STUDIES

ON

ORGANOMETAL—NITROGEN

BONDS

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Preface

This dissertation has been carried out during 1973-1975 as a doctrate thesis under the direction of

Professor Dr. Yoshio Ishii

at the Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University.

This thesis presents the " STUDIES ON ORGANOMETAL-NITROGEN BONDS ", in which the interaction of the group IV organometallic amine with unsaturated compounds containing heteroatom, and that of group VIII transition metal with nitrogen-halogen bond are investigated.

The author wishes to express his sincere gratitude to Professor Yoshio Ishii for his kind and fruitful suggestions and encouragement throughout the course of this work. The author also would like to make his grateful acknowledgement to Dr. Kenji Itoh and Dr. Isamu Matsuda for their profound interest, and their helpful suggestions, and criticisms. He thanks Mr. Masayasu Ohashi, Mr. Kenji Hirai, and Mr. Junichi Yamada for their collaboration. He is indebted to Miss Nagisa Mizuno for the measurement of the NMR spectra. He extends his gratitude to Mr. Yoshitaka Kuroda and Dr. Imao Nagasaka for their encouragement. And he wishes to express his profound debt to the rest of all members in the Professor Ishii's Laboratory for their valuable discussions and hearty cooperation with him.

Finally, an acknowledgement must be made to his parents for their encouragement and understanding.

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CONTENTS

INTRODUCTION

The chemistry of the organometallic compounds containing metal-nitrogen bond has recently attracted the attention of a number of chemists in the world.

On the electronic basis, the metal-nitrogen bonds are roughly classified into following three types: (1) bonds with large ionic character, (2) nearly covalent bonds, (3) coordinate bonds with the lone pair electron. Type 1 and 2 are frequently observed in organometallic compounds of main group elements. Most transition metal ammine or imine complexes and amine adducts of organoborane are good example of type 3. In this thesis, the studies on the preparation and reactivity of several metal amides are described.

It was found out in the last decade that the group IV metal-nitrogen bond added to various kind of polar unsaturated bonds. Some of these reactions provide a synthetic potential in the carbon-nitrogen bond formation during organic trans-formations. Chapter I is devoted to the elucidation of reactivity of group IV metal-nitrogen bond, and to the application of its specific character to a synthesis of heterocyclic compounds. A selective synthesis of s-triazinone or biuret was attained under the controlled reaction conditions in the addition reaction of N-tri-methylstannyl(diphenylmethylene)amine with heterocumulene. On a way to explore new heterocycles synthesis with the above organostannylamine, diketene molecule was discovered to function as a new synthon. Imidazolidine synthesis facilitated by the driving force of the " affinity difference " between N-Si and O-Si is mentioned as the second new heterocycle preparation. The (p-d)π overlap between group IV metal and a heteroatom is an essential subject from the viewpoint of physical chemistry. This interaction has been suggested by many evidence, *i. e.* the shapes of molecule, spectroscopic properties, basicity, *etc.*. The importance of (p-d)π overlap has, however, been hardly estimated by means of MO calculation. In order to elucidate the mechanism of the cycloaddition of N-trimethylsilyl(diphenylmethylene)amine with two moles of isocyanates, a semi-empirical SCF-MO calculation (CNDO/2 approximation) was performed in Chapter I. The result of the calculation shows the presence of a substantial (p-d)π overlap in a N-Si bond of the silylamine.

Chapter II is devoted to the chemistry of transition metal-nitrogen bonds. The coordination of lone pair electrons of the nitrogen atom to the metal atom is

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recognized as the general bonding mode in the transition metal-nitrogen bonds. Recently, the nitrene complexes as well as carbene complexes have become a new frontier of the organometallic chemistry from the viewpoint of the stabilization of the reactive intermediates. They have been studied extensively, and the large volume of information is now available on the nitrene complexes. Whereas the interaction of organic azide with transition metal was as yet almost one route to reach a nitrene complex, a new attempt to prepare nitrene complex by reductive dehalogenation of *gem*-dichloramine with low valent transition metal was envisaged in this study. Thus the reaction of N,N-dichloramine with diiron enneacarbonyl or tetrakis(triphenyl-phosphine)palladium generated corresponding isocyanates or phosphinimine *via* a nitrene intermediate, respectively. The successful stabilization of nitrene generated from N,N-dichlorocyclohexylamine with palladiacyclopentadiene was reported in the last section of Chapter II.

In Chapter III, a new palladium-catalyzed C-C bond formation is described in the case of the cyclotrimerization of two acetylenes with an olefin. Cyclotrimeriza-tion of dimethyl acetylenedicarboxylate and olefin catalyzed coordinatively unsaturat-ed palladiacyclopentadiene and an isolation of the intermediate complex of this cata-lytic process were investigated.

CHAPTER I

REACTIONS OF GROUP IV ORGANOMETALLIC AMINES

WITH UNSATURATED BOND CONTAINING HETEROATOM

In this chapter, the interactions of the Group IV Metal-Nitrogen bonds with various unsaturated bonds containing heteroatom are mentioned.

1 Stepwise Addition of Isocyanates and Isothiocyanates with N-Trimethylstannyl-(diphenylmethylene)amine

In a paper on the insertion reaction of N-trimethylsilyl(diphenylmethylene)-amine with isocyanates or isothiocyanates, it was reported that the amine with isocyanates in a 1/2 ratio yielded 3,4-dihydro-1,3-dialkyl-4,4-diphenyl-6-trimethyl-siloxy-1,3,5-triazin-2(1H)-one by a polar [4+2] cycloaddition.[1]

Ph$_2$C=NSiMe$_3$ $\xrightarrow{\text{R-NCO}}$ Ph$_2$C=N-C(=O)-NRSiMe$_3$ $\updownarrow$ Ph$_2$C=N-C(=NR)-OSiMe$_3$ $\xrightarrow{\text{R'-NCO}}$

R=R'=Me and Ph
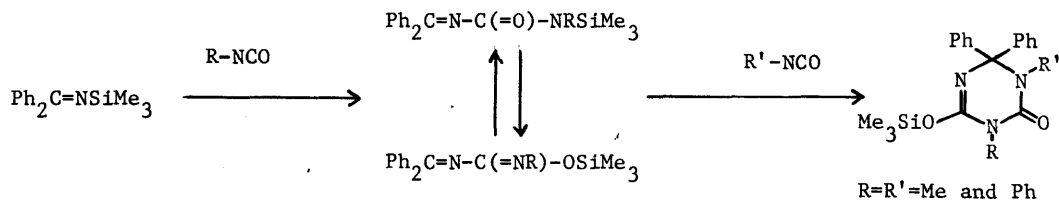
Several reactions of N-organostannyl(alkylidene)amines have been reported. Harrison[2] found many insertion reactions of Ph$_2$C=NSnBu$_3$ with unsaturated bonds including isocyanates and isothiocyanates. We were interested in the fact that the Sn-O bond of aldehyde adducts added to isocyanates or isothiocyanates resulting in consecutive insertion products.

Ph$_2$C=NSnBu$_3$ $\xrightarrow{\text{R-CHO}}$ Bu$_3$Sn-O-CHR-N=CPh$_2$ $\xrightarrow{\text{R'-C=N=X}}$ Bu$_3$Sn-NR'-C(=X)-OCHR-N=CPh$_2$ $\updownarrow$ Bu$_3$Sn-X-C(=NR')-OCHR-N=CPh$_2$
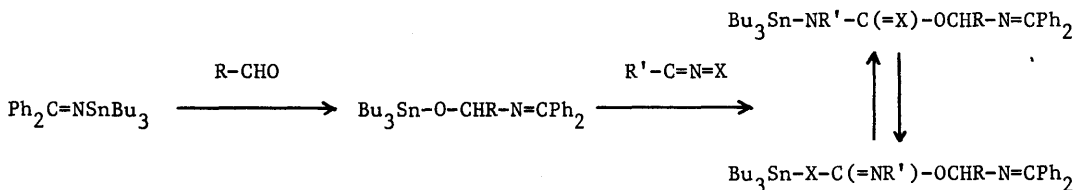
Lappert *et al.*[3] investigated various hydrogen abstraction, and insertion reactions of R$_2$C=NSnMe$_3$. They pointed out two aspects of the insertion reactions;

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(1) the N-H bond of trace $Ph_2C=NH$ showed a catalytic action, (2) the nucleophilic attack of the nitrogen atom was the primary step, resulting in a polar intermediate.

This section deals with the stepwise reactions of N-trimethylstannyl(diphenyl-methylene)amine, $Ph_2C=N-SnMe_3$, with $R-N=C=X$ (X=O and S) in order to determine whether the stepwise reaction is a polar [4+2] cycloaddition or a consecutive insertion reaction.

1-1   Structure of 1/1 Insertion Products

Equimolar reaction of $Ph_2C=NSnMe_3$ with $R-N=C=X$ gave the corresponding insertion products, $Ph_2C=N-C(=X)-NRSnMe_3$ (Ia—Ie) in line with results reported.[2,3] Spectroscopic data for 1/1 insertion products are shown in Table 1.

