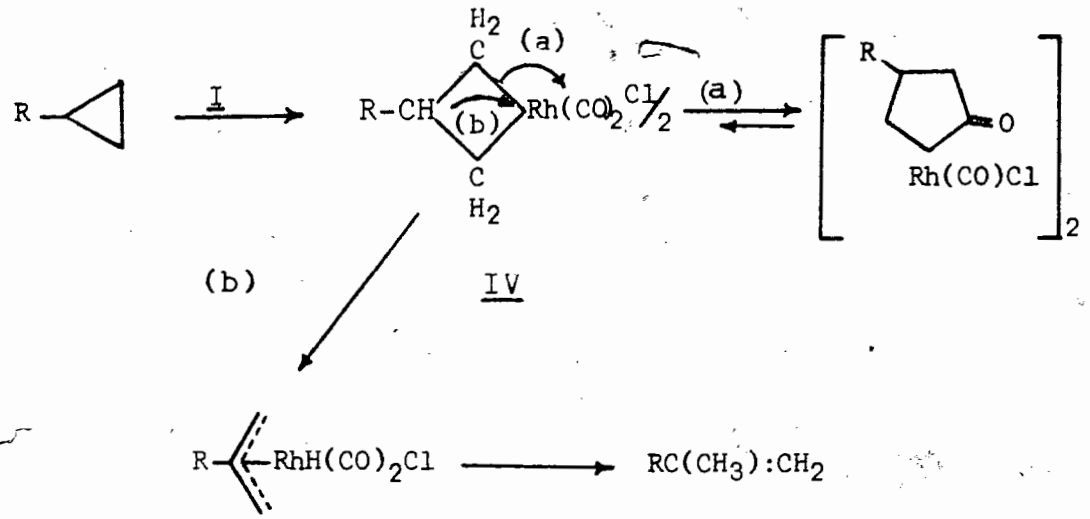
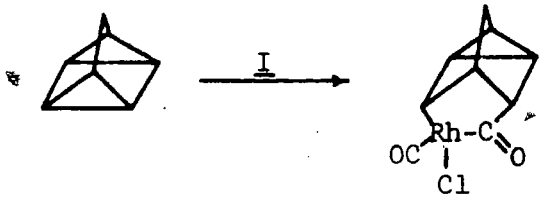


Figure 1: Reaction of Complex I with Monosubstituted Cyclopropanes

Similar reactions with I in which acyl rhodium adducts were isolated have been reported for quadricyclane (9) and tricyclooctane (10). The intermediates proposed for these reactions and attendant isomerizations catalyzed by other Rh^I complexes are analogous to IV.



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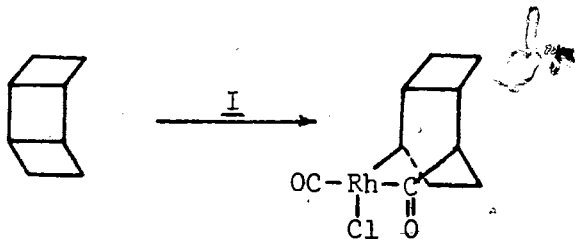
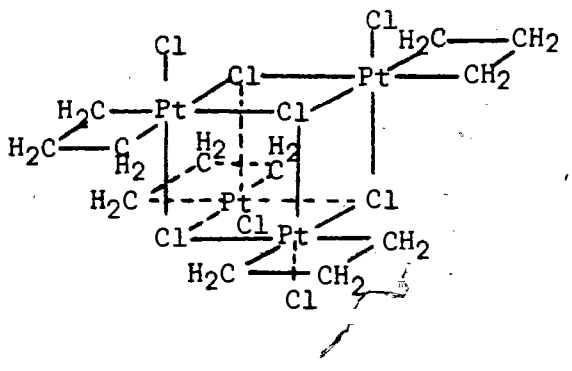
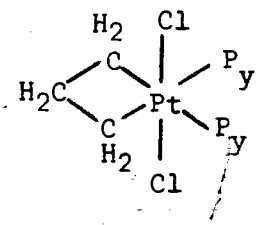


(10)

The insertion of the Pt^{II} complex, II, into substituted cyclopropanes is reported to give an insoluble polymeric product in high yield. The parent cyclopropane adduct $C_3H_6PtCl_2$ was first described by Tipper[11], and formulated as the tetramer V on the basis of spectral data,[12] and X-ray data[12,14] of the bis-pyridine derivative VI.

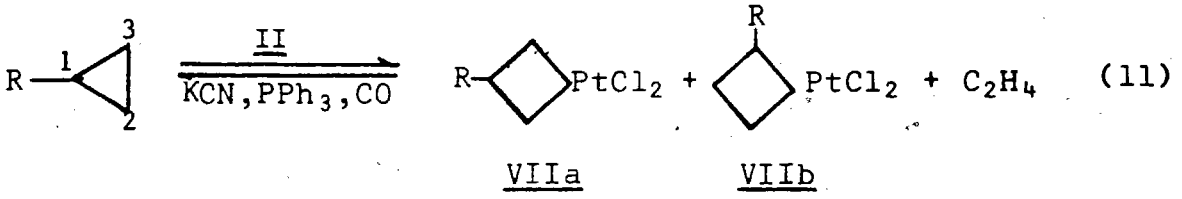


V



VI

McQuillin[15,16,17] and coworkers have studied the effect of substituents on the reactivity and selectivity of cyclopropanes toward II and have found that electron-donating groups on the cyclopropyl ring facilitate the insertion of Pt^{II} (complex II) into the C-C bond (11).



Furthermore, the insertion reaction occurs with marked selectivity at the least substituted cyclopropyl bond. The structures of the adducts were established as VIIa and VIIb by examination of the n.m.r. spectra of their bis-pyridine derivatives.

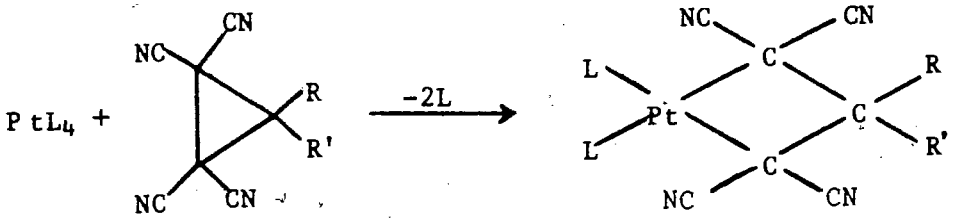
Reactions of C-C single bonds with Pt^{o} and Pd^{o} have also been observed but are confined to compounds in which one of the carbons is either part of a cyano function or is highly substituted by cyano groups (12)[18], (13)[19], (14)[20].

$$Pd \text{ or } Pt(PPh_3)_4 + N{\equiv}C\text{-}C{\equiv}N \xrightarrow[3\ hrs]{100^{o}C} CNPt(PPh_3)_2CN \qquad (12)$$

$$Pt(PPh_3)_4 + CH_3\text{-}C(CN)_3 \rightarrow Pt(CN)(PPh_3)_2C(CN)_2CH_3 \qquad (13)$$

$$Pt(PEt_3)_3 + C_6H_5\text{-}CN \rightarrow \begin{matrix} Et_3P & & C_6H_5 \\ & \diagdown\ \diagup & \\ & Pt & \\ & \diagup\ \diagdown & \\ NC & & PEt_3 \end{matrix} \qquad (14)$$

The recently reported[21] reaction of $Pt(PPh_3)_2C_2H_4$ or ML_n (n = 3,4; M = Pd or Pt; L = phosphines or triarylarsines) with tetracyanocyclopropane gives metallocyclobutane derivatives (15).



(15)

IX

The structure of the metallocyclobutane complex was deduced from i.r., n.m.r., and X-ray diffraction data[22] (IX: L = PPh_3; R=R'=H).

The mechanism for oxidative addition reactions is currently under dispute, undoubtedly due to the broad classification of such reactions. Two general mechanisms have been

proposed to describe the oxidative addition reactions of square planar d^8 complexes of Ir^I and Rh^I. A one-step concerted mechanism, based on orbital symmetry arguments, has been postulated by Pearson[23] for the reaction of $Ir(CO)ZL_2$ (Z = Cl, I, SCN; L = PPh_3, PPh_2Me) in dichloroethane with CH_3I, which explains the occurrence of both cis-and trans-addition products (Figure 2).

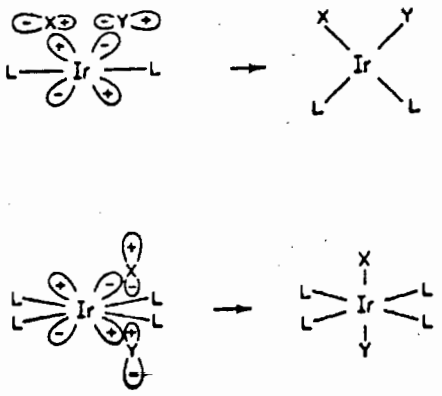
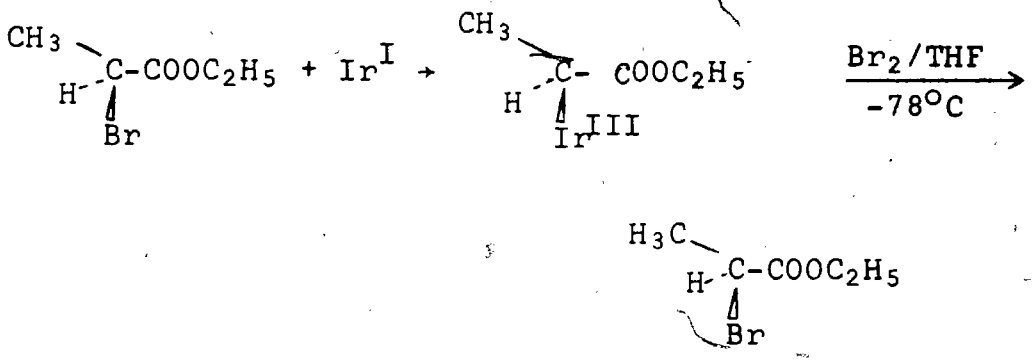


Figure 2: Pearson's Mechanism for cis and trans-Addition of Ir^I to Alkyl Halides.

Evidence for the one-step, concerted process is indicated by the failure to incorporate $^{131}I^-$ into the product, and by the addition of CH_3I gas to solid complexes, where formation of ionic intermediates can reasonably be excluded. In addition, Pearson observed that there is retention of configuration at the reacting carbon of optically active $CH_3\text{-}\overset{Br}{\underset{|}{C}}HCOOC_2H_5$ during its addition to $Ir(CO)Cl(PMePh_2)_2$ (16).

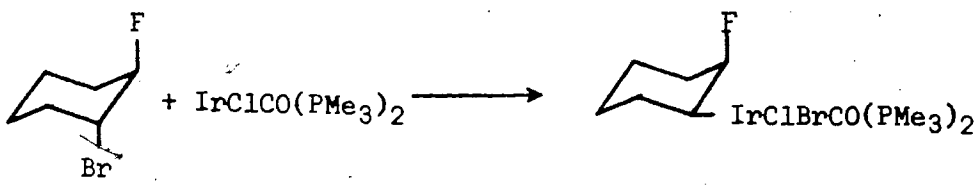


(16)

The assumption made in this deduction was that cleavage of the Ir-alkyl bond of the addition product, $Ir(CO)Cl(PMePh_2)_2(CH_3CHCOOC_2H_5)Br$, with bromine proceeded with retention of configuration. Since there are related metal alkyl bond cleavages[24,25,26] effected with bromine which involve inversion of configuration of the alkyl carbon, further work is necessary to define the stereochemistry of this reaction. Osborn[30] has repeated this experiment and found that the purified Ir^{III} product (cf. 16) showed only negligible optical activity under a variety of experimental conditions.

Another mechanism, which accounts for the observed trend toward increased reactivity of the metal complexes with increasing ligand basicity, involves an SN2 process in which the metal complex acts as a nucleophile. This model predicts inversion of configuration at the reacting carbon atom of an alkyl halide, and either cis or trans addition to the metal. The only oxidative addition of an alkyl halide to a d^8 complex

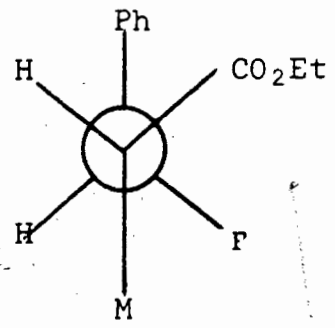
thought to involve inversion of configuration at carbon was reported by Osborn[27] and coworkers. They analyzed the reaction mixture obtained from addition of trans-1-bromo-2-fluorocyclohexane to $Ir(CO)Cl(PPh_3)_2$ and $Ir(CO)Cl(PMe_3)_2$ by n.m.r. and concluded that the addition product possessed cis cyclohexyl stereochemistry, resulting from inversion at the carbon undergoing reaction (17).