The appearance of satellites of the methylamino proton signals in the case of Ia and Ib (R=Me) suggests that the trimethyltin group is attached to the nitrogen atom. However, the values of $J_{Sn-N-CH}$ (Ia, 24 Hz; Ib, 12 Hz) are much lower than those of Me_3SnNMe_2 (J^{117}=39.2 Hz and J^{119}=41.0 Hz).[4]
The depression of the coupling constant is consistent
with the weakening of the Sn-N bond by the coordina-
tion of the lone pair to the tin atom. This is also
strongly supported by the low frequency of the carbonyl
stretching bands of the isocyanate adducts (Ia, Ic, and Ie).

$$Ph_2C=N-C \underset{\underset{R}{N}}{\overset{X}{<}} SnMe_3$$
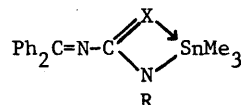
I: R=Me and Ph, X=O
   and S

Table 1.   1/1 Adducts: $Ph_2C=N-C(=X)-NR-SnMe_3$

	R	X	Yield (%)	$\nu_{C=N}$ $\nu_{C=O}$ (cm^{-1})		τ_{CH_3}-Sn ($J^{117/119}$; Hz)	τ_{CH_3}-N ($J_{Sn-N-C-H}$; Hz)
Ia	Me	O	80	1627	1600	9.79 (55.5/57.0)[a]	7.47 (24.0)
Ib	Me	S	80	1622		9.68 (54.8/56.5)[b]	7.38 (12.0)
Ic[c]	Ph	O	97	1621	1589	9.73 (55.0/58.0)[a]	
Id	Ph	S	99	1616		9.60 (56.1/58.5)[b]	
Ie	PhCO	O	95	1626	1673 1603	9.68 (55.5/58.0)[b]	

a) Benzene solution. b) Carbon tetrachloride solution. c) Prepared by Lappert *et al.*[3]

It is reasonable to conclude that the coordination of the sulfur atom of Ib
($J_{Sn-N-CH}$=12 Hz) is stronger than that of oxygen atom of Ia ($J_{Sn-N-CH}$=24 Hz).
Diphenylmethylenealkyl-ureas or -thioureas, $Ph_2C=N-C(=X)-NHR$, were obtained
by the destannylation of Ia—Ie with ethanethiol.   Their UV spectra showed $\pi \rightarrow \pi^*$
transition bands around 248-258 nm characteristic of the heterodiene linkage
($>C=N-\overset{|}{C}=N$).

1-2   Consecutive Reactions of 1/1 Adducts

The subsequent addition of the second heterocumulene to the 1/1 adducts can
occur in two ways: a polar [4+2] cycloaddition yielding 3,4-dihydro-1,3-dialkyl-
4,4-diphenyl-6-trimethylstannoxy-1,3,5-triazin-2(1H)-one (II), and a consecutive
insertion of the second het~~~~mulene into the Sn-N bond of the 1/1 adduct giving
either of the two possible linear insertion products, III or IV.   By destannyla-
tion II gives hexahydro-1,3-dialkyl-4,4-diphenyl-1,3,5-triazin-2,4-dione (V), and
both linear adducts III and IV afford the same N,N'-dialkylmethylenebiuret (VI).
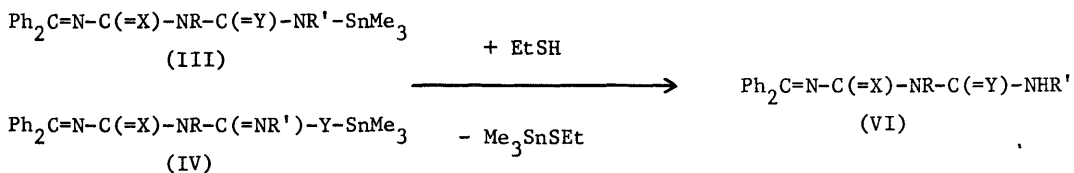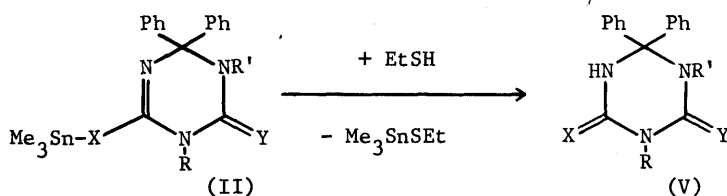
Both the two pathways are actually operating, and the primary heterocumulene
component of 1/1 insertion reactions plays the most important role in controlling
the subsequent reactions.

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1-2-1   Annelation Reactions of Isocyanate 1/1 Adducts

When the isocyanate 1/1 adduct (Ia or Ib) was treated with methyl or phenyl isocyanate, crystalline products were isolated in good yields.   They were concluded to be 1/2 adducts by analyses, NMR and IR spectra.   The destannylation of isolated 1/2 adducts proceeded quantitatively by means of ethanethiol.   None of the destannylation products showed a $\pi \rightarrow \pi^*$ transition due to a heterodiene linkage, $\supset C=N-\overset{|}{C}=O$.   This supports the cyclic structure (V: X=Y=O) and is not consistent with the linear structure (VI: X=Y=O).   Much stronger evidence of the cyclic structure (V) was obtained from the mass spectra of the destannylation products. Two destannylation products (runs a and c) showed peaks due to $[Ph_2C=N-CH_3]^+$ (m/e=195) and $[Ph_2C=N=CH_2]^+$ (m/e=194).   The appearance of these peaks suggests the direct bonding of diphenylmethylene with the alkylamino group (R'-N) introduced by the second isocyanate, and are explained by the cyclic structure (V). The destannylation product of run b (order of addition: methyl then phenyl isocyanate) showed M^+- MeNCO peak (m/e=300).   The presence of M^+- MeNCO is fully consistent with structure (V), because fragmentation of the linear structure (VI) should occur from the terminal position (only M^+- PhNCO would appear; direct elimination of the central component M^+- MeNCO, not being detectable).   The IR spectrum of run d is also consistent with the cyclic structure (V: R=R'=Ph, X=Y=O); the carbonyl stretching frequencies at 1730 and 1657 cm^{-1} were similar to those of 1,3,5-triazindiones (1720 and 1680 cm^{-1}).[5]   Mixed mps, analyses, IR, and NMR spectra were the same as those of authentic hexahydro-1,3-dialkyl-6,6-diphenyl-1,3,5-triazin-2,4-dione (V).[1]   Thus, the consecutive insertion process, giving III or IV then VI, is excluded, and the annelation products of isocyanate 1/1 adducts with the second isocyanate are concluded to be 3,4-dihydro-1,3-dialkyl-4,4-diphenyl-6-trimethylstannoxy-1,3,5-triazin-2(1H)-one (IIa—IId) by a polar [4+2] cycloaddition.   The treatment of IIa —— IId with ethanethiol gave the corresponding hexahydro-1,3-dialkyl-6,6-diphenyl-1,3,5-triazin-2,4-dione (Va—Vd) quantitatively.   This method provides a synthetic route for the preparation of triazindiones with three different substituents on the nitrogen atoms such as Vb and Vc.

R-NCO

$$Ph_2C=N-SnMe_3 \longrightarrow Ph_2C=N-C(=O)-NR-SnMe_3$$

(Ia) R=Me, (Ic) R=Ph

[4+2] | R'-NCO

Ph   Ph
 N   NR'
Me_3Sn-O N   O
              R
(IIa) R=R'=Me

+ EtSH
────────────→
− Me_3SnSEt

Ph   Ph
HN   NR'
O   N   O
     R

(IIa) R=R'=Me   (Va) R=R'=Me
(IIb) R=Me, R'=Ph   (Vb) R=Me, R'=Ph
(IIc) R=Ph, R'=Me   (Vc) R=Ph, R'=Me
(IId) R=R'=Ph   (Vd) R=R'=Ph
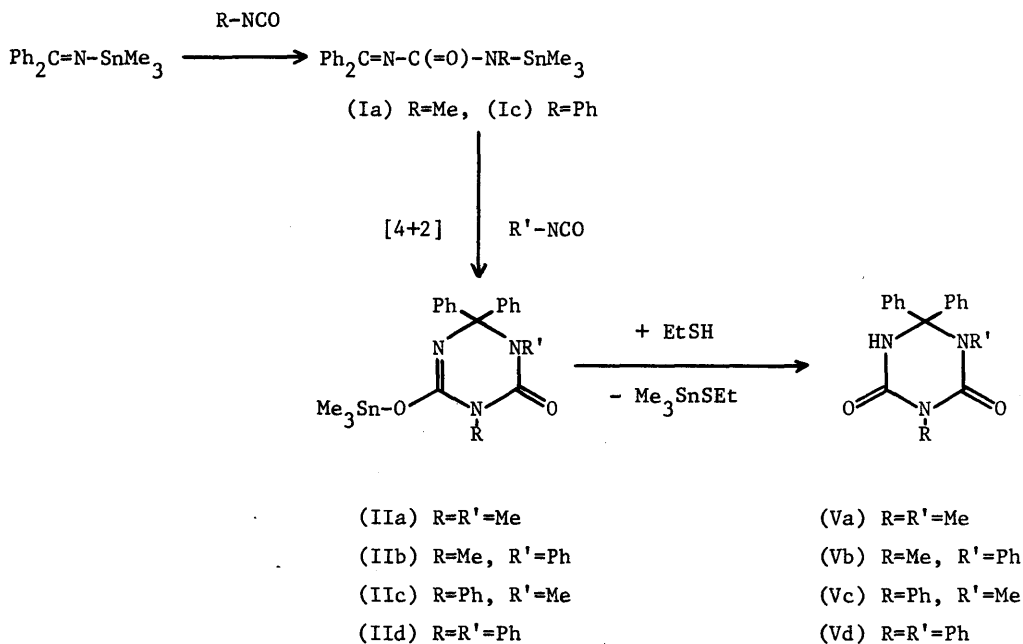
The yields and properties of these [4+2] cycloaddition products (IIa—IId) and their destannylation products (Va—Vd) are summarized in Table 2 and 3.

Table 2. The [4+2] cycloaddition of isocyanate adducts

	Yield (%)	Mp (°C)	ν_{max} (cm^{-1})	τ_{CH_3-Sn} ($J^{117/119}$)	τ_{CH_3-N}
IIa	77	149.0-152.0	1688, 1621	9.89 (56.0/58.0)	7.41, 6.75
IIb	76	169.0-172.0	1686, 1624	9.83 (54.5/57.0)	6.73
IIc	46	179.0-181.0	1692, 1630	9.90 (55.5/57.5)	7.38
IId	96	166.0-167.0	1731, 1697	9.88 (53.0/55.3)	

Table 3. Destannylation products of II

	Yield	Mp (°C)	$\nu_{C=O}$ (cm^{-1})	τ_{CH_3-N}
Va	quant.	238.0-239.0	1723, 1648	7.29, 7.03
Vb	quant.	240.0-241.0	1720, 1674	6.93
Vc	quant.	264.0-265.0	1729, 1663	7.22
Vd	quant.	215.0-216.0	1730, 1657	

An atempt to react phenyl isothiocyanate with isocyanate 1/1 adducts (Ia and Ic) was unsuccessful, resulting in the recovery of starting materials. The less reactive phenyl isothiocyanate cannot add to 1/1 isocyanate adducts (Ia and Ic), since the nucleophilicity of the nitrogen atom in Ia or Ic is depressed by the electron-withdrawing group.

1-2-2   Insertion Reactions of Isothiocyanate 1/1 Adducts

Further reactions of Ib or Id (isothiocyanate 1/1 adducts) with other iso-cyanates were found to proceed by a consecutive insertion reaction in a similar manner to those reported by Harrison.[2]   The demetallation products of 1/2 adducts were concluded to be N-diphenylmethylene-N,N'-dialkylthio- or -dithiobiuret, which showed apparent $\pi \rightarrow \pi^*$ transitions due to the heterodiene linkage, $\supset C=N-\overset{|}{C}=S$, around $269 \sim 292$ nm ($\log \varepsilon \cong 4$).   The fragmentation pattern of the destannylation products from the reaction of Ib with methyl isocyanate is consistent with the linear struc-ture (VI), $[Ph_2C=N-C=S]^+$ (m/e=224), $[Ph_2C=N]^+$ (m/e=180), $[Ph_2C=N-C(=S)-NMe]^+$ (m/e=253).   Thus a further reaction of isothiocyanate adducts (Ib or Id) with either isocyanate or isothiocyanate should give the corresponding linear products (III or IV).   No ^{117}Sn, or ^{119}Sn satellite band corresponding to the CH_3-N proton signal was observed in the NMR spectra of the products obtained in the case of runs e and f.   Only linear structure (IV) is consistent with these spectroscopic properties.

$$Ph_2C=N-SnMe_3 \xrightarrow{R-NCS} Ph_2C=N-C \underset{S}{\overset{N-R}{<}} SnMe_3$$

(Ib) R=Me | (Id) R=Ph

R'-NCX   (X=O,S)

+EtSH

$$Ph_2C=N-C(=S)-NR-C(=NR')-X-SnMe_3 \xrightarrow[-Me_3SnSEt]{} Ph_2C=N-C(=S)-NR-C(=X)-NHR'$$

(IVe) R=R'=Me, X=S   (VIe) R=R'=Me, X=S
(IVf) R=R'=Me, X=O   (VIf) R=R'=Me, X=O
(IVg) R=R'=Ph, X=O   (VIg) R=R'=Ph, X=O
(IVh) R=Me, R'=Ph, X=S   (VIh) R=Me, R'=Ph, X=S

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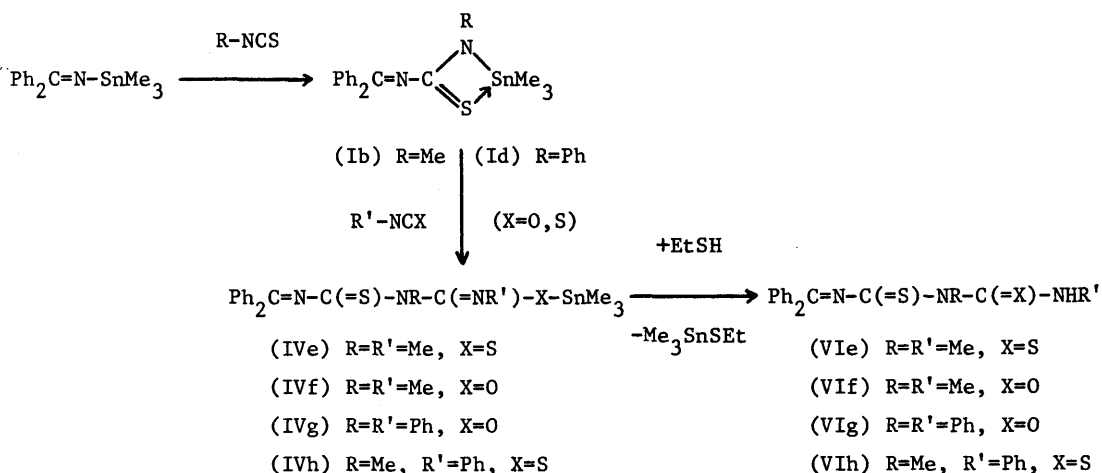
The consecutive insertion products of isothiocyanate 1/1 adducts (IVe—IVh) and their destannylation products (VIe—VIh) are summarized in Table 4 and 5.

Table 4. Consecutive insertion to isothiocyanate 1/1 adducts

	Yield (%)	Mp (°C)	ν_{max}[a] (cm^{-1})	$\tau_{CH_3-Sn}(J^{117}/^{119})$[a]	τ_{CH_3-N}[a]
IVe	84	158.0-160.0	1597, 1371	9.72 (57.0/59.0)	6.93, 6.31
IVf	67	163.0-166.0	1683, 1603	9.76 (55.0/57.0)	7.39, 6.66
IVg	100	165.0-166.0	1698, 1355	9.72 (55.5/58.5)	
IVh		not isolated			

a) Benzene solution.

Table 5. Destannylation products of IV

	Yield (%)	Mp (°C)	$\nu_{C=O}$ $\nu_{C=N}$ $\nu_{C=S}$[a] (cm^{-1})	λ_{max}[b] (nm)	τ_{CH_3-N}[c]
VIe	q. y.[d]	242.0-244.0	1531, 1290	278	6.79, 6.36
VIf	q. y.[d]	241.0-242.0	1692, 1533, 1296	269	7.20, 6.65
VIg	q. y.[d]	252.0-254.0	1703, 1513, 1240	279	
VIh	80[e]	213.0-215.0	1521, 1287	292	6.36

a) KBr disk. b) Ethanol solution. c) Deuterochloroform solution.
d) quantitative yield. e) Overall yield from Ib.

1-2-3   Mechanism of the Subsequent Reaction of the 1/1 Adducts

The drastic variation of the addition depending on the first component of the 1/1 adducts is illustrated by the following scheme.   The primary step of the addition of the Sn-N bond to the heterocumulene was assumed to occur by the nucleophilic attack of the nitrogen atom[3] giving a zwitter-ionic intermediate.

SnMe₃ at top:

$$\overset{1\ 2}{Ph_2C=N}\overset{3}{-C}\overset{SnMe_3}{\underset{4}{-N}}-R \qquad + \qquad \overset{6\ 5}{R'-N=C=Y}$$

with X below the C of [I].

[I]

R'
N
‖
—
Y

Ph_2C
‖
N
C
‖
X

R
N⁺—SnMe₃

[4+2]
cycloaddition
reaction   X=O   X=S   insertion
                  Y=O   Y=O, S   reaction

R'
N
Ph₂   O
N
NR
[II]
O-SnMe₃

+ EtSH
− Me₃SnSEt

R'
N
Ph₂   O
N
HN   NR
O   [V]

R'
N
Ph₂C   Y-SnMe₃
‖
N   NR
[IV]
S

+ EtSH
− Me₃SnSEt

R'
HN   Y
Ph₂C
‖
N   NR
[VI]
S

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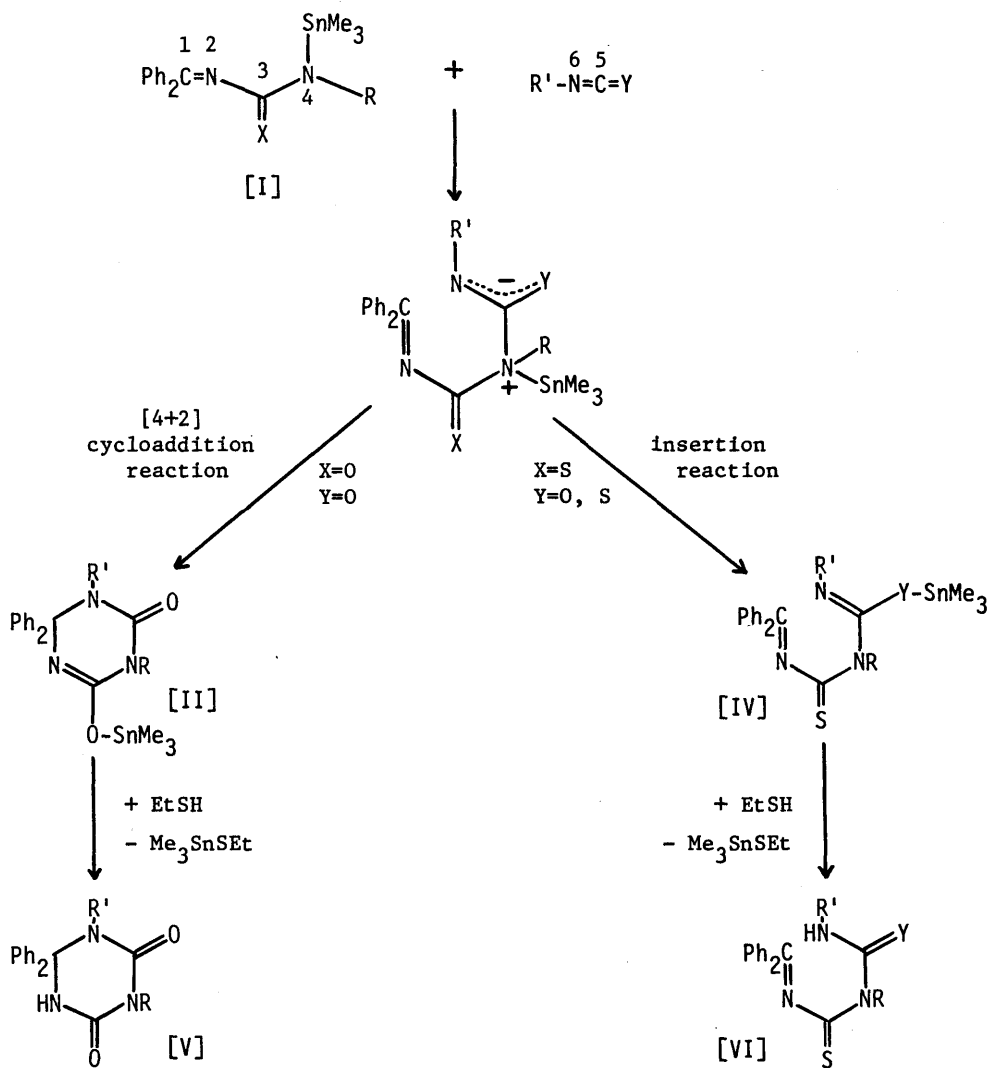
When X=O (run a—d) the positive charge on C(1) is enhanced largely by the
conjugated carbonyl group and is stabilized by resonance with the two phenyl rings.
Thus the nucleophilic ring closure occurs between N(6) and C(1).   The following
migration of the trimethylstannyl group from the ammonium nitrogen to the oxygen
atom yields the 1,3,5-triazin-2(1H)-one derivatives (IIa—IId).   The positive
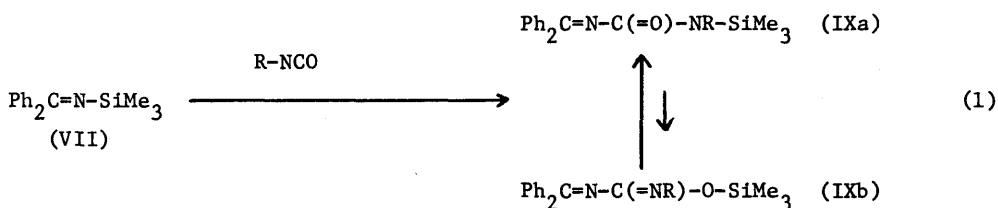charge on C(1) is small when X=S (run e—h), since the thiocarbonyl group is weakly
electron-withdrawing as compared with the carbonyl group.   Consequently, the anionic
center (Y) captures the electrophilic trimethylstannyl group giving the corresponding
consecutive insertion products (IVe—IVh).   In Harrison's case,[2] the aldehyde ad-
ducts did not have an electron-withdrawing group at C(3), and the formal charge on
C(1) is consequently zero.   The [4+2] cycloaddition reaction would therefore be
impossible.