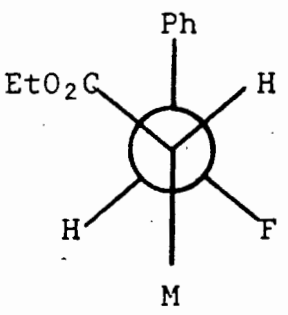


(17)

Jensen and Knickel[28] were unable to repeat this work, finding no reaction under the reported conditions, nor under conditions appreciably more drastic. Osborn[29] has repeated this work and found that the observed reaction did proceed but only in the presence of impurities or radical initiators such as AIBN or peroxide. Reinvestigation of the stereochemistry of the reaction revealed that both cis and trans 1-bromo-2-fluorocyclohexane gave the same adduct. Thus, this process appears to be radical in nature and involves organic radical intermediates capable of loss of stereochemistry at the reacting carbon atom.

Additional evidence for a free radical pathway comes from the reaction of $IrClCO(PMe_3)_2$ with $C_6H_5CHFCHBrCOOEt$ (Xa).[30] The n.m.r. spectra (^1H, ^{19}F, ^{13}C) of the isolated adduct indicated it to be consistent with configuration XIb. However, the n.m.r. spectrum of the reaction mixture before work-up





Xa M = Br

XIa M = $IrClBrCO(PMe_3)_2$

Xb M = Br

XIb M = $IrClBrCO\ P(Me_3)_2$

shows the presence of both species (XIa and XIb) in the ratio of 1:4.5. The same ratio is obtained with Xb. Similar reactions have been reported[30-32] for Pt^o and Pd^o complexes, and both chain and non-chain[33] free radical mechanisms have been proposed. These additions are characterized by decreases in reaction rates by radical scavengers and by loss of stereochemistry at carbon. Kramer and Osborn[32] have proposed a generalized reaction scheme (Figure 3) for alkyl halide addition to Pt^o complexes. The scheme allows for several routes depending on the reactivity of the alkyl halide, the

nucleophilicity of the metal complex, the ability of the metal complex to undergo one-electron transfer processes,[34] steric effects and ligand exchange processes.

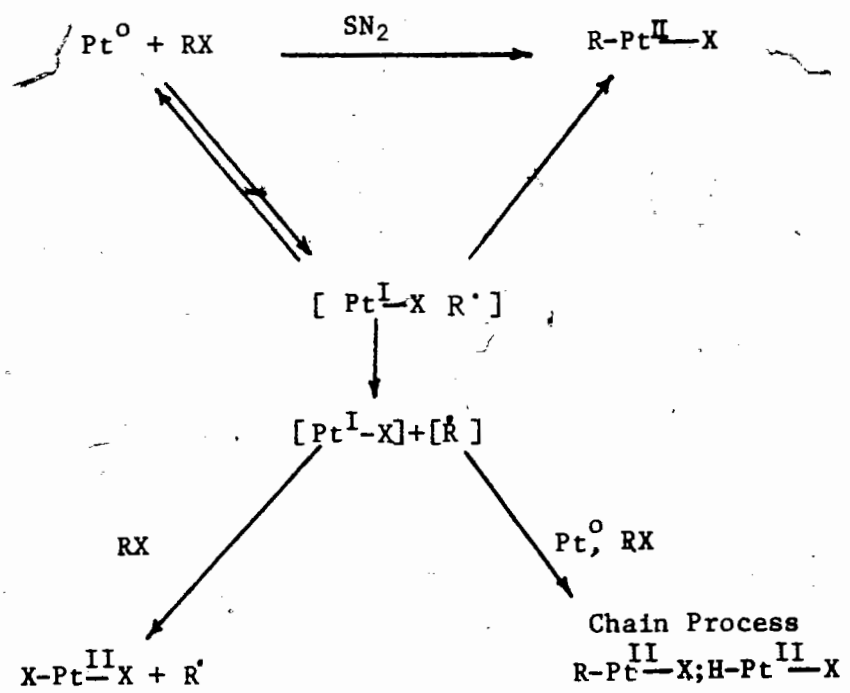
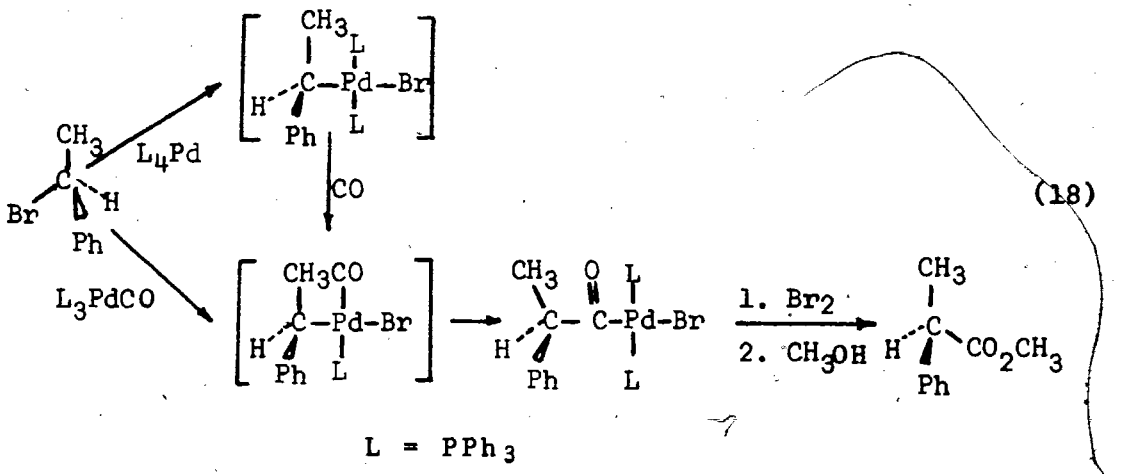


Figure 3: Generalized Osborn Mechanism for Reaction of Pt^{o} with Alkyl Halides.

Supporting evidence for the SN2 mechanism during oxidative additions of d^8 complexes has been recently reported by Collman [35] for a macrocyclic Rh^{I} complex and by Ugo [36] for $IrCl(CO)(PEt_nPh_{3-n})_2$ (n=1,2) and $IrCl(CO)[P(p\text{-}Z\text{-}C_6H_4)_3]_2$ (Z=Cl,F,H,CH_3,OCH_3).

For the related d^{10} complexes, Stille[37,38] has reported inversion of configuration at the reacting carbon atom during the addition of alkyl halides to Pd^{o} complexes. He used optically active α-phenylethyl bromine and $PdCO(PPh_3)_3$ or $Pd(PPh_3)_4$ under a CO atmosphere (18).



(18)

In this reaction sequence carbonyl tris(triphenylphosphine) palladium (0) undergoes oxidative addition to give an intermediate, followed by intramolecular carbon monoxide insertion to afford a stable acylpalladium complex. The assumption is made in this work that the carbonyl insertion occurs with 100% retention of configuration. It was determined that under these conditions the stereospecificity of the oxidative addition process was approximately 90-95%. The same authors

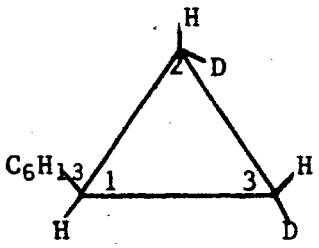
also report the reaction of optically active 1-phenyl-2,2,2-trifluoroethyl chloride with $Pd(PPh_3)_4$ to give a stable complex $Pd(PPh_3)_2[PhCH(CF_3)]Cl$ that exhibited little or no optical rotation. This outcome is reminiscent of Osborn's radical processes. An SN2 mechanism has also been implicated in the reaction of Pt^o and Pd^o complexes with tetracyano cyclopropanes[21] to give metallocyclobutane addition products.

There is to date no conclusive stereochemical evidence which enables one to differentiate among the proposed mechanisms. It would seem likely from the existing literature that the mechanism of oxidative addition could vary, depending on the metal complex and adding species.

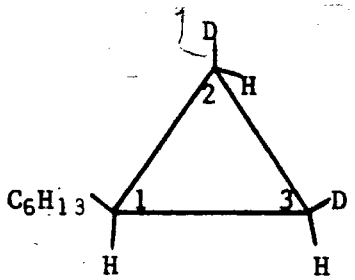
The goal of the present investigation was to design a reactive hydrocarbon capable of C-C addition to a transition metal complex, which would yield an adduct amenable to spectroscopic determination of the stereochemistry of the addition at both reactive C-C centers of the hydrocarbon. For reasons which are detailed below, we chose to synthesize a pair of deuterated alkylcyclopropanes. These molecules possess C-C bonds reactive in the oxidative addition process and are expected to yield products which could be examined by n.m.r. spectroscopy. It was hoped that the stereochemical outcome of the addition process could be determined by examination of the n.m.r. spectra of these adducts.

Results

Since the reaction of Pt^{II} (complex II) has been reported to proceed well with monosubstituted cyclopropanes [16,17] at the least substituted cyclopropyl C_2-C_3 bond, the synthesis of compounds XII and XIII stereospecifically deuterated at C_2 and C_3 was undertaken.



XII



XIII

A priori, there are three stereochemical courses which could be observed during addition of the Pt^{II} complex to a C_2-C_3 bond of such cyclopropanes; these are (Fig. 4):

a) Retention of configuration (R,R) at both carbon centres (C_2 and C_3);

b) Inversion of configuration (I,I) at both carbon centres (C_2, C_3);

and c) Retention of configuration at one centre, inversion at the other (R,I).

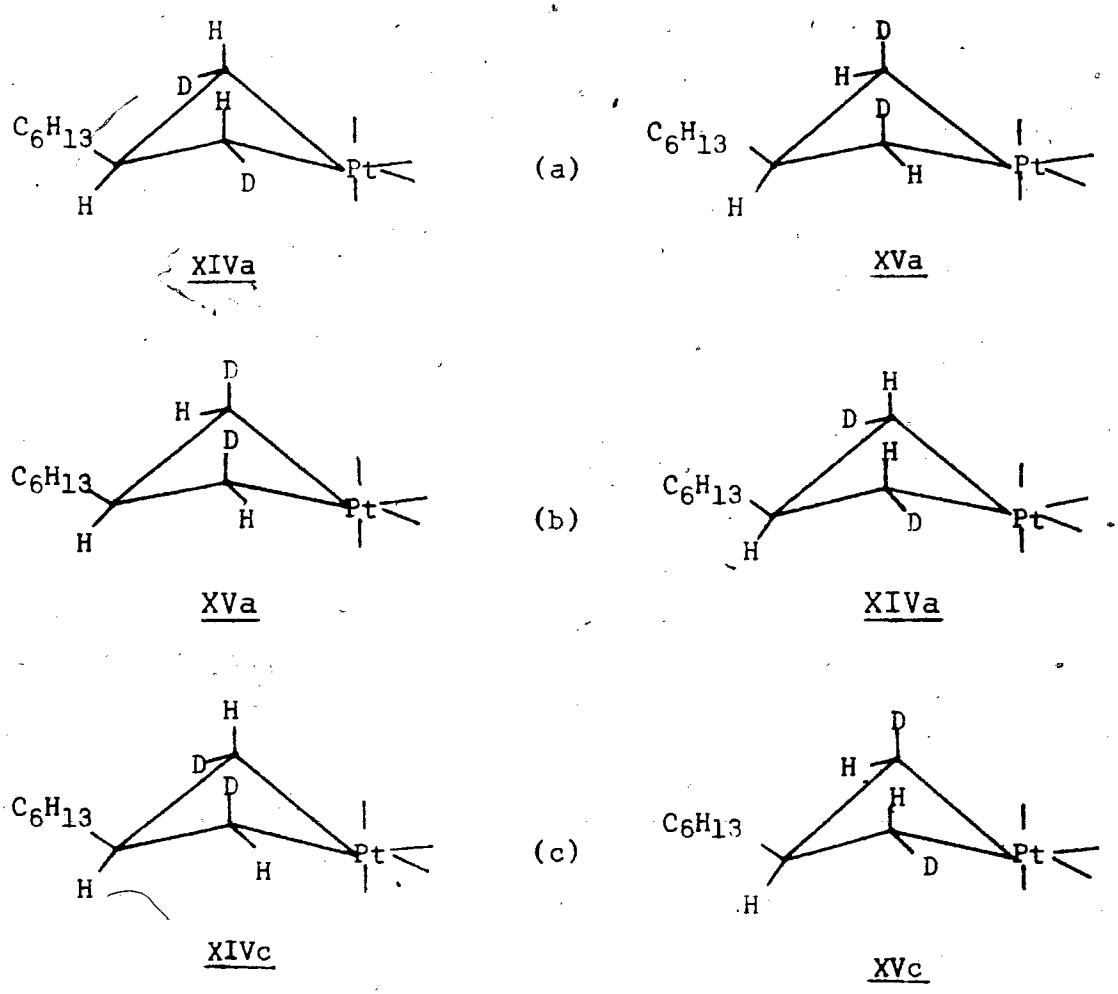


Figure 4. Possible Products of Reaction of Complex II with XII and XIII.

a) Retention at both C_2 and C_3 (R,R).

b) Inversion at both C_2 and C_3 (I,I).

c) Retention at one carbon, inversion at another (R,I).

It was desired that the distinction between these three possibilities be evident upon examination of the n.m.r. spectra of the addition products. Two stereochemical probes based on n.m.r. spectral parameters were considered. A difference in chemical shifts between the cyclopropyl hydrogens (C_2 and C_3) cis and trans to the n-alkyl substituent of monoalkyl cyclopropanes has been reported.[39] Significant differences in the coupling constants of cis- and trans-cyclopropyl hydrogens have also been established[40].

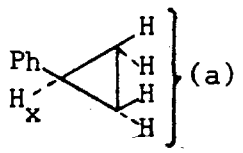
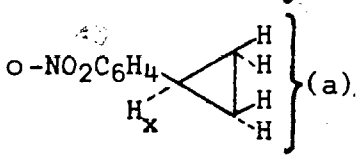
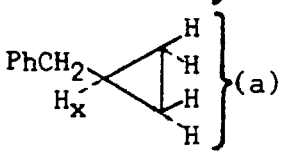
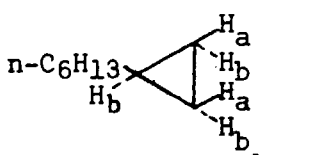
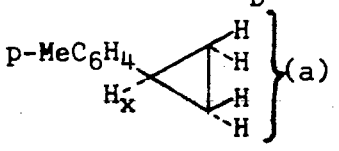
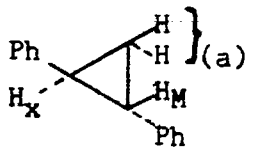
It is known that alkyl groups have a shielding effect due to their magnetic anisotropy.[39] It has been observed that the absorption peaks of cyclopropyl hydrogens cis to alkyl substituents are shifted upfield than those of their trans counterparts. This effect is also exhibited by the Pt^{II} adducts of cyclopropanes as indicated by the n.m.r. data[17] for a series of cyclopropanes and their corresponding Pt^{II} $Cl_2(py)_2$ adducts and shown in Table 1. A trend also obvious from this table is that all cyclopropyl methylene proton peaks are shifted downfield by approximately the same value as one proceeds from the cyclopropane to the adduct.

The coupling constants of cis and trans cyclopropyl hydrogens have been studied by a number of workers[40] and are summarized in Table 2. As is evident from the table, the coupling between vicinal cis-cyclopropyl hydrogens is 8 to

11 Hz , whereas that for vicinal trans hydrogens is 5 to 8 Hz. Vicinal cyclobutyl hydrogen couplings show similar[44] behavior (see Table 3) in that coupling between vicinal cis hydrogens is greater than that between trans hydrogens.

Table 1

Downfield Proton Chemical Shifts for $PtCl_2(py)_2$ Trimethylene Derivatives in Comparison With the Parent Cyclopropanes†

Cyclopropane	τ	Complex τ	Δ
	H_a 9.28 H_x 8.20	7.03 5.90	2.25 2.30
	H_a 9.14 H_x 7.64	7.02 5.44	2.1 2.2
	H_a 9.6 H_x 8.99	7.30 6.79	2.3 2.2
	H_a 10.0 H_b 9.6	7.58 7.25	2.42 2.35
	H_a 9.3 H_x 8.20	7.05 5.07	2.15 3.13
	H_a 8.65 H_m } 7.90 H_x }	6.80 4.88 5.25	1.85 3.02 2.65

† Δ p.p.m. in $CDCl_3$

TABLE 2

^1H-^1H Coupling Constants in Cyclopropane Derivatives[40]

Compound	Solvent	Coupling Constants, c.p.s.		
		J_{gem}	J_{cis}	J_{trans}
1-Phenyl-1-bromocyclopropane	Neat	-5.9 ± 0.2	+10.5 ± 0.3	+7.0 ±0.2
1,1-Dimethylcyclopropanecarboxylic acid	Neat	-4.3 ± .3	+8.0 ± .3	+5.6 ± .3
Dimethyl 1-methylcyclopropane-cis-1,2-dicarboxylate	Neat	-4.7 ± .2	+8.6 ± .2	+6.3 ± .2
Dimethyl 1-methylcyclopropane-trans-1,2-dicarboxylate	Neat	-4.2 ± .2	+8.8 ± .2	+6.6 ± .2
1,1-Dichlorocyclopropane	Benzene	-6.0 ± 2.0	+11.2 ± .5	+8.0 ± .5
1,1-Dimethylcyclopropane	Benzene	-4.5 ± 1.0	+9.2 ± .5	+5.4 ± .5

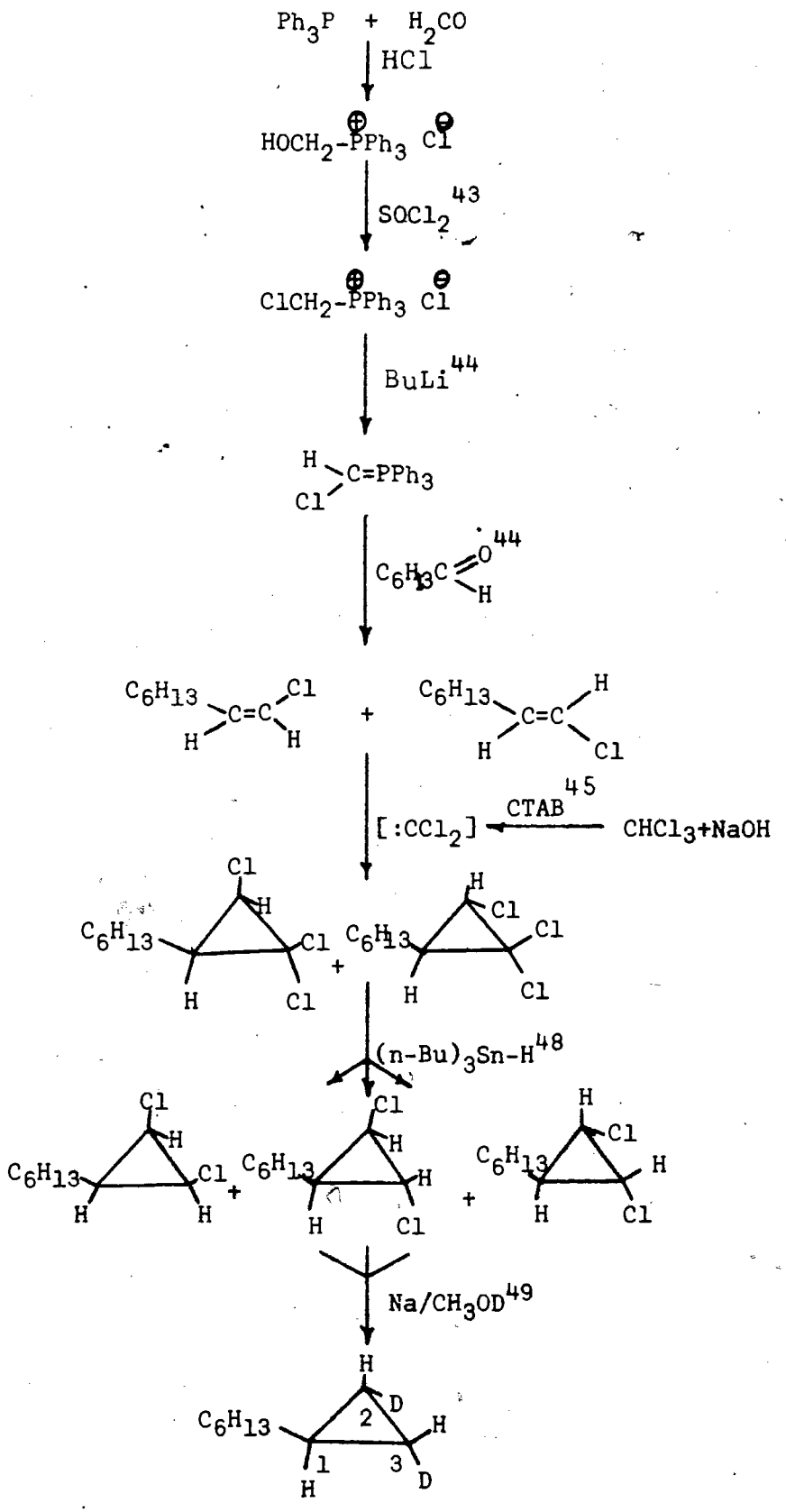
TABLE 3

Vicinal ^1H-^1H Couplings in Four Membered Rings[41]

Compound	J_{cis}	J_{trans}
cyclobutane	10.4 (Hz)	4.9 (Hz)
cyclobutanone	10.0	6.4
thietane	8.9	6.3
oxetane	8.7	6.7
azetidine	8.4	6.0
thiatane-1,1-dioxide	10.3	6.3

Our initial efforts were directed at unequivocal syntheses of n-hexylcyclopropane and its stereospecifically deuterated analogs XII and XIII. The synthesis of n-hexylcyclopropane was carried out according to the procedure of Simmons and Smith[42]. The synthesis of XII proceeded from reaction of a mixture of cis and trans 1-chloro-oct-1-enes[44] and dichlorocarbene generated in the presence of a phase transfer agent (cetyltrimethylammonium bromide)[45] (CTBA). The mixture of hexyltrichlorocyclopropanes thus generated was reduced to the dichloro stage by reaction with tri-n-butyltin hydride[48]. Deuterium was placed in the molecule stereospecifically trans to the hexyl substituent by reduction of the dichlorocyclopropane isomers generated above with sodium in methanol-OD. This reduction is known to yield products in which deuterium is placed in the least hindered position at each chlorine containing carbon[49] (Figure 5).

In the present case, analysis of the deuterated product (principally cyclopropane XII) by mass spectroscopy revealed 92% D_2 and 8% D_1. Analysis by n.m.r. revealed that the dideuterio species (XII) was contaminated to the extent of 9% with XIII or the isomer in which the deuteriums were trans to one another. The total contamination due to XIII and isomers having C_2 or C_3 protons trans to the hexyl group was 17% by n.m.r. analysis.