2   Semi-empirical SCF-MO Studies on Cyclization Reaction of Silylimine
       with Isocyanates

     Recently, organosilicon compounds have been frequently utilized to organic
syntheses.   The most popular examples are the stabilization of enolate anion,[6]
pseudo-Wittig reaction of α-organosilylcarbanions,[7] an annelation, and homolo-
gation with vinylsilanes.[8]   On the other hand, organosilylamines or imines were
found to play substantial role in the synthesis of some heterocycles.[9]
In the previous paper on the insertion reaction of N-trimethylsilyl(diphenyl-
methylene)amine with isocyanates or isothiocyanates,[1] reactions of silylamines
with isocyanates in a 1/2 molar ratio yielded exclusively 3,4-dihydro-1,3-dialkyl-
4,4-diphenyl-6-trimethylsiloxy-1,3,5-triazin-2(1H)-one (VIII) by a polar [4+2]
cycloaddition.   The conclusion of the paper was summarized as follows;
(1) Treatment of the amine (VII) with equimolar amounts of isocyanates (R-NCO;
     R=Me or Ph) gave the equilibrium mixture of 1/1 adducts between amide (IXa)
     and imidate (IXb).   The variable temperature NMR study indicated that
     the equilibrium lies so far to the amide-form (IXa) around room temperature
     (eq 1).

$$Ph_2C=N-SiMe_3 \xrightarrow{\ R-NCO\ } \begin{array}{c} Ph_2C=N-C(=O)-NR-SiMe_3 \quad (IXa) \\ \uparrow\downarrow \\ Ph_2C=N-C(=NR)-O-SiMe_3 \quad (IXb) \end{array} \qquad (1)$$

(VII)

(2) The 3,4-dihydro-4,4-diphenyl-6-trimethylsiloxy-1,3,5-triazin-2(1H)-one (VIII) was obtained exclusively in a quantitative yield by a polar [4+2] cycloaddition of 1/1 adduct with another mole of isocyanate (R'-NCO). In these cycloaddition reaction, the formation of oxadiazinone (X) was completely depressed (eq 2).

$$IXa \text{ or } IXb \xrightarrow{\ R'-NCO\ } \qquad (2)$$

(X)

(VIII)
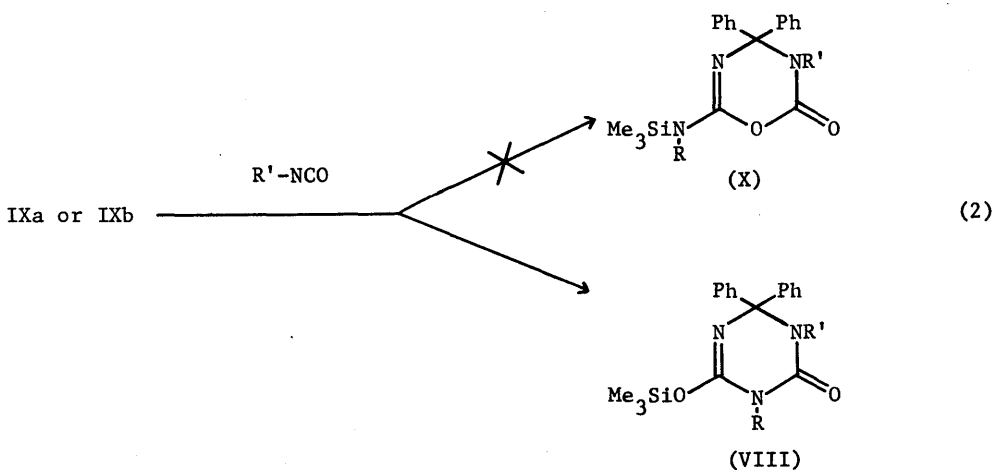
It is also reported that the tin analogue of VII, $Ph_2C=N-SnMe_3$, reacts with 2 moles of isocyanates in the same manner to give 3,4-dihydro-1,3-dialkyl-4,4-diphenyl-6-trimethylstannoxy-1,3,5-triazin-2(1H)-one (II). In this section, a semi-empirical SCF-MO calculation of model compounds and systems, (A)~(D) in Fig. 1, is reported in order to investigate the mechanism of [4+2] cycloaddition of 1/1 adduct (IX) with isocyanate. The suitability of a supposed path (Diels-Alder reaction) and the possibility of another path will be down for discussion by modifying IXa and IXb to (A) and (B) for simplification of the calculation.

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In the all model compounds, the dimethylmethyleneamino groups (Ph$_2$C=N-) and the trimethylsilyl groups were replaced by methyleneamino groups (H$_2$C=N-) and hydrosilyl groups (H$_3$Si-) in order to facilitate the calculation. In spite of these simplifications, MO calculations on these models gave reasonable and sufficient results.

2-1   Geometry of Model Compounds

The MO calculations were performed using the CNDO/2-Type MO method.[10]   The model compounds were shown in Fig. 1.
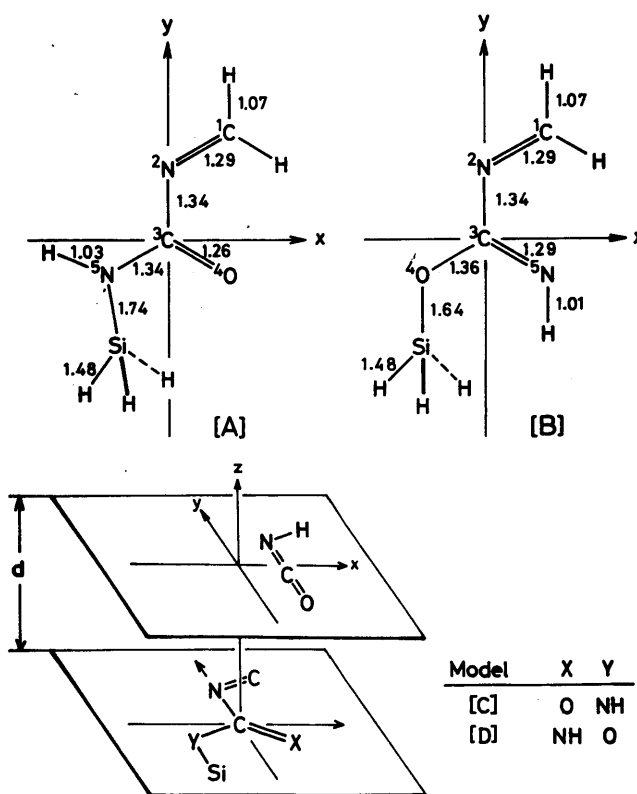

Fig. 1.   Geometry of Model Compounds

Compounds (A) and (B) are the model compounds for IXa and IXb, respectively.
(C) and (D) are the models of the transition state of cycloaddition of 1/1 adduct
(IXa or IXb) with isocyanates.   Bond lengths of model compounds were cited from
" The Tables of Interatomic Distances and Configuration in Molecules and Ions ".[11]
In the model compounds (B) and (D), idealized angles of 120° were used for the
Si-O-C bond angle.   Models (C) and (D) are transition state of the concerted [4+2]
cycloaddition caused by the approach of HNCO molecule from the top of (A) and (B),
respectively.   The MO calculations were achieved on the assumption of two cases
where the intermolecular distances are 1.5 Å and 3.0 Å.

2-2   Results of MO Calculations

2-2-1   Electronic Structure of 1/1 Adducts

     The total energy and charge density for model starting materials (A) and (B)
are given in Table 6 and 7.