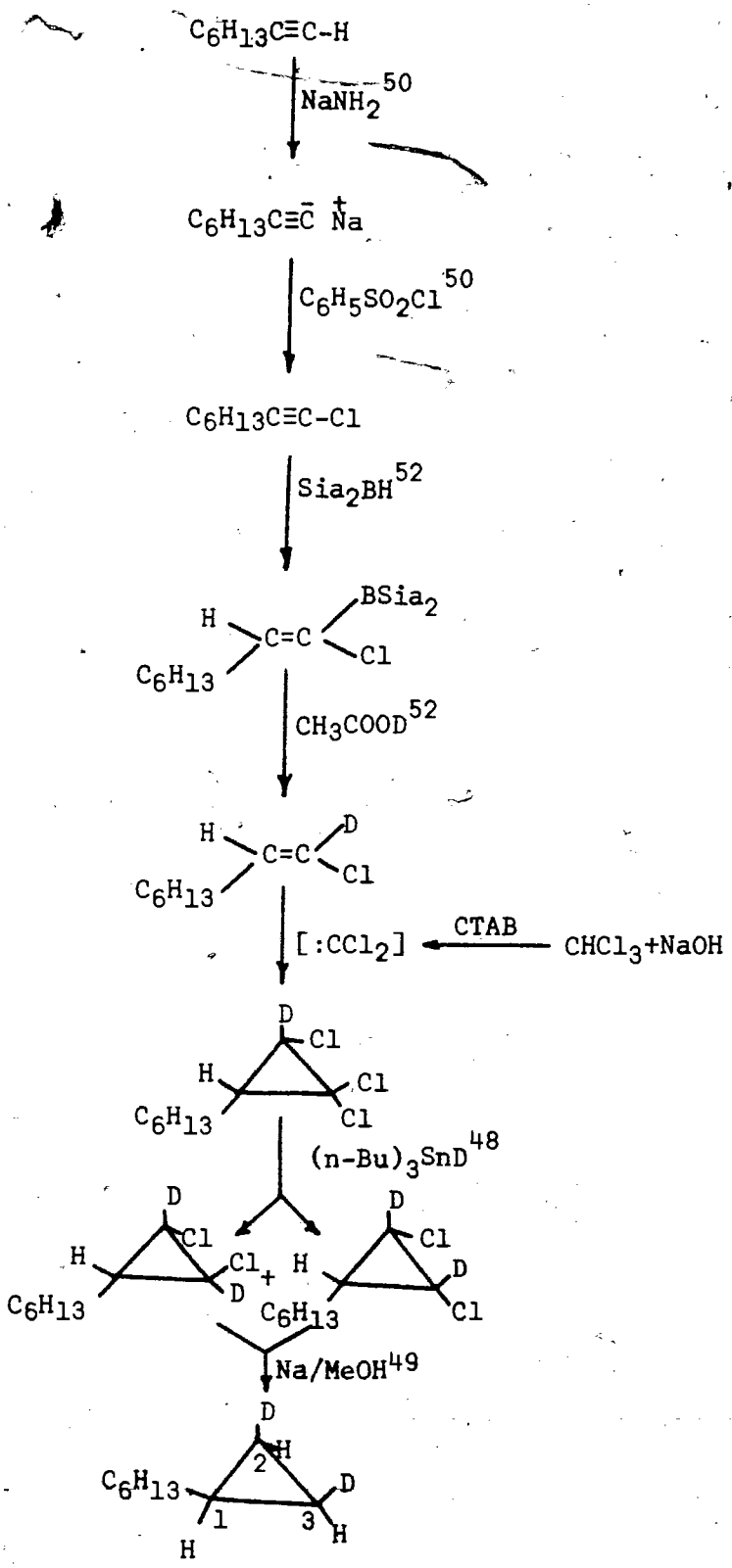
XII

Figure 5: Synthesis of XII

The synthesis of XIII proceeded from 1-deuterio-1-chlorooct-1-ene[50-52]. This olefin was prepared by reaction of disiamylborane with 1-chlorooct-1-yne[52] followed by hydrolysis of the vinyl borane in acetic acid-OD[52]. The deuterated chlorooctene thus produced was allowed to react with dichlorocarbene as above and the hexyltrichlorocyclopropane produced was reduced to the dichloro stage by reaction with tri-n-butyltin deuteride[48]. This sequence placed one deuterium at each of the chlorinated carbons (C_2 and C_3). Reduction of the dichlorodideuteriocyclopropanes with sodium in methanol[49] gave predominantly XIII. Mass spectroscopic analysis of the deuterated product produced by this sequence revealed 73% D_2 and 27% D_1. Since nuclear magnetic resonance analysis revealed 28% contamination of XIII by isomers containing protons at C_2 and C_3 cis to the hexyl group, one may deduce that, within experimental limits of detection, XIII was contaminated only with the monodeuterio species (Figure 6).

Each of XII, XIII, and n-hexylcyclopropane were reacted with Pt^{II} (complex II) under the conditions used by Powell and McQuillin[17]. The insoluble yellow products thus formed were reacted with pyridine to give the corresponding bispyridine adducts[17]. These adducts were then analyzed by 220 MHz n.m.r. to determine the stereochemistry of the insertion reaction.

From the preceeding arguments, the chemical shifts for the 2,3-cis-hydrogens of XII should be further upfield



XIII

Figure 6: Synthesis of XIII

than the 2,3-trans hydrogens of XIII. Thus the chemical shifts of the C_2 and C_3 hydrogens in the derived $Pt^{II}Cl_2(Py)_2$ adducts should depend on the stereochemical outcome of the reaction of each deuterated cyclopropane with Pt^{II} (complex II). If the reaction proceeds with

a) total retention, then δ_{H_2,H_3} of the adduct from XII will be less than δ_{H_2,H_3} of the adduct derived from XIII;

b) total inversion, then δ_{H_2,H_3} of the adduct from XII will be greater than δ_{H_2,H_3} of the adduct derived from XIII;

c) retention at one center and inversion at another center, then the spectra of adducts derived from XII and XIII will be identical.

The distinction between the three possible courses based on the coupling constant differences follows an equally definitive argument.

Thus for the case where $J_{cis} > J_{trans}$ in the derived adducts, if the reaction proceeds with

a) total retention, then $J_{1,2}$ and $J_{1,3}$ in the adduct derived from XII will be less than $J_{1,2}$ and $J_{1,3}$ in the adduct derived from XIII;

b) total inversion, then $J_{1,2}$ and $J_{1,3}$ in the adduct derived from XII will be greater than $J_{1,2}$ and $J_{1,3}$ in the adduct derived from XIII.

c) retention at one center, and inversion at the other center then the H_2 and H_3 hydrogens in the

adducts derived from both XII and XIII will exhibit both cis and trans coupling with H_1.

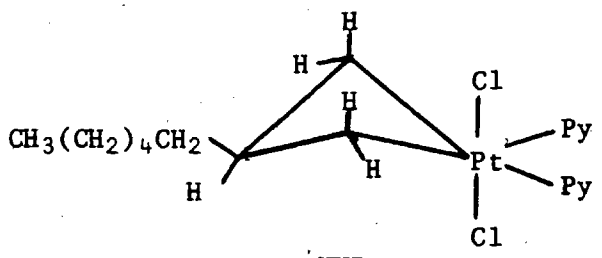
The ^1H n.m.r. spectra of XII (Figure 7), XIII (Figure 8), and n-hexylcyclopropane revealed the presence of a quartet at δ 1.08 (J=7 Hz) assigned to the CH_2 group α to the ring, a broad multiplet at δ 1.20 assigned to the remaining n-hexyl methylene hydrogens, a methyl group appearing as a triplet at δ 0.83 (J=6.7 Hz) and a one hydrogen multiplet at δ 0.50 attributable to H_1. The ^1H n.m.r. spectrum of n-hexylcyclopropane revealed the C_2 and C_3 hydrogens cis to the hexyl group as a multiplet centered at δ 0.1 and the hydrogens trans to the hexyl group as a multiplet centered at δ 0.27[17]. In the spectrum of XII (Figure 7), the signal due to the cis-2,3 hydrogens appears as a doublet ($J_{1,2(3)}$=5 Hz), and that due to the trans-2,3-hydrogens as a reduced size multiplet (17% of cis). The n.m.r. spectrum of XIII (Figure 8) revealed the signal of the trans-2,3-hydrogens to be 28% that of the trans-2,3-hydrogens which gave a doublet signal ($J_{1,2(3)}$=8 Hz).

The $Pt_2Cl_2(Py)_2$ adducts of n-hexylcyclopropane, XII and XIII revealed common ^1H-n.m.r. signals due to coordinated pyridine (δ 6.5-8.9) and n-hexyl groups (CH_3, δ 0.80; $(CH_2)_4$, δ 1.25; CH_2-ring, δ 1.75). The n.m.r. spectrum of XVI (Figure 9,9a), the adduct of n-hexylcyclopropane, exhibited a multiplet signal at δ 3.39 assigned to H_1. The ring methylene hydrogen signals appear as quartets at δ 2.95 (cis-2,3-H) and δ 3.22 (trans-2,3-H) with ^{195}Pt quartet satellites. The coupling of the cis-2,3-hydrogens with H_1 was observed to be

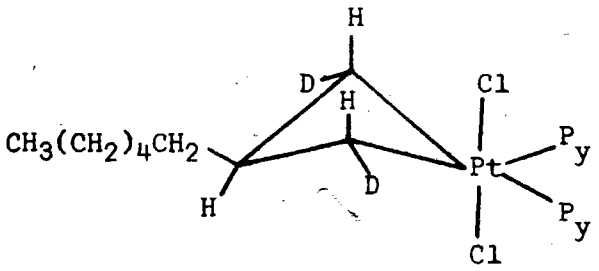
9.0 Hz and coupling with ^{195}Pt 86 Hz. Coupling of the trans-2,3-hydrogens with H_1 was 7.5 Hz and with ^{195}Pt 82 Hz. The above assignments are consistent with the shieldings[17,39] and couplings observed in other three-[40,55] and four-[41] membered rings and with those previously reported for XVI[17].

Examination of the n.m.r. spectrum of the $PtCl_2(Py)_2$ adduct (XVII, Figure 10) derived from XII revealed the signal due to the cis-2,3-hydrogens as a doublet ($J_{1,2(3)}$=9.0 Hz) at δ 2.91 with ^{195}Pt satellites. A signal (δ 3.18) due to trans-2,3-hydrogens revealed that contamination was the same as in XII. This observation unequivocally establishes the structure of the adduct of XII as XVII. Similarly the n.m.r. spectrum of the adduct XVIII (Figure 11) derived from XIII revealed a doublet ($J_{1,2(3)}$=7.5 Hz) signal at δ 3.18 with ^{195}Pt satellites due to the trans-2,3-hydrogens. Contamination by isomers containing cis-2,3-hydrogens was the same (28%) as that noted in XIII. These observations define the structure of the adduct of XIII as XVIII. The expected splitting for cyclopropyl hydrogens in XVII and XVIII is shown in Figure 12.

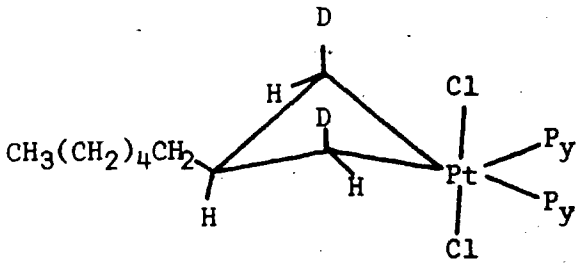
Within the limits of detection of our n.m.r. method, the addition of Pt^{II} (complex II) to cyclopropanes XII and XIII proceeds stereospecifically with retention of configuration at the two unhindered ring carbons.



XVI



XVII



XVIII

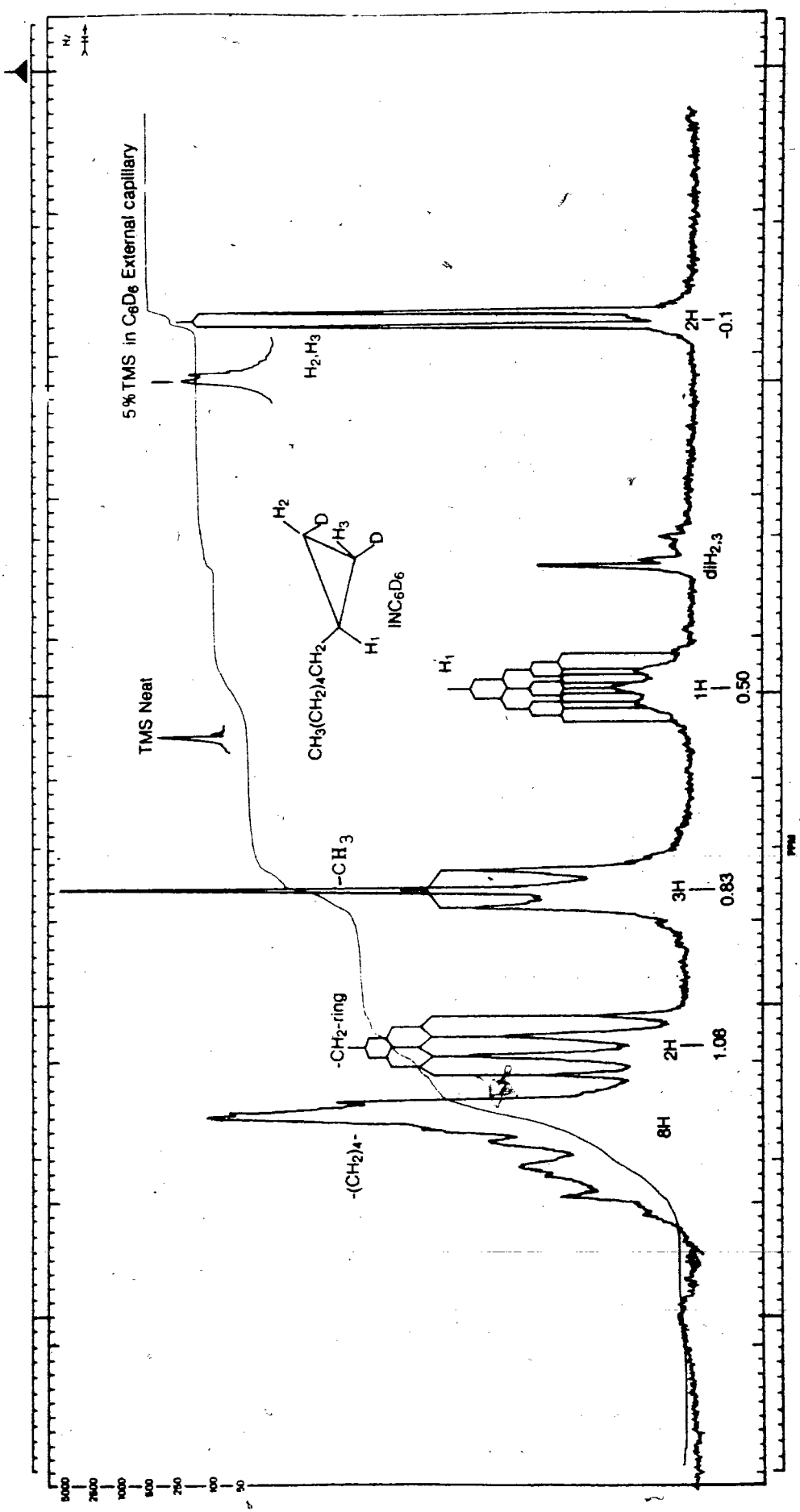


Figure 7: N.M.R. Spectrum of Compound XII.