Table 6.   Total energy and charge density of (A) and (B)
(including only s- and p-orbitals)

Compound		(A)	(B)
Total Energy (a.u.)		−63.8217	−63.7580
Charge Density	C(1)	0.134946	0.116158
	N(2)	−0.190879	−0.161022
	C(3)	0.418649	0.374949
	O(4)	−0.401554	−0.416604
	N(5)	−0.330310	−0.342385
	Si	0.795397	0.907679

Table 7.   Total energy and charge density of (A) and (B)
(including 3d-orbital of Si)

Compound		(A)	(B)
Total Energy (a.u.)		−64.3051	−64.2096
Charge Density	C(1)	0.159241	0.140298
	N(2)	−0.185400	−0.152471
	C(3)	0.477349	0.436605
	O(4)	−0.338779	−0.345436
	N(5)	−0.275616	−0.297138
	Si	0.358697	0.521925

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From the comparison of the total energy, it is clear that (A) is more stable than (B)
by 0.0637 a.u. in the calculation   including only 2s- and p-orbitals, and by
0.0955 a.u. in that of further incorporation of 3d-orbitals of silicon atom.
These results agreed well with the NMR data that showed an equilibrium between IXa
and IXb laid so far to IXa.   Whereas the value of positive charge on the silicon
atom is too large in the calculation including only s- and p-orbitals, the value is
lowered to a reasonable one by the introduction of 3d-orbital of silicon into the cal-
culation.

2-2-2   Polar [4+2] Cycloaddition Reaction of 1/1 Adduct with Isocyanate

    The cycloaddition to give six-membered heterocycles was assumed to proceed *via*
Diels-Alder process.   The total energy and charge density of the modeled transition
states, where the intermolecular distance between 1/1 adduct and isocyanic acid was
3.0 Å and 1.5 Å, were shown in Table 8 and 9.

Table 8.   Total energy and charge density of (C) and (D); d=3.0 Å
(including 3d-orbital of Si)

Model		(C-30)	(D-30)
Total Energy (a.u.)		-101.973	-101.866
Charge Density	C(1)	0.156004	0.137259
	N(2)	-0.183545	-0.150557
	C(3)	0.476360	0.435396
	O(4)	-0.345769	-0.346317
	N(5)	-0.275861	-0.306153
	Si	0.315039	0.489034
	N(6)	-0.318310	-0.316135
	C(7)	0.465584	0.463171
	O(8)	-0.264364	-0.274244

Table 9.   Total energy and charge density of (C) and (D); d=1.5 Å
(including 3d-orbital of Si)

Model		(C-15)	(D-15)
Total Energy (a.u.)		-102.061	-101.901
Charge Density	C(1)	0.217656	0.198448
	N(2)	-0.214636	-0.172532
	C(3)	0.563605	0.498754
	O(4)	-0.324717	-0.347344
	N(5)	-0.296834	-0.282547
	Si	0.306655	0.491475
	N(6)	-0.474970	-0.460598
	C(7)	0.579343	0.556683
	O(8)	-0.342273	-0.388562

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The 1/1 adduct and isocyanic acid are concluded to be scarcely perturbed in the case of d=3.0 Å, because charge density was unchanged despite of the approach of HNCO molecule till d=3.0 Å (Table 7 and 8). When two reactants approach to 1.5 Å, the transition state (C) is stabilized greater extent than (D). The energy differences between (C-30) and (C-15) and that between (D-30) and (D-15) are 0.088 and 0.035 a.u., respectively. If the [4+2] cycloaddition proceeds *via* a transition state (C), oxadiazinone (X) should be obtained, which is in contradiction to the experimental observation that triazinone (VIII) was the predominant product. Triazinone (VIII) would be formed *via* a transition state (D) which is less stable than (C). Consequently, the [4+2] cycloaddition does not proceed *via* a Diels-Alder path as (C) or (D), but takes place perhaps *via* a stepwise mechanism. We briefly discuss about the latter possibility as follows. The central carbon atom of isocyanic acid possesses large positive charge, and plays a role as an electrophilic center. It is, therefore, important to understand the character of the highest occupied MO of nucleophiles in order to elucidate the reaction mechanism. The highest occupied MO of (A), which was concluded to be the more stable tautomer based both on experimental (NMR) observation and on the MO calculation (Table 7), is shown in Table 10.

Eigen vector cited in Table 10 indicates that the highest occupied MO is regarded as the lone pair on the nitrogen atom bonded to H_3Si group, although it is somewhat delocalized over the heterodiene linkage; $\supset C=N-\overset{|}{C}=O$ skeleton.

Accordingly, the nucleophilic attack of the lone pair of N(5) to the central carbon C(7) of isocyanic acid should occur at the first stage of the reaction. This C-N bond formation gives zwitter-ionic intermediate XI, which induces the nucleophilic ring closure between N(6) and C(1). These results are illustrated in the following scheme.

Table 10. Highest occupied MO of (A)

MO energy	−0.510278 a.u.

Atomic orbital		Eigen Vector
C(1)	2s	0.015578
	$2p_x$	−0.061317
	p_y	0.075909
	p_z	0.120061
N(2)	2s	−0.058096
	$2p_x$	0.234949
	p_y	−0.323414
	p_z	0.095620
C(3)	2s	0.040571
	$2p_x$	−0.062145
	p_y	0.166488
	p_z	−0.123592
O(4)	2s	0.008847
	$2p_x$	0.029505
	p_y	−0.386390
	p_z	−0.475998
N(5)	2s	−0.067857
	$2p_x$	0.126082
	p_y	−0.257498
	p_z	0.341959

16
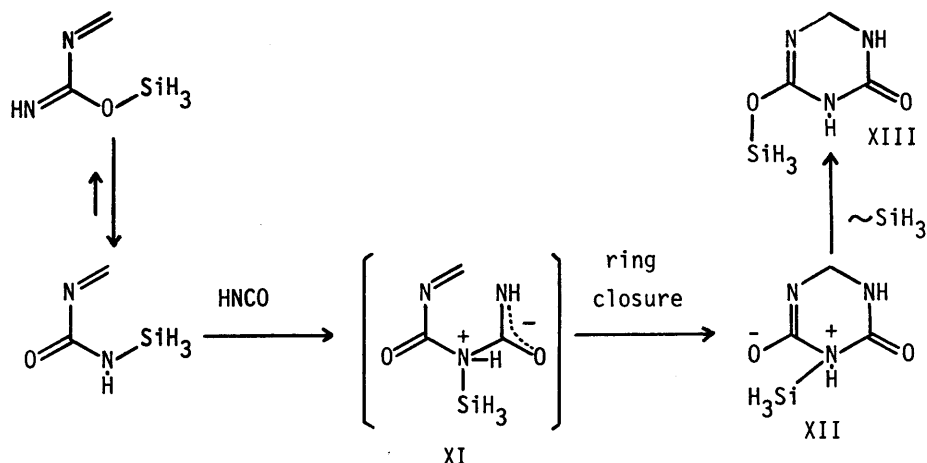
The migration of the silyl group from the ammonium nitrogen to oxyanion of XII occurs at the final stage yielding 1,3,5-triazin-2(1H)-one (XIII).

2-2-3   Feasibility of the 1,3-Silyl Group Migration and (2p-3d)π Interaction

The 1,3-migration of trimethylsilyl group between nitrogen and oxygen atoms was observed by means of NMR study of the 1/1 adduct of silylamine (VII) with iso-cyanate.   In Fig. 2, E_{Si-O} or E_{Si-N} represents bonding interaction between silicon and oxygen or nitrogen atom. The negative value of E_{Si-O} or E_{Si-N} indicates the substantial bonding interaction.   The more the absolute value of E_{Si-O} or E_{Si-N} increases, the stronger the interaction between Si and O or N will be ensued.

The MO calculation for the model compounds (A) and (B) shows that the silicon atom could interact with the heteroatom located at γ-position as shown in Fig. 2.   This large through-space interaction would be an important driving force of the 1,3-migration of

E_{Si-N}=-0.727908 a.u. E_{Si-O}=-0.591414 a.u.

E_{Si-O}=-0.210850 a.u. E_{Si-N}=-0.196592 a.u.

Fig. 2   Bonding interaction between
        Si and O(4) or N(5)

silyl group.   Finally, the presence of large (p-d)π interaction was supported by comparing the electronic structure consisting of only s- and p-orbitals with that of s-, p-, and 3d-orbitals.   The electronic structure of (A) and (B) are shown in Table 11.   And π-bond order of (A) and (B) calculated including 3d-orbital of Si atom

Table 11. Electronic structures of (A) and (B)

Compound	(A)		(B)	
	including d-orbital	only s- and p-orbitals	including d-orbital	only s- and p-orbitals
E_{N-Si}	-0.727908	-0.468620		
E_{O-Si}			-0.591414	-0.364630
π-bond order $3d_{yz}(Si)-2p_z$(N or O)	0.370832		0.371438	
Charge Density on Si	0.358697	0.795397	0.521925	0.907679
Total Energy (a.u.)	-64.3051	-63.8217	-64.2096	-63.7580

are shown in Fig. 3. The result suggests both positive charge density on Si and total energy are depressed by the introduction of 3d-orbital into MO calculation. This means that lone pair electrons on an adjacent heteroatom flows into the vacant 3d-orbital of silicon atom. Consequently, through-conjugation from C(1) to Si(6) becomes possible, and stabilizes the total energy of the model compounds (A) and (B).
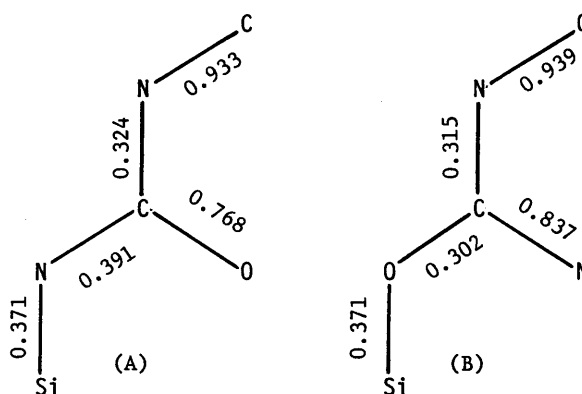
Fig. 3 π-Bond order of (A) and (B)
(p_z-p_z, p_z-d_{yz})

3   The Reaction of N-Trimethylsilyl- and -stannyl(diphenylmethylene)amine with Diketene

N-Trimethylsilyl- and -stannyl(diphenylmethylene)amine; $Ph_2C=N-MMe_3$ [(VII) for M=Si and (XIV) for M=Sn] have been reported to induce insertion and consecutive cyclization reactions with heterocumulene compounds,[1,2,3,12] aldehydes,[2] and acrylonitrile.[2]   Diketene is an attractive component for the preparation of six-membered heterocyclic compounds, because the acyl-oxygen bond cleavage of diketene provides a synthetic equivalence of acetylketene; $CH_3CO-CH=C=O$.   For example, the addition

of diketene to some carbodiimides and the parent diphenylmethyleneamine gave the corresponding oxazinone derivatives (XV)[13] and (XVI),[14] respectively.
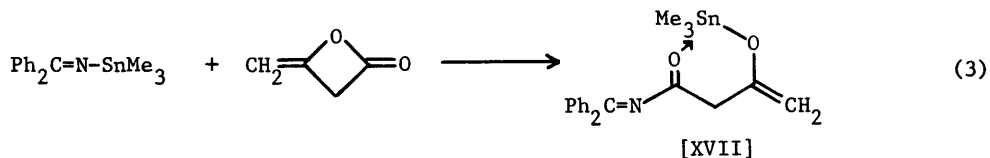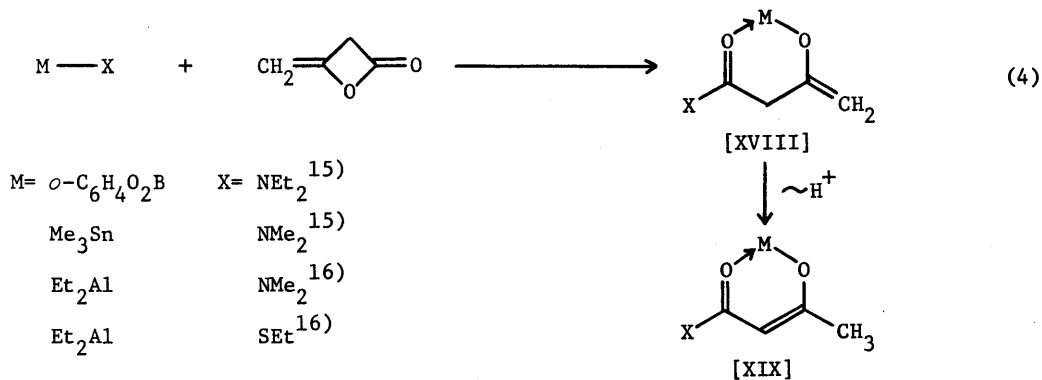
In this section, an insertion of diketene to the metal-nitrogen bond of VII and XIV, and the subsequent cyclization reactions by way of demetallation treatment are described. The difference of products in both insertion and demetallation steps by changing the metal atom is discussed.
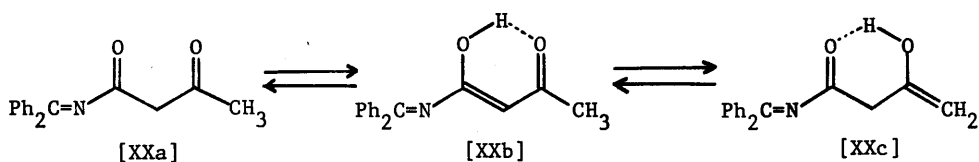

(XV)   (XVI)
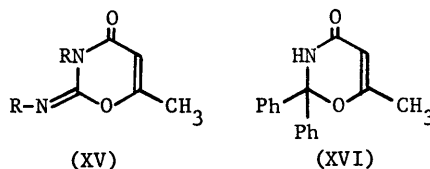
3-1   The Reaction of N-Trimethylstannyl(diphenylmethylene)amine

N-Trimethylstannyl(diphenylmethylene)amine; $Ph_2C=N-SnMe_3$ (XIV) reacted exothermically with equimolar amounts of diketene to give the 1/1 adduct (XVII) as the fairly air-stable crystals in 96% yield. The strong IR absorption band around 1574 cm^{-1} indicates the presence of the carbonyl oxygen atom coordinated to the organotin moiety. Another absorption band at 1673 cm^{-1} was assigned to the C=N stretching frequency. The ^1H NMR spectrum of 1/1 adduct (XVII) showed resonance peaks at τ7.05 (2H, m), 5.71 (1H, d, J=1.5 Hz), and 4.43 (1H, m), which were assigned to the methylene and terminal vinylic protons, respectively. The above spectroscopic results are consistent with the depicted structure XVII in Eq. 3.

The participation of the diphenylmethylene group in the 1/1 reaction may be ruled out, since any cyclic product which includes the diphenylmethylene group in the ring skeleton was not obtained at all. Organometallic insertion reactions of diketene have been reported [15,16] to give only one product XIX, which involves intramolecular 1,3-shift of a central methylene proton from XVIII (eq 4).

$$Ph_2C=N-SnMe_3 \quad + \quad CH_2 \overset{O}{=\!=} =O \quad \longrightarrow$$

[XVII]

(3)

19

M —— X + CH$_2$=⬠=O ⟶ [structure XVIII] (4)

[XVIII]

↓ ~H$^+$

[XIX]

M= o-C$_6$H$_4$O$_2$B   X= NEt$_2$ [15)]

Me$_3$Sn   NMe$_2$ [15)]
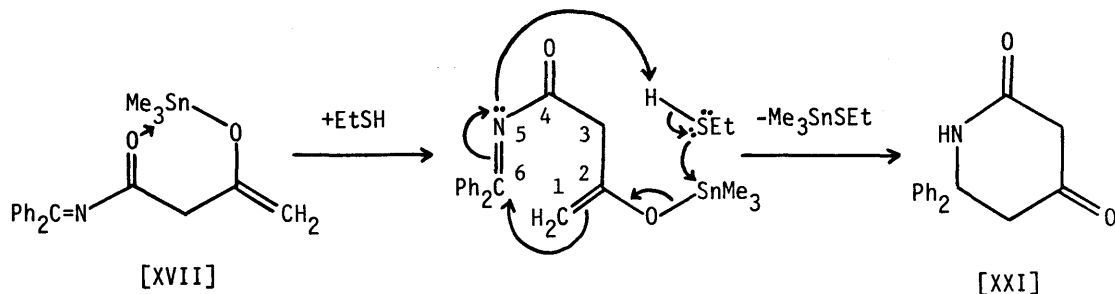
Et$_2$Al   NMe$_2$ [16)]

Et$_2$Al   SEt [16)]

It is noteworthy that the product (XVII) obtained in the reaction of N-trimethyl-stannyl(diphenylmethylene)amine with diketene is the first stable organometallic insertion product which does not induce a 1,3-proton shift. The structure of XVII is also confirmed by the following destannylation reaction. Ethanethiol was added to the 1/1 adduct (XVII) in order to substitute the trimethylstannyl group with proton. The expected products were the isomers XXa XXc; however, the ^{1}H NMR spectrum of the obtained destannylation product exhibited unexpectedly neither methyl protons nor vinylic protons. Only two pairs of methylene protons (τ6.95, 2H, s, and τ6.68, 2H, s) and the one proton attached to the nitrogen atom (τ2.32, 1H, s, confirmed by D$_2$O exchange) were observed.

Ph$_2$C=N [structure XXa] CH$_3$ ⇌ Ph$_2$C=N [structure XXb] CH$_3$ ⇌ Ph$_2$C=N [structure XXc] CH$_2$

[XXa]   [XXb]   [XXc]

Moreover, two strong absorption bands at 1728 and 1661 cm^{-1} are assigned to a ketone and an amide carbonyl stretching frequencies, respectively. The above-mentioned spectroscopic results are consistent with 6,6-diphenylpiperidin-2,4-dione (XXI), whose formation is shown in Scheme 1. The addition of ethanethiol firstly causes the cleavage of the intramolecular coordinated structure because of the difference in the affinity of the tin atom toward oxygen and sulfur atoms.
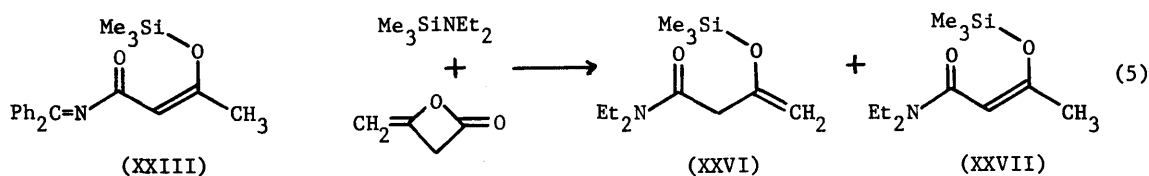
Scheme 1.

Me₃Sn、

[Structure of XVII: Ph₂C=N attached, with Me₃Sn-O and O-CH₂ arrangement]

Ph₂C=N

[XVII]

+EtSH →

[Central cyclic intermediate structure with numbering 1-6, N at 5, Ph₂C at 6, H₂C, with arrows showing electron movement, H-SEt and SnMe₃ and O labels]

-Me₃SnSEt →

[Structure of XXI: six-membered ring with O at top, HN, Ph₂, and =O]

[XXI]

Then the ring closure is induced exclusively by the nucleophilic attack of the ter-
minal carbon atom C(1) to the *exo* double bond at C(6), accompanied by the elimina-
tion of trimethylstannyl ethylsulfide. In the present case, diketene behaves as
a component ĊO-CH₂CO-ĊH₂ to [4+2] cycloaddition. This is quite different from
the general behavior of diketene which acts as synthetic equivalence of acetylketene,
CH₃CO-CH=C=O, as described before.