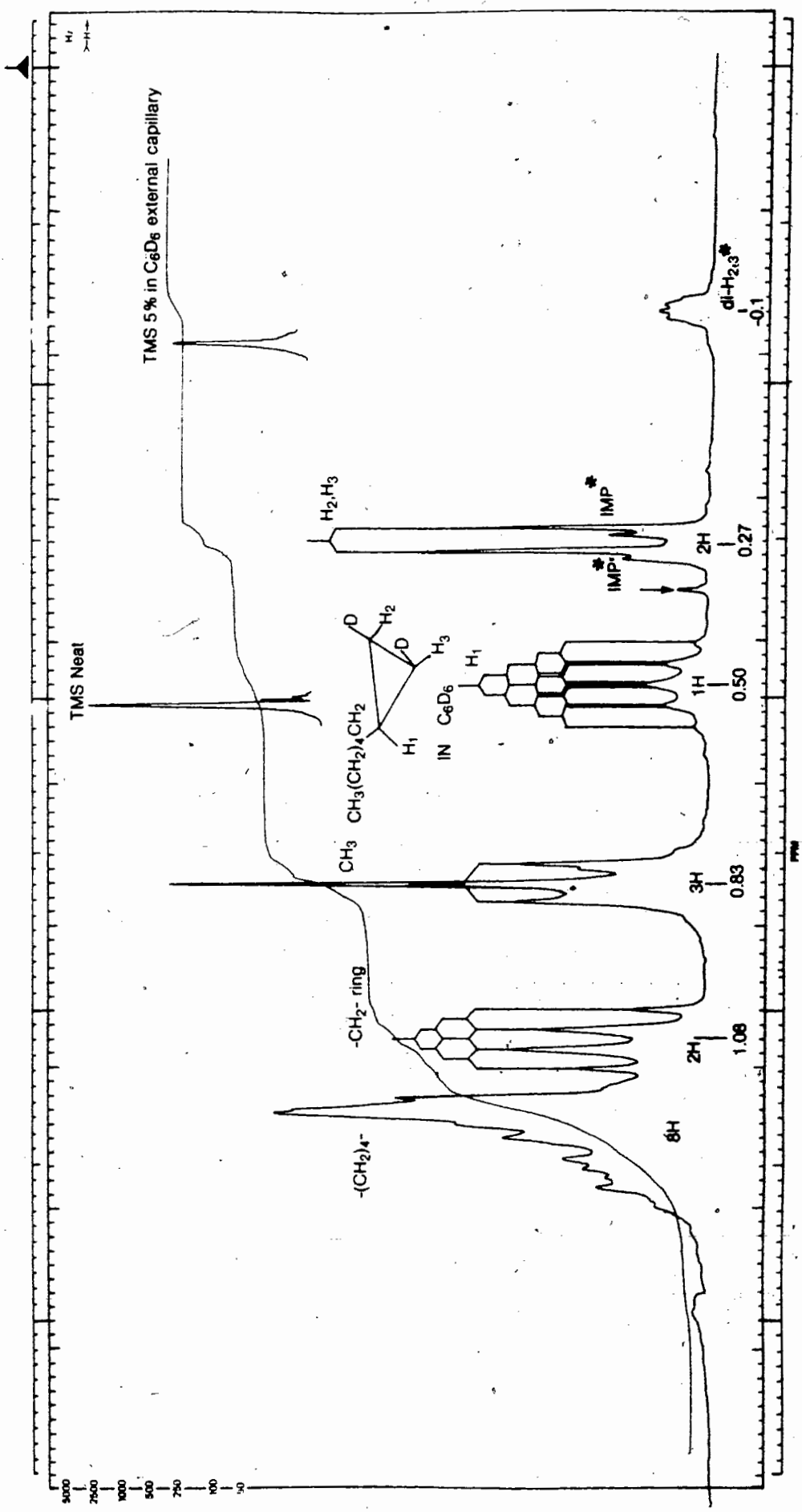


Figure 8: N.M.R. Spectrum of Compound XIII.

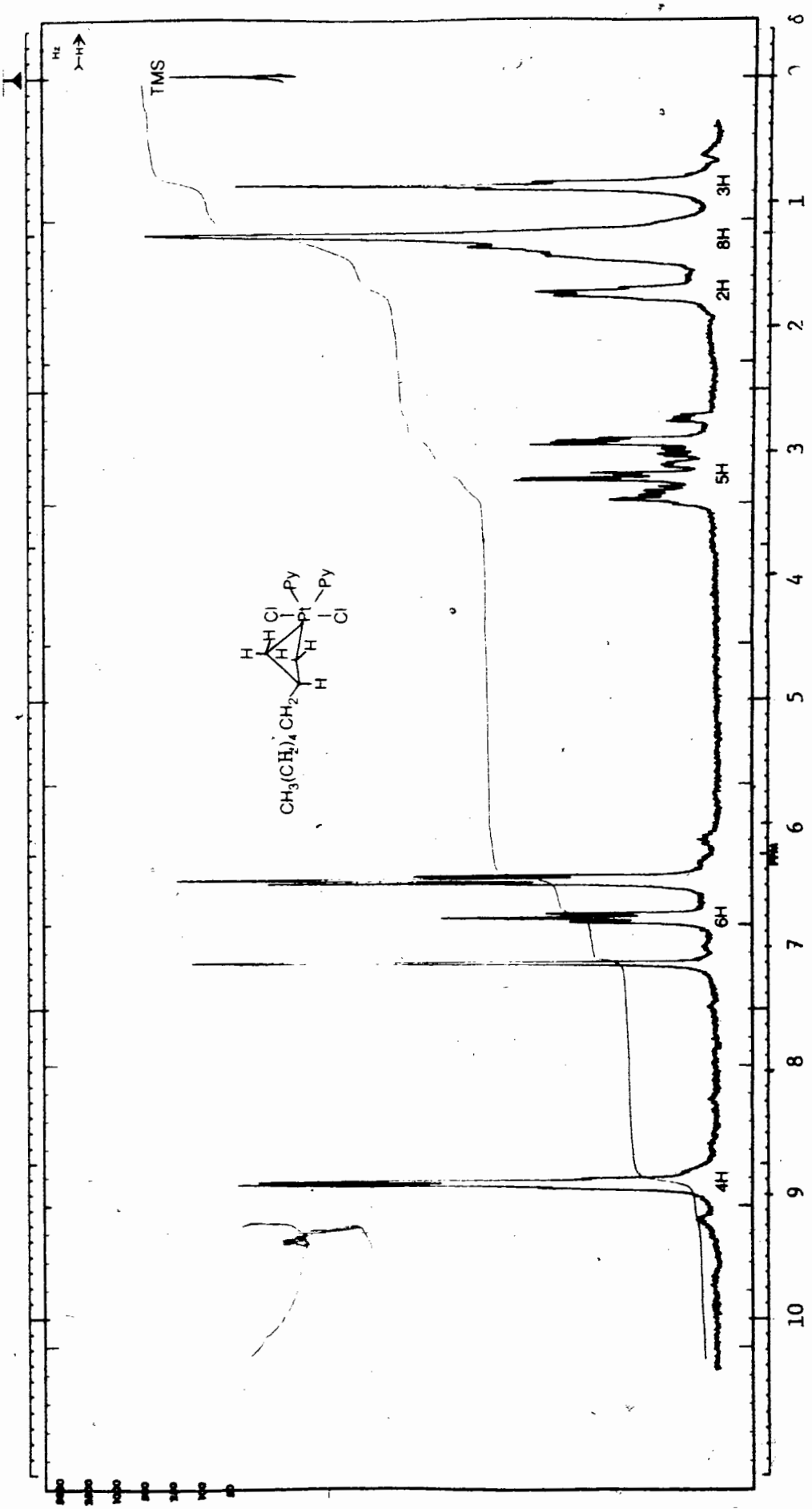


Figure 9: N.M.R. Spectrum of Complex XVI.

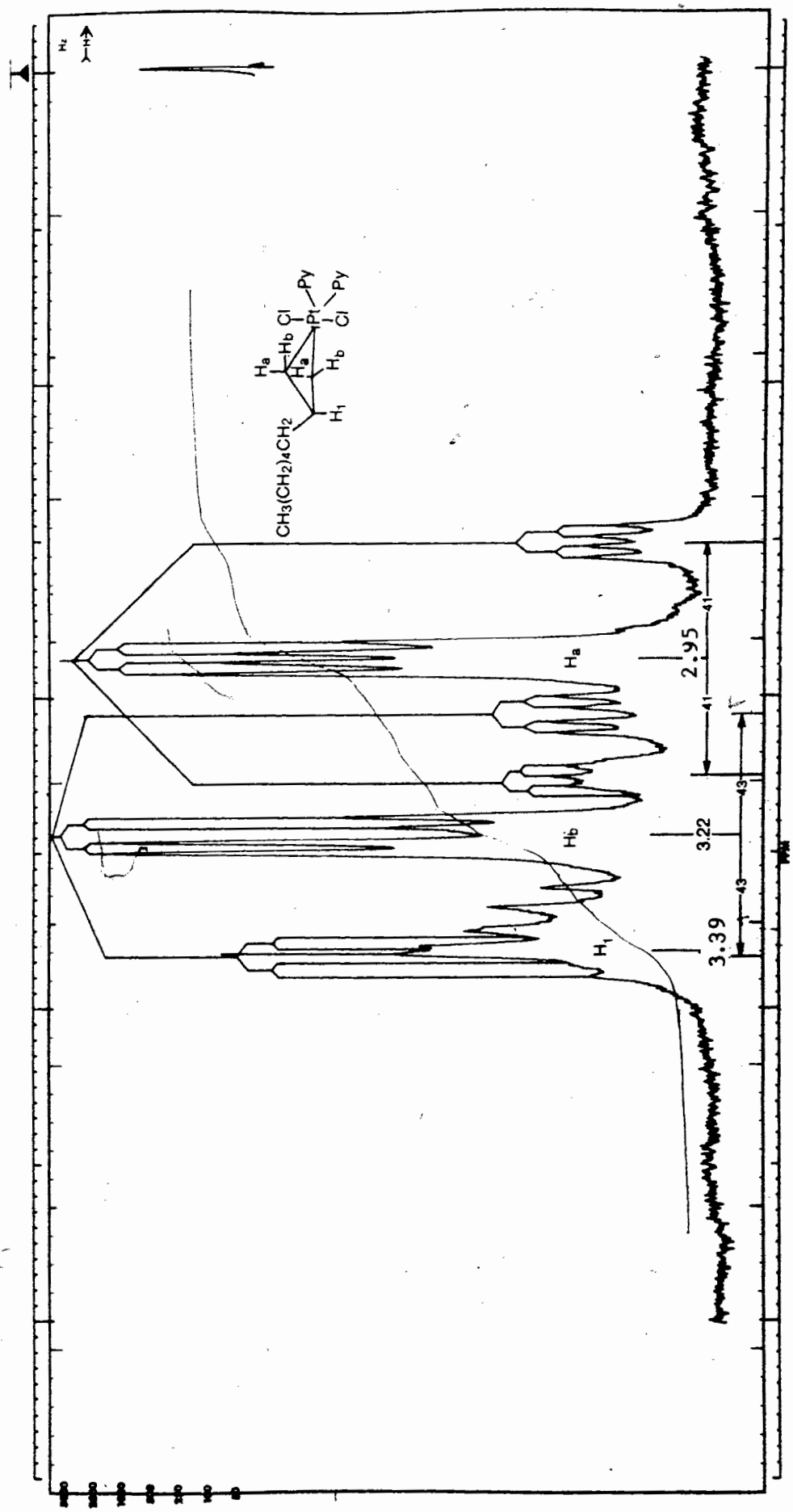


Figure 9a: Detailed N.M.R. Spectrum of Complex XVI

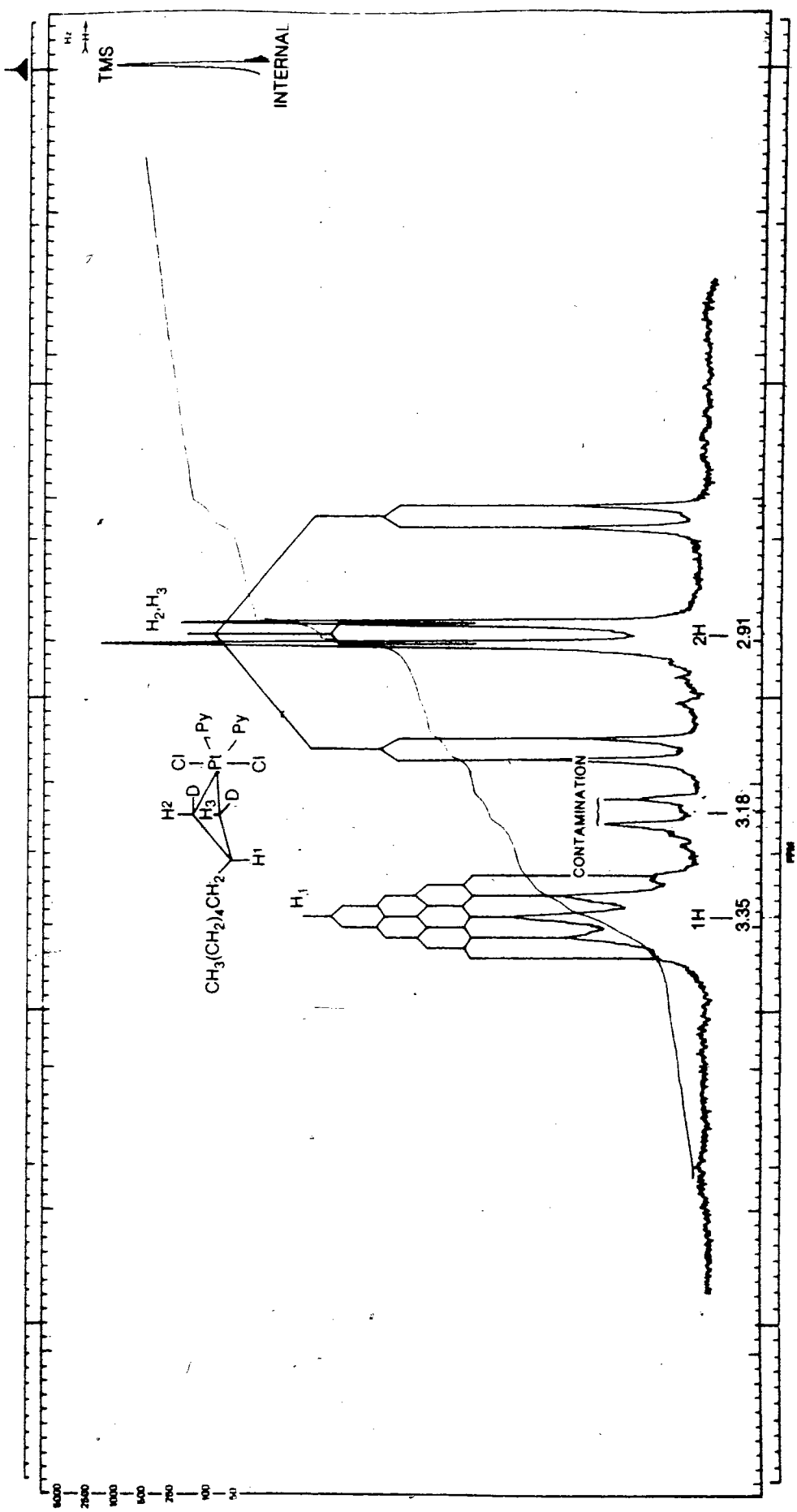


Figure 10: N.M.R. Spectrum of Complex XVII.

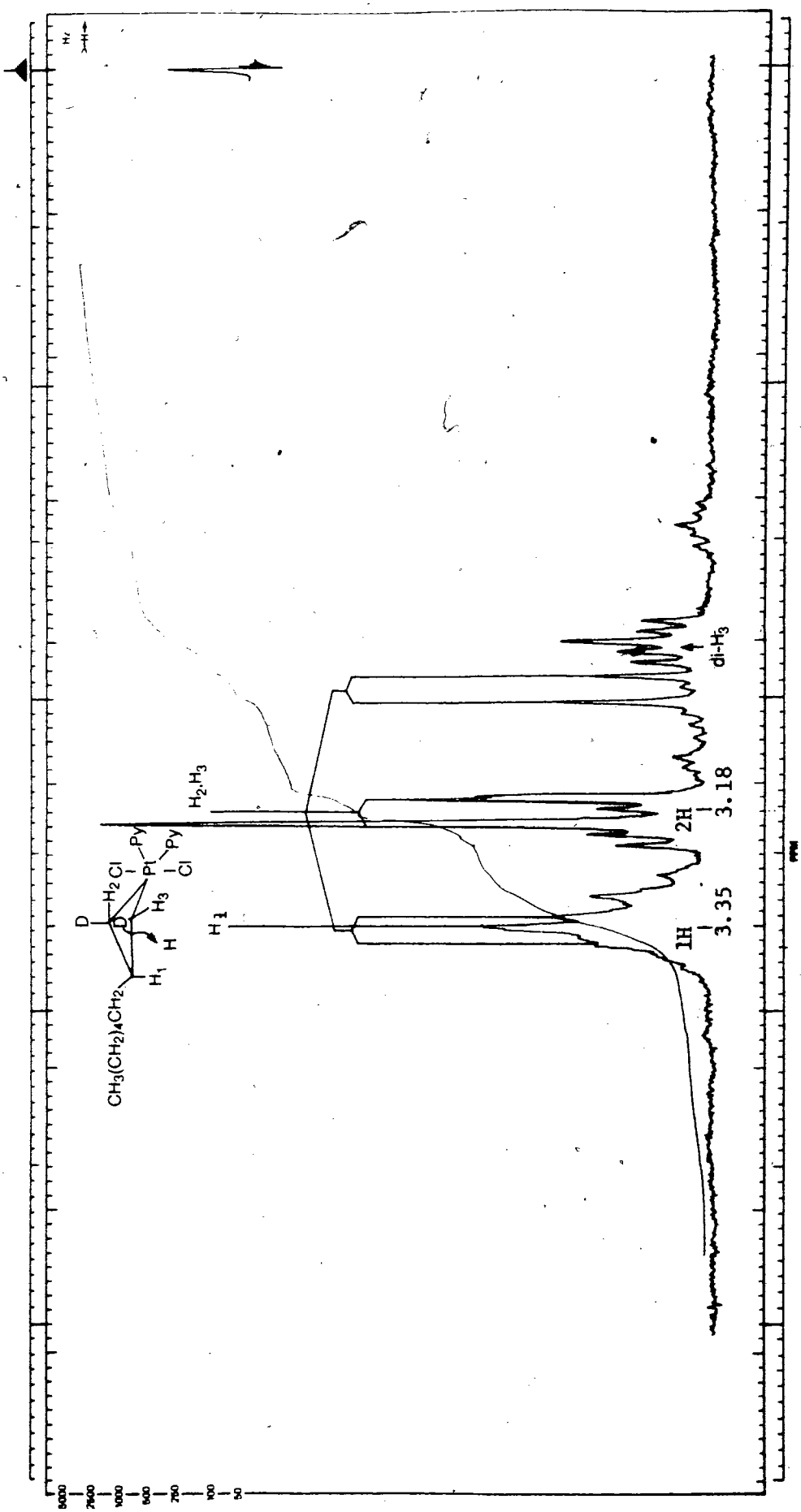


Figure 11: N.M.R. Spectrum of Complex XVIII.

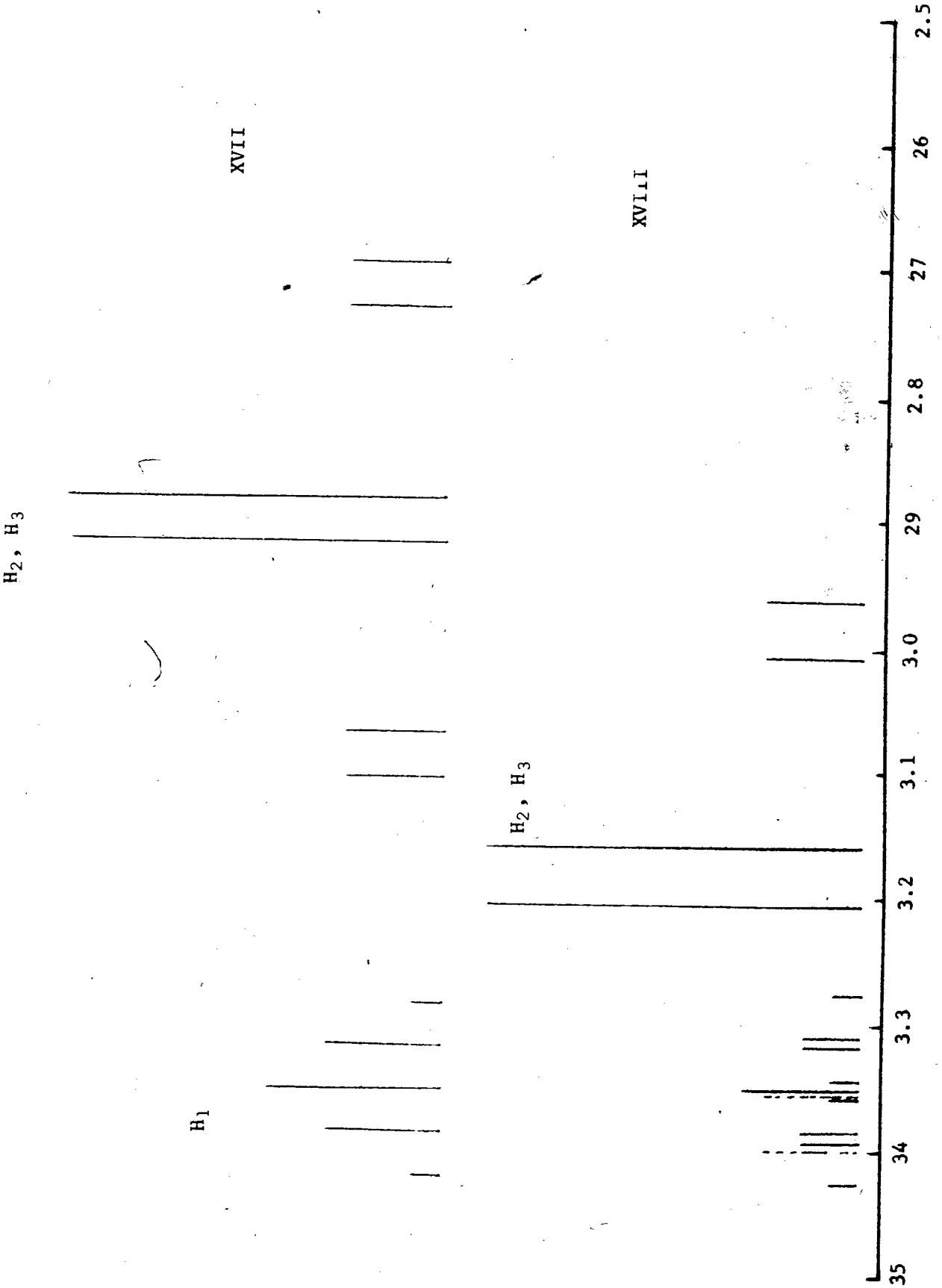
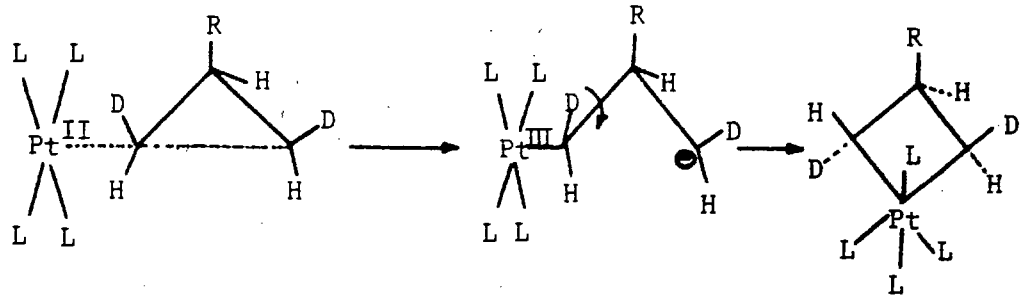


Figure 12: Expected N.M.R. Patterns for Cyclopropyl Hydrogens of Complex XVII and Complex XVIII.

Discussion

The mechanisms proposed for oxidative addition reactions of transition metal complexes vary from SN2 displacement processes, in which the central metal atom acts as a nucleophilic centre, to the involvement of a metal atom which behaves as a Lewis acid to give a carbonium ion intermediate. Free radical processes and one step concerted pathways also have been proposed. Although all of the above pathways have been considered in the literature[2], it will become clear from the following that only a concerted process is consistent with the stereochemical outcome of the reaction of substituted cyclopropanes with Pt^{II} (complex II).