3-2   The Reaction of N-Trimethylsilyl(diphenylmethylene)amine

    N-Trimethylsilyl(diphenylmethylene)amine (VII) reacted with diketene under more
vigorous condition than the tin analogue (XIV) (60 °C, 14 hr). The 1/1 reaction
mixture was purified by vacuum distillation (bp 108.0-116.0 °C/ 0.02 mmHg) and was
confirmed as a 1/1 adduct by analysis, whereas the adduct did not show a simple ^{1}H
NMR spectrum (Fig. 4). The detailed measurement of the proton ratio and coupling
patterns revealed the presence of three isomers XXII, XXIV, and XXV, structures of
which were given in Scheme 2. There is the possibility of the presence of the struc-
ture XXIII in the 1/1 adduct as reported in the paper[17] that diketene reacted with
equimolar amounts of trimethylsilyldiethylamine to give the mixture of XXVI and XXVII
as shown in Eq. 5.

[Structure XXIII: Me₃Si-O, Ph₂C=N with CO-CH=C-CH₃]

(XXIII)

[Structure: Me₃SiNEt₂ + CH₂=C(O)=O (diketene)] →

[Structure XXVI: Me₃Si-O, Et₂N with CO-CH₂CO-CH₂]

(XXVI)

+

[Structure XXVII: Me₃Si-O, Et₂N with CO-CH=C-CH₃]

(XXVII)

(5)

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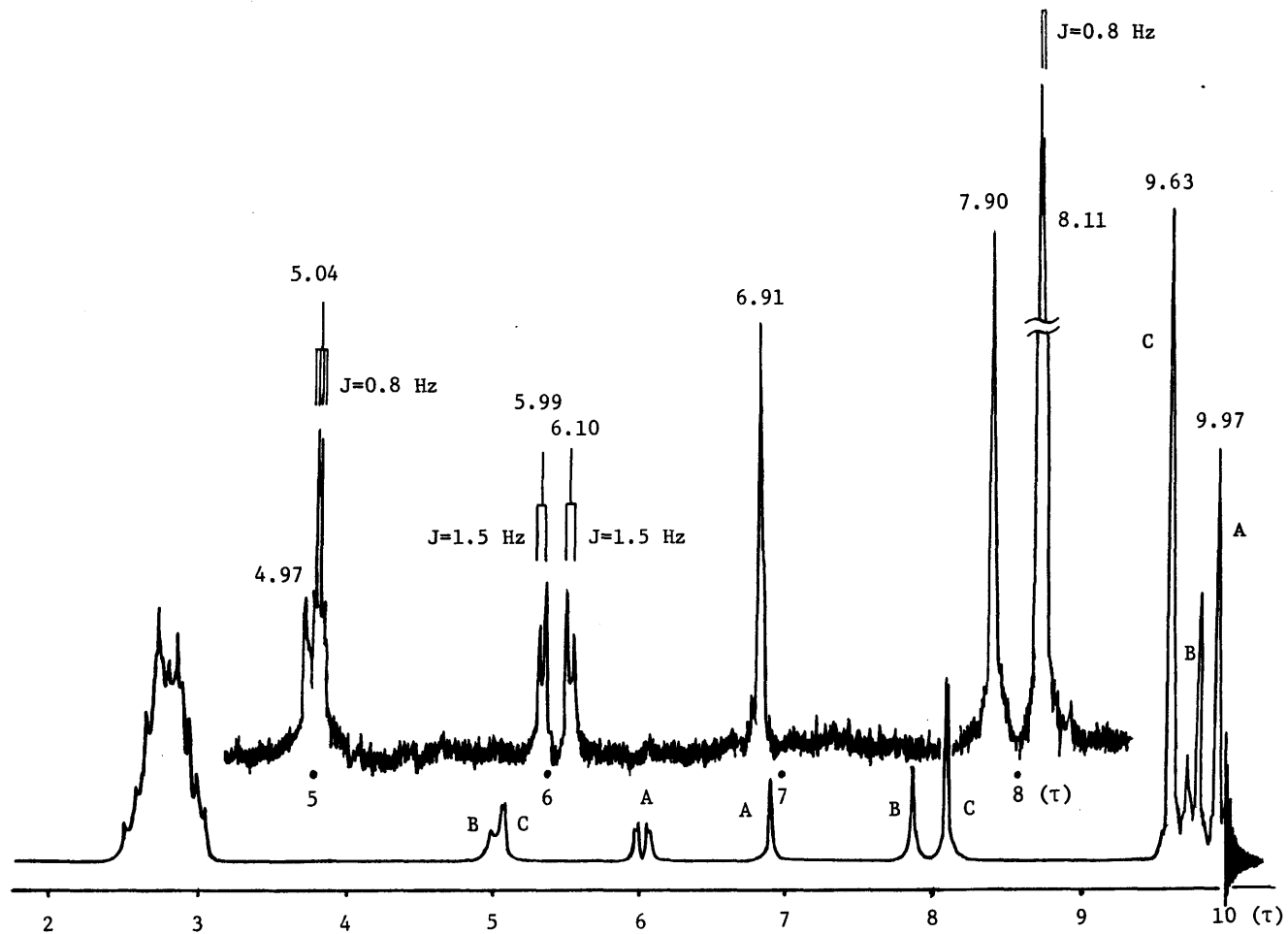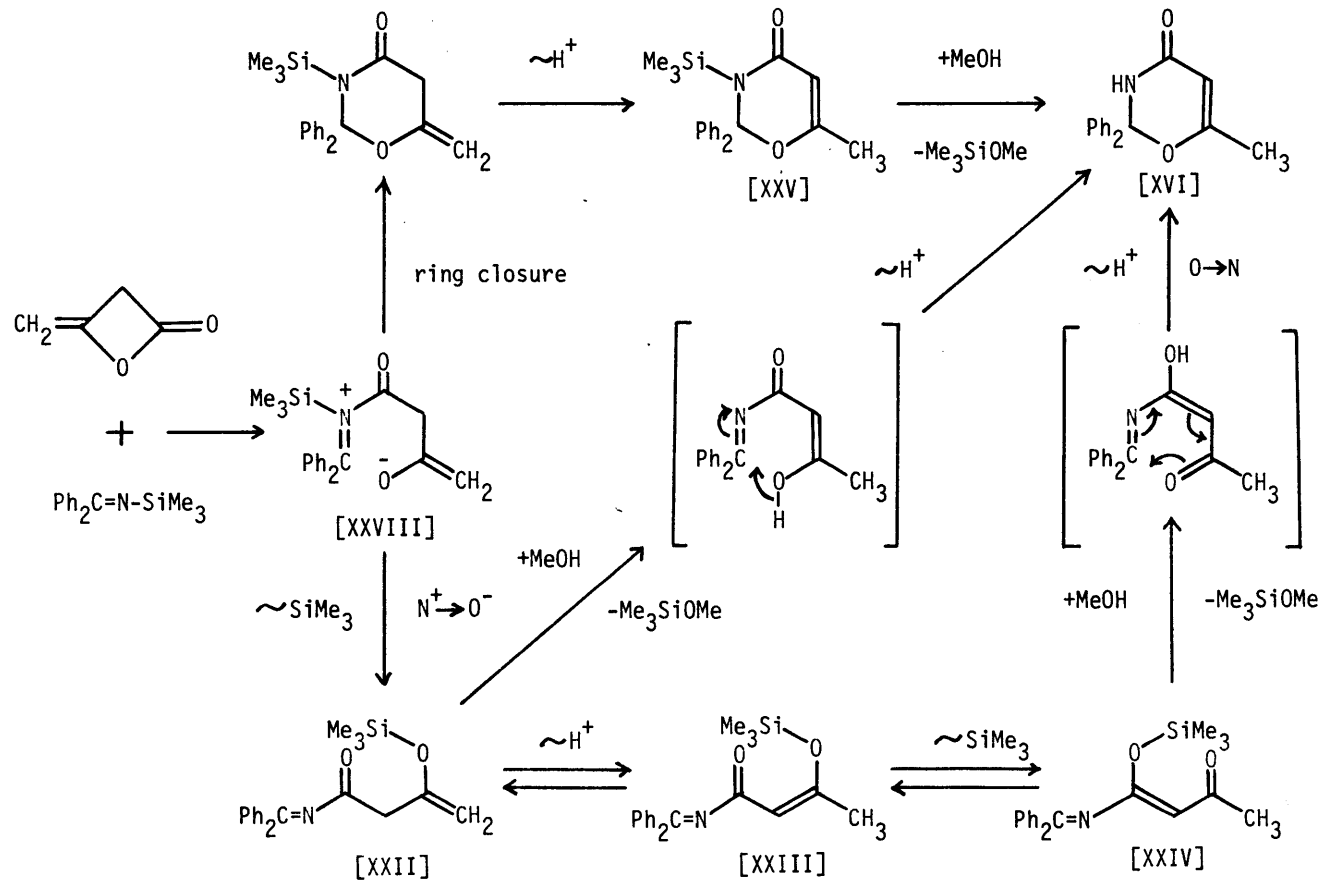Fig. 4. The ^{1}H NMR spectrum of distilled mixture (in CCl_4). Resonance peaks A, B, and C were attributed to XXII, XXIV, and XXV, respectively.