The SN2 mechanism proposed by Halpern[56] involves attack of a nucleophilic metal centre at a cyclopropyl corner followed by cleavage of a C-C bond, as shown below for the present system.



Such a mechanism predicts inversion of configuration of at least one carbon centre. This process has been brought into serious

consideration by various features of the kinetics of known SN2 reactions, and appears to be in good agreement with the addition of alkyl halides to a variety of metal complexes. An SN2 mechanism has also been implicated in the oxidative addition of very nucleophilic metal centres $((R_3P)_3Pt)$ to C-C single bonds[19,20,21]. The stereochemical prediction of inversion at one reactive center is, however, contrary to the observation of complete retention of configuration at both carbon centers of the cyclopropanes used in the present study. Furthermore, no reaction was observed between mono-substituted cyclopropanes and metal complexes more nucleophilic than II (e.g. $Pt(PPh_3)_4$, $Pt(PPh_3)_3$).

The free radical mechanism proposed by Osborn[29-32] for Ir^I and Pt^o addition to alkyl halogen bonds must also be ruled out on the basis of the stereochemistry observed in the present study. A radical process would result in loss of stereochemistry as has been observed by Osborn.[29-32]

Another plausible route for oxidative additions which has been implied in isomerization reactions for catalysis of strained cyclic hydrocarbons, involves the formation of carbonium ion intermediates. This mechanism has been extensively studied by Gassman[57], Paquette[58], Dauben[59], and Masumune[60], for a variety of transition metal complexes (such as

$[Rh(CO)_2Cl]_2$, $Pd(C_6H_5CN)_2Cl_2$, $[Ir(CO)_3Cl]_2$, Ag^+ etc.). In the reaction of $[Rh(CO)_2Cl]_2$ with bicyclobutanes, the transition metal complex[57,60] behaves initially as a very specific Lewis acid species which attacks the bicyclobutane moiety, producing cleavage of a side bond to give the most stable carbonium ion. The intermediate (Figure 13) then rearranges or can be trapped with MeOH solvent.

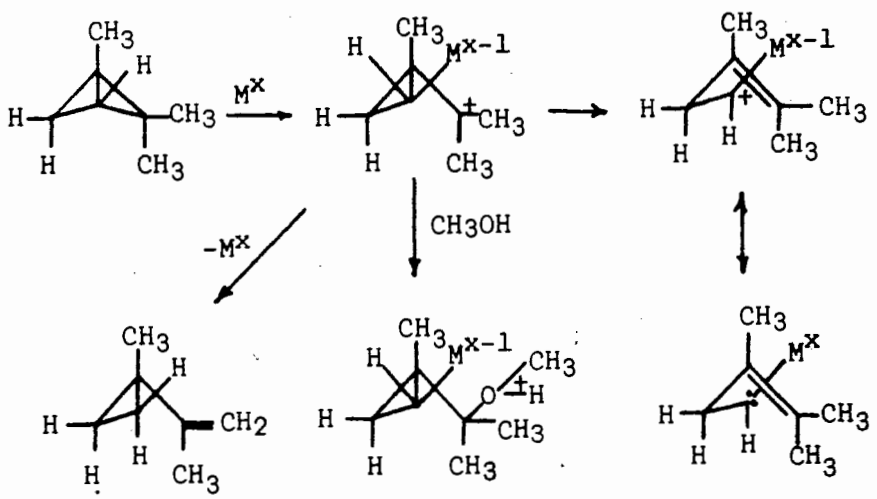


Figure 13: Gassman's Mechanism for Bicyclobutane Rearrangement.

Paquette[58] and Dauben[59] have proposed a different intermediate which also explains the products obtained.

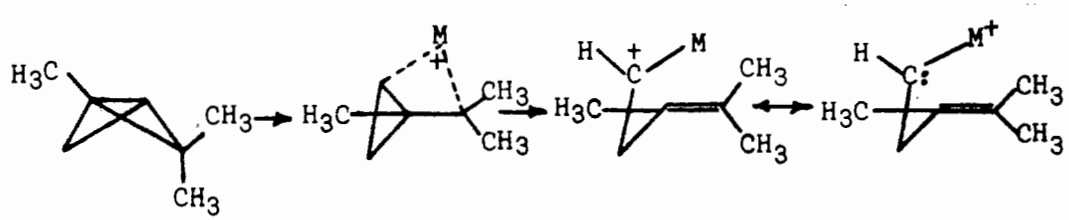


Figure 14: Paquette and Dauben Mechanism for Bicyclobutane Rearrangement.

The reaction pathways available for an electrophilic addition process of Pt^{II} (complex II) to a substituted cyclopropane are shown in Figure 15. Initial attack of Pt^{II} could be at the corner of the cyclopropane ring or at the edge which may be ultimately cleaved[61]. Although this mechanism is in agreement with the reaction rates of substituted cyclopropanes with Pt^{II} (complex II)[17] and substituted cyclopropanes[5] with Rh^{I}, the formation of a free carbonium ion in our system would undoubtedly result in the formation of isomeric products with respect to the deuterium positions. Furthermore, the product resulting from cleavage of the 1,2-bond would be preferred over that from the 2,3-bond since the former results from the more stable carbonium ion (Figure 15). Neither of these predictions were observed in the present investigation.

The only mechanism which is in full agreement with the stereochemical outcome appears to be a one-step concerted cycloaddition as outlined by Pearson[23]. Such a mechanism can be envisioned as a donation of electrons from the cyclopropane C-C bond to an empty d orbital on Pt^{II} and π-back donation into an antibonding level of the cyclopropane. This model has been challenged[22] since it does not readily explain the puckering observed in the metallocyclobutane ring of IX.

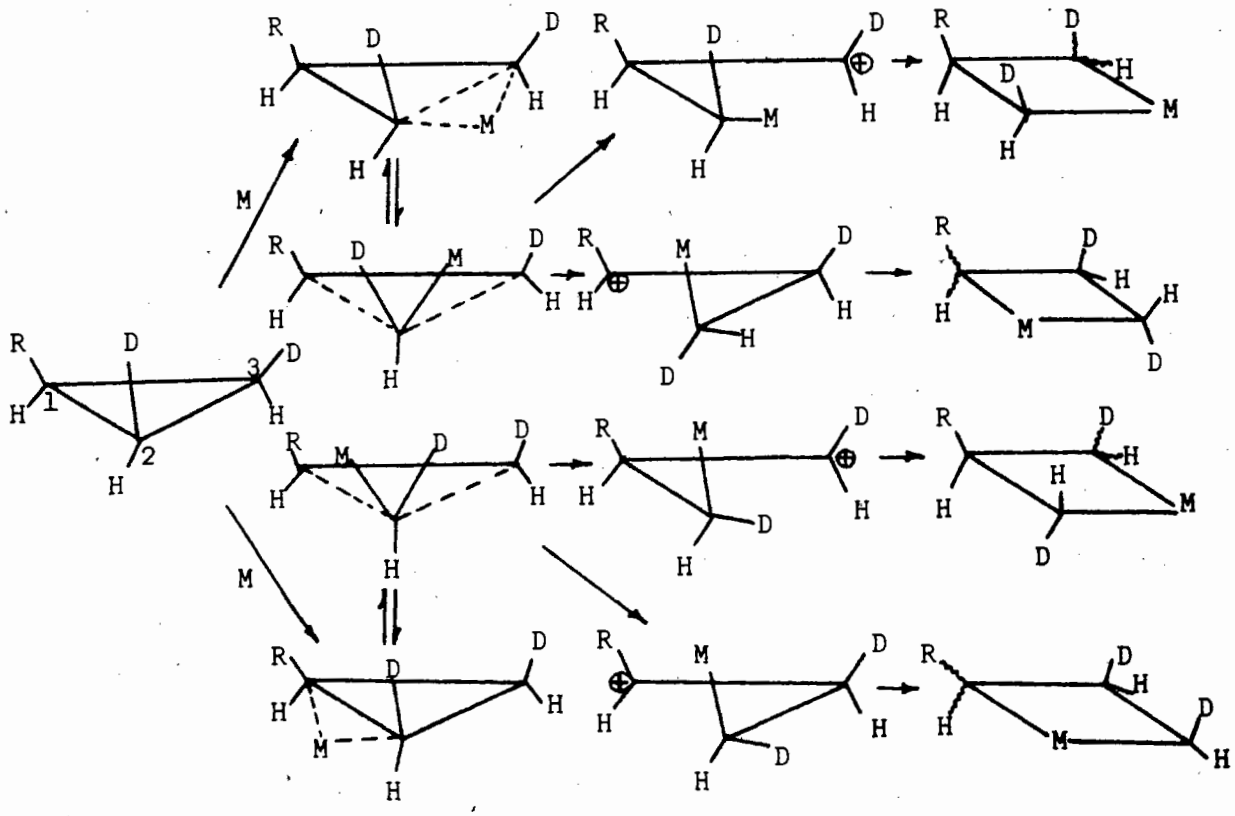
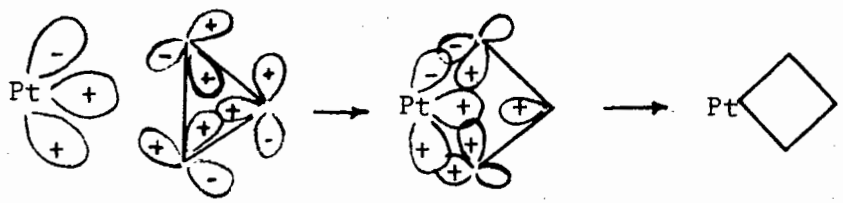


Figure 15: Application of Carboniun Ion Mechanism to Present Addition Process (R = n-C_6H_{13}, M = Pt).



This mechanism implies retention of configuration at both carbon centers, and the metal atom behaving as a weak Lewis acid (in agreement with the products obtained).

Our results represent the first stereochemical evidence for a concerted cycloaddition mechanism during the oxidative addition of a transition metal complex to a strained C-C single bond.

Experimental

Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double focusing mass spectrometer using an ionization voltage of 80 eV. NMR spectra were obtained on Varian A56/60 and XL 100 spectrometers using $CDCl_3$ as solvent and TMS as an internal standard ($\delta 0$) unless otherwise stated. I.R. spectra were obtained either as neat films or KBr pellets using a Perkin-Elmer 457 spectrophotometer. Melting point determinations were carried out using a Fisher-Johns melting point apparatus and are uncorrected. GLC analyses were done using a 6' x 1/8" column packed with 20% SE-30 on Chromosorb G(100/120 mesh) unless otherwise specified.

Synthesis of trans-1-n-hexyl-cis-2,3-dideuteriocyclopropane

Preparation of Chloromethyltriphenylphosphonium chloride[43]

Into triphenylphosphine (131.1 g, 0.5 m) and 15 g (0.5 m) of paraformaldehyde in 250 ml of dry ether was passed a stream of hydrogen chloride gas until no further precipitate formation was noted (ca. 2 hrs). The white precipitate that formed was filtered, dried in vacuo, and dissolved in 300 ml of dichloromethane. To this solution was added 90 g (0.75 mole) of thionyl chloride. The solution was refluxed for 30 minutes and the volatile components were removed in vacuo, the remaining pale green residue was dissolved in hot dichloromethane and precipitated by addition of

hot ethyl acetate. The precipitate was dried in vacuo to give 150 g (84%) of chloromethyltriphenylphosphonium chloride, m.p. 262-64°C; lit.[43] m.p. 260-61°C.

Preparation of Cis and Trans-1-chlorooct-1-ene[44]

A solution of 34.7 g (100 mmol) of chloromethyl triphenylphosphonium chloride in 50 ml of dry glyme was prepared and cooled in a dry ice-acetone bath while 60 ml of 2M butyllithium in hexane was added dropwise with stirring over a period of 1 hr. The reaction mixture became red and copious quantities of white precipitate formed. While maintaining the reaction mixture at -50°C, heptanal (14.9 g, 12 m) was added. The mixture was allowed to warm to room temperature then refluxed for 16 hrs. The reaction mixture was filtered, the solvent removed in vacuo, and the residue distilled to yield 30-35% of a mixture of cis-, and trans-1-chlorooct-1-ene. B.p. 43-67°C (2.5 mm Hg). G.l.c. analysis showed two major components, n.m.r. of mixture δ ($CDCl_3$) 0.9 (3H,t,CH_3,J=5Hz), 1.3 (8H,b,$(C\underline{H}_2)_4$-), 2.1 (2H,m,$C\underline{H}_2$-C=C), and 5.9 (2H,m, $\underline{H}>C=C<\frac{H}{Cl}$). M.S. (Calcd. for $C_8H_{15}Cl$, M^+ 146): 146 (M^+, 18%), 148 (M^++2, 5.7% M^+/M^++2 = 100/32), 43 (M^+ - $(CH_2)_3CH=CHCl$), 100%).