Me₃Si–N, O (ring closure)

~H⁺

+MeOH
-Me₃SiOMe

[XXV]

[XVI]

CH₂=⟨⟩=O

+

Ph₂C=N-SiMe₃

Me₃Si–N⁺

[XXVIII]

~SiMe₃   N⁺→O⁻

+MeOH
-Me₃SiOMe

~H⁺

~H⁺   O→N

+MeOH   -Me₃SiOMe

Me₃Si–O

Ph₂C=N CH₂

[XXII]

~H⁺

Me₃Si–O

Ph₂C=N CH₃

[XXIII]

~SiMe₃

O–SiMe₃

Ph₂C=N CH₃

[XXIV]

However, it can be excluded because of the absence of the allyl coupling which is expected in the structure XXIII. The observed isomer ratio in the 1/1 adducts was dependent on the reaction temperature as shown in Table 12.

Table 12.

Reaction temp. (°C)	Total yield of XXII, XXIV, and XXV (%)	Isomer ratio XXII : XXIV : XXV		
60	73	3.5 :	1.0 :	8.0
115	68	0.9 :	1.0 :	1.3
120	71	0.4 :	1.0 :	0.8

The isomer ratio of XXII and XXV decreased, and that of XXIV increased as the elevation of the reaction temperature. This result definitely showed XXII and XXV were convertible to XXIV, which would be ther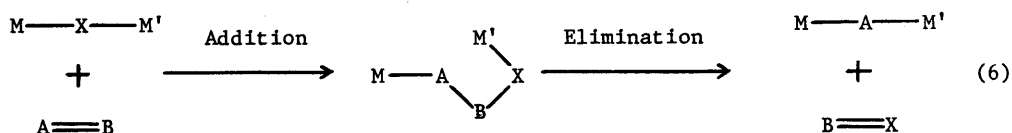modynamically the most stable product. Although the 1/1 adduct is composed of three isomers, XXII, XXIV, and XXV, only 2,2-diphenyl-3,4-dihydro-6-methyl-2(1H)-1,3-oxazin-4-one (XVI) was isolated on desilylation reaction. The yields are quantitative from the methanolysis of the purified 1/1 adduct, and 72 % from the methanolysis of the 1/1 reaction mixture.
The XVI has been prepared by [4+2] cycloaddition reaction of the parent amine; Ph$_2$C=NH with diketene.[14] . The above results are summarized in Scheme 2. The first step is a nucleophilic attack of the nitrogen atom in N-trimethylsilyl(diphenyl-methylene)amine to the carbonyl carbon of diketene. In the second step, two paths are possible. First possibility is the migration of the trimethylsilyl group from the nitrogen to the oxyanion in XXVIII to give XXII and XXIV. Secondly, a direct ring closure accompanying a 1,3-prototropy gives XXV, similar to a reaction of the parent diphenylmethyleneamine with diketene.[14] It is extremely interesting that two isomeric heterocyclic compounds; XXI and XVI may be obtained from diketene only by changing the organometallic moiety in another component; N-organometallyldiphenyl-methyleneamine.

4   Modified Synthesis of Imidazolidines with N,N'-Bis(trimethylsilyl)-
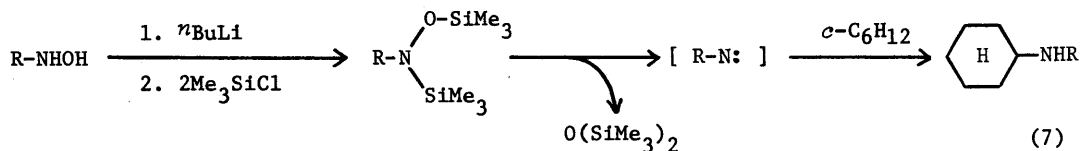   1,2-diamines

    Addition reaction of the metallic oxides, amides, and sulfides (M—X: M=Si, Ge,

; X=O, N, S) to unsaturated bonds (A=B) has been investigated to study the reactiv-
y of organometallic compounds and to obtain new compounds with a heteroatom.
en the heteroatom is bound to two organometallic entity, namely, the compound ab-
eviated in the general formula as M-X-M' is used, addition is often followed by
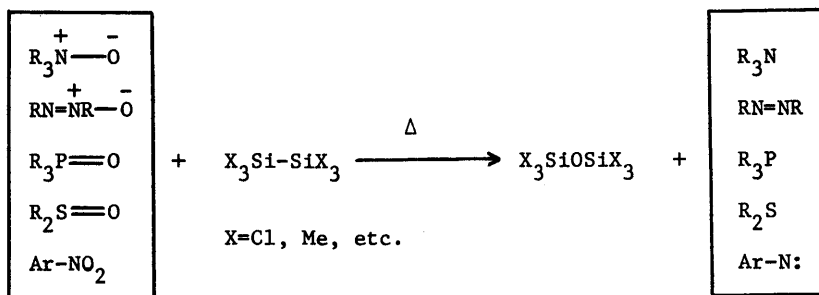bsequent elimination of M-A-M' in some cases (eq 6).

$$
\begin{array}{ccc}
\begin{matrix} M\!-\!\!-\!\!-X\!-\!\!-\!\!-M' \\ + \\ A\!=\!\!=\!\!=B \end{matrix} & \xrightarrow{\text{Addition}} & M\!-\!\!-\!A\begin{matrix} M' \\ \diagdown \\ \diagup \\ B \end{matrix}X & \xrightarrow{\text{Elimination}} & \begin{matrix} M\!-\!\!-\!\!-A\!-\!\!-\!\!-M' \\ + \\ B\!=\!\!=\!\!=X \end{matrix} & (6)
\end{array}
$$

e most important driving force in either β-addition-β-elimination (M=Me$_3$Si,[18, 19]
$_3$Ge,[20] and Me$_3$Sn[18, 21] X=NMe), or β-addition-ω-elimination (M=^{n}Bu$_3$Sn; X=O(CH$_2$)$_n$O,[22]
(CH$_2$)$_2$O,[23] NR(CH$_2$)$_2$NR[23]) would be the organometallic affinity differences be-
een product (with stable M-Y bonds) and starting materials (with labile M-X bonds).[24]

It is now well recognized that silicon is an excellent oxygenophile, and as such,
host of useful synthetic methods have been developed which exploit this property.[25]
r example, nitrene generation *via* a pyrolysis of N,O-bis(trimethylsilyl)hydroxylamine
s reported by F. P. Tsui *et al.* (eq 7).[26]

$$
\text{R-NHOH} \xrightarrow[\text{2. 2Me}_3\text{SiCl}]{\text{1. }^n\text{BuLi}} \text{R-N}\begin{matrix}\diagup \text{O-SiMe}_3 \\ \diagdown \text{SiMe}_3\end{matrix} \longrightarrow [\text{ R-N: }] \xrightarrow{c\text{-C}_6\text{H}_{12}} \langle \text{H} \rangle\!-\!\text{NHR}
$$
$$
\searrow \text{O(SiMe}_3)_2 \qquad\qquad (7)
$$

was suggested that the driving force for α-deoxysilylation is the bond formation
tween oxygen and the nitrogen-bound silicon.   Disilane was known to function as
ficient reducing agent for various organic[27, 28, 29] (and inorganic[30]) nitrogen
ide as well as phosphine oxide,[27, 31] sulfoxide,[27] and aryl nitro compounds.[32]

$$
\begin{array}{ccc}
\boxed{\begin{matrix} \overset{+}{R_3N}\!-\!\overset{-}{O} \\ \overset{+}{RN=NR}\!-\!\overset{-}{O} \\ R_3P\!=\!\!=O \\ R_2S\!=\!\!=O \\ Ar\text{-}NO_2 \end{matrix}} & + \quad X_3Si\text{-}SiX_3 \xrightarrow{\Delta} X_3SiOSiX_3 \quad + & \boxed{\begin{matrix} R_3N \\ RN=NR \\ R_3P \\ R_2S \\ Ar\text{-}N: \end{matrix}} \\
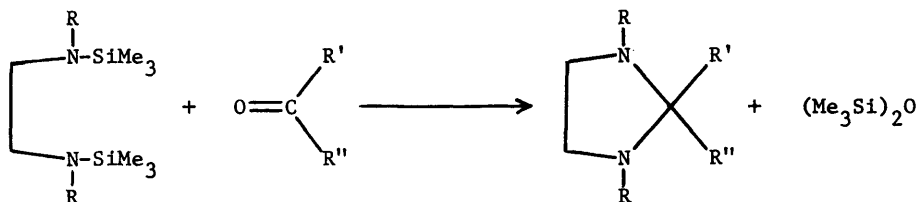& X=Cl, \text{ Me, etc.} &
\end{array}
$$

Recently, D. A. Evans *et al.* reported[33] that methylthiotrimethylsilane reacts spontaneously with aldehydes and ketones at 0 °C to give dimethylthioketals without the requirement of acid catalysis in an excellent yield.

$$2 \text{ MeS-SiMe}_3 \quad + \quad \underset{R}{\overset{R'}{\diagdown}} C=0 \quad \longrightarrow \quad \underset{R}{\overset{R'}{\diagdown}} C \underset{\text{SMe}}{\overset{\text{SMe}}{\diagup}} \quad + \quad O(SiMe_3)_2$$

In this section, the modified preparation of imidazolidine skeleton by means of N,N-bis(trimethylsilyl)ethylene- and -*o*-phenylenediamines is described. Imidazolidine derivatives have been synthesized by a dehydration condensation between diamine and carbonyl compounds. This preparative reaction, however, is reversible and removal of generated water is required to complete the reaction. This operation takes generally long time and is inadequate to prepare water-sensitive homologues. Elimination of unreactive hexamethyldisiloxane should favor an irreversible generation of imidazolidine under mild reaction conditions. In addition, the present manipulation is easy to carry out simple separation of hexamethyldisiloxane *in vacuo*. These condensation reactions constitute an extension of addition-elimination reactions of main group organometallics from the standpoint of organometallic chemistry. This work is devoted to examine the possibility of utilization of the strong silicon-oxygen bond formation (a hard-hard interaction) in the imidazolidine cyclizations, because it was previously elucidated that an inverse soft-soft interaction of tin-sulfur bond formation had substantial synthetic potential in iminocarbonylation or cyclization to thione-carbonate and spiro