Preparation of 1,1,2-trichloro-3-n-hexylcyclopropane[45]

A solution of 1-chlorooct-1-ene (7.5 g) and cetyltrimethyl-

ammonium bromide (CTAB), ca. 0.2 g) in 18 g of chloroform was prepared and heated under a N_2 blanket to 50°C. A solution of 17 g of NaOH in 17 ml H_2O was added dropwise over a period of 15 min. The progress of the reaction was monitored by removing samples from the organic layer and subjecting them to g.l.c. (170°C). The reaction was allowed to proceed until no further decrease in 1-chlorooct-1-ene was observed after addition of more base.

The reaction mixture was diluted with 100 ml H_2O, acidified with 10% H_2SO_4 and extracted with ethyl ether (3 x 100 ml). The solvent was dried over anhydrous $MgSO_4$, removed in vacuo, and the residue distilled under reduced pressure to give 67% yield of 1,1,2-trichloro-3-n-hexylcyclopropane; b.p. 95-96°C (5 mm Hg). N.m.r. $\delta(CDCl_3)$: 0.9 (3H,t,J=4.5 Hz, CH_3), 1.5 (11H,b,-$(CH_2)_5$- and C_1-H, 3.1 (0.5 H,b,cis-C(H)(Cl)), 3.6 (0.5 H,d), J=8.5 Hz, trans C(Cl)(H)). M.S. (at 15 eV. calcd. for $C_9H_{15}Cl_3$,M^+, 228): 193 (M^+-Cl,10%) 157 (M^+-2Cl,68%), 122 (100%).

Preparation of Tri-n-butyltin Hydride

Reduction of tri-n-butyltin chloride with lithium aluminum hydride according to H.G. Kuivila[46] and Birnaum[47] gave tri-n-butyltin hydride in 87% yield; b.p. 70-72°C (0.2 mm Hg), lit.[45] 68-74°/0.2 mm Hg. I.R. ν^{max}_{film} 1810 cm^{-1} (Sn-H).

Preparation of 1,2-Dichloro-3-n-hexylcyclopropane

Reduction of 1,1,2-trichloro-3-n-hexylcyclopropane was accomplished by the use of tri-n-butyltin hydride according to the method of D. Seyferth[48]. To 1,1,2-trichloro-3-n-hexylcyclopropane (4.0 g, .02 mole) neat, was added tri-n-butyltin hydride (5.82 g, 0.02 mole). The reaction was maintained at 115°C and monitored by g.l.c. (180°C) by following the disappearance of the starting compound. G.l.c. analysis after reaction for 0.5 hrs revealed the appearance of three new peaks of shorter retention times than those of the starting trichloro-cyclopropane attributed to the three possible products of a single reductive process. The reaction was allowed to proceed until the starting material was exhausted (ca. 3.5 hrs). The mixture was distilled at 0.1 mm Hg, collecting several fractions between 61° to 112°C. The overall yield of distillate was 80%; n.m.r. δ ($CDCl_3$); δ 1.0 (3H,t,J=4.5 Hz,-CH_3); 1.4 (11H, b.d., J=8 Hz, (-CH_2-)$_5$ and C_3-H); 2.9 and 3.2 (2H,m,cis and trans, C_1-H and C_2-H).

Reduction of 1,2-dichloro-3-n-hexylcyclopropane to trans-1-n-hexyl-cis-2,3-dideuteriocyclopropane (XII)

The reaction was carried out according to M.R. Willcott[49] and V.H. Cargle with minor modifications. In a typical reaction, 1,2-dichloro-3-n-hexylcyclopropane (2-3 gm) in 15 ml

of methanol-OD and deuterium oxide (1%) were mixed under nitrogen. Clean pieces of sodium were added to the mixture and allowed to react under a positive N_2 atmosphere. The progress of the reaction was followed by g.l.c. (180°C) and allowed to proceed until the starting material was exhausted or no further consumption of starting material was observed upon further addition of sodium.

The mixture was diluted with water, extracted with hexane, dried over anhydrous $MgSO_4$, and distilled at atmospheric pressure. Fractions distilling in the range 120-140°C were collected and pooled giving an overall yield of trans-1-n-hexyl-cis-2,3-dideuteriocyclopropane of 20-30%. G.l.c. analysis of the fraction with b.p. 135-140°C showed one component. N.m.r. as shown in Figure 7. $\delta(C_6D_6)$: (external TMS) -0.1 (2H;d,J=5 Hz,$C_{2,3}$-H), 0.5 (1H, b.m., J=5 Hz, C_1-H); 0.3 (3H, t,J=4.5 Hz, -CH_3), 1.2 (10H, $(CH_2)_5$). M.S. (calcd. for $C_8H_{16}D_2$, M^+ 128): 128 (M^+, 19% , D_0=0%, D_1=8%, D_2=92%).

Synthesis of cis-1-n-hexyl(cis-2,3-dideuterio)cyclopropane (XIII).

Preparation of 1-chloro-oct-1-yne

This procedure was adapted from H.G. Viehe.[50] To 200 ml of dry tetrahydrofuran (THF) was added 8.5 g sodium amide. This solution was warmed and to it was added, dropwise, 1-octyne (22 g) and additional THF as required to keep the solution homogeneous. The mixture was refluxed until

gas evolution ceased (ca. 1 hr), cooled to room temperature, treated with benzenesulfonyl chloride, (dropwise addition of 36 g in 25 ml THF) and stirred for an additional 2 hrs.

The resulting reaction mixture was diluted with 100 ml of water and extracted into ether. The ether extract was dried over anhydrous $MgSO_4$ and the solvent removed in vacuo. Distillation of the residue yielded 50% of 1-chlorooct-1-yne, b.p. 40-44°C (6 mm Hg). Lit.[51] 61-62°C (17 mm Hg); N.m.r. δ ($CDCl_3$): 0.92 (3H,t,J=5 Hz, CH_3); 1.4 (8H, b. $(CH_2)_4$), 2.2 (2H,t,J=6 Hz, CH_2-C=C-Cl). I.R. ν_{film}^{max} 2920, 2832, 2224, 1460, 1430, 1380, 1035, and 725 cm^{-1}

Preparation of cis-1-chloro-1-deuteriooct-1-ene

The method of preparation of the chlorodeuteriooctene is adopted from H.C. Brown and G. Zweifel.[52] A solution, under argon, containing sodium borohydride (1.9 g) in 25 ml of dry diglyme and 2-methylbut-2-ene (9.5 g) was cooled to 0°C, flushed with argon, and freshly distilled boron trifluoride-etherate (9.2 g) in 10 ml of diglyme was added dropwise while maintaining the temperature below 10°C. Stirring (0-5°C) was continued for 2 hrs. After this time 1-chlorooct-1-yne (7.25 g) was added (at 5-10°C) and the reaction mixture was stirred for 0.5 hrs at 0-5°C, then for 2.5 hrs at r.t.

Acetic acid-D_1 (12 ml) was added at 0-5°C and the reaction stirred for an additional 2.5 hrs. Dilution with

water (150 ml) and extraction with ether yielded an ether extract which was washed with dilute NaOH and subsequently several times with water. Removal of the ether *in vacuo* and distillation of the residue at reduced pressure gave a clear liquid, b.p. 53-56° (8 mm Hg). G.l.c. analysis revealed this fraction contained a major component (ca. 90%) and a minor component due to starting material. N.m.r. δ ($CDCl_3$): 0.9 (3H,t,J=4Hz, $\underline{CH_3}$); 1.3 (8H,b, $(\underline{CH_2})_4$); 2.2 (2H,d,J=7 Hz, $-\underline{CH_2}-C=C_1-$), 5.8 (1H,m,$C_{2-}\underline{H}$). M.S. (calcd. for $C_8H_{14}DCl$, M^+, 147), 147(M^+, 16%; D_0 21%, D_1 79%, D_2 0%), 43 ($M^+-(CH_2)_3CH=CDCl$) 100%).

Preparation of 1,1,2-trichloro-2-deuterio-3-n-hexylcyclopropane

A solution containing *cis*-1-chloro-1-deuterio-1-octene (7.5 g) and cetyl trimethylammonium bromide (CTAB)[45] in 20 ml of chloroform was heated to 50-55°C. A solution of 20 g NaOH in 20 ml of water was added dropwise. The progress of the reaction was monitored by g.l.c (170°C) and allowed to proceed until no further decrease in concentration of starting material was noted upon further addition of base. The reaction mixture was cooled to room temperature, diluted with water (100 ml), acidified with 10% H_2SO_4 and extracted into ether. Solvent removal and distillation under reduced pressure afforded 1,1,2-trichloro-2-deuterio-3-n-hexylcyclopro-

pane as a clear liquid. b.p. 70-75° (0.1 mm Hg). G.l.c. at 170°C showed the product to consist mainly of one component with minor impurities. M.S. (at 15 eV.) (calcd. for $C_9H_{14}DCl_3$, M^+, 229), 194 (M^+-Cl,20%), 123 (100%).

Reduction of 1,1,2-trichloro-2-deuterio-3-n-hexylcyclopropane

The reaction was carried out under nitrogen and using tri-n-butyltin deuteride[46-48]. The progress of the reaction was followed by g.l.c. using a 6' x 1/8" 5% Carbowax column at 180°C. Work-up as previously described and distillation gave a main fraction b.p. 65-85° (0.1 mm Hg) consisting of approximately 80% of two isomeric products along with some unreacted starting material and minor impurities. This mixture was subjected to sodium and alcohol reduction without further purification.

Reduction of 1,2-dichloro-1,2-dideuterio-3-n-hexylcyclopropane

Crude n-hexyl-dichloro-dideuteriocyclopropane (3 g) was added to 25 ml of methanol containing 1% water. While keeping the reaction under N_2, clean pieces of sodium (~100 mg) were added to the mixture and allowed to react at r.t. with constant stirring. The progress of the reaction was followed by g.l.c. and terminated when no further reaction of the starting material was observed.

The mixture was diluted with water (100 ml), extracted with ether, the organic layer dried over anhydrous $MgSO_4$, and

distilled at atmospheric pressure to give 40% of cis-1-n-hexyl-cis-2,3-dideuteriocyclopropane, 95% pure by g.l.p.c.; b.p. 133-135°C; n.m.r. as in Figure 8. M.S. (at 15 eV.) (Calcd. $C_9H_{16}D_2$, 128), 128(M^+; D_0 0%, D_1 27%, D_2 73%).

Preparation of tetrachloro(diethylene)diplatinum (II) (Zeise's Dimer)

The dimeric complex was prepared from $K_2(PtCl_4)$ by the method of Chatt and Searle[64]. Recrystallization from hot toluene gave a microcrystalline yellow-orange product; m.p. (darkens) 190°C; dec. 205-210°C (lit.[64] dec. 210°C); I.R. ν^{max}_{KBr}: 1412 (C=C), 1250, 1019, 225, 485 and 335 (PtCl) cm^{-1}.

Reaction of Zeise's Dimer with Cyclopropanes to give Dichloro(2-n-hexylpropane-1,3-diyl)platinum

In a typical reaction, Zeise's Dimer (200 mg, 0.34 mmol) and n-hexylcyclopropane (200 mg, 1.55 mmol) in 5-10 ml of ether was stirred under reflux for 8 hrs. During the course of the reaction, the orange coloured Zeise's Dimer was replaced by a pale yellow precipitate. The precipitate was filtered, washed with ether and dried to give 230 mg (85%) of a pale yellow powder; m.p. 120-5°C(darkens), lit.[17] (dec) 120°C;

Preparation of trans-dichlorobispyridine(2-n-hexylpropane-1,3-diyl)platinum derivatives.

Method A

Dichloro(2-n-hexylpropane-1,3-diyl)platinum (100 mg) was cooled in an ice-water bath followed by the addition of ice-cold pyridine sufficient for dissolution. The solution was allowed to warm to r.t. then added dropwise and with constant stirring to 100 ml of cold H_2O. The resulting milky suspension was centrifuged, the water decanted and the yellow precipitate dissolved in $CHCl_3$. Removal of the $CHCl_3$ *in vacuo* gave a pale yellow solid. Recrystallization from benzene-pet. ether gave a pale yellow crystalline solid which exhibited one spot on thin layer chromatography (Silica Gel HF254, $CHCl_3$). M.p. 124-6°C (darkens), lit.[17] darkens 125°C, dec 220°C; n.m.r. as in Figs 9-11.

Method B

As described by Powell and McQuillin[17] 100 mg of the platinum complexes were dissolved in 1 g of $CHCl_3$ containing 100 mg of pyridine and stirred for five minutes. The resulting yellow solution was chromatographed on a Silica Gel column (30 x 1.5 cm) using $CHCl_3$ as the eluting solvent. Two yellow bands were visible on the column. The corresponding fractions were combined, and the solvent was removed to give the desired product from the first band and trace amounts of a yellow solid from the second band.

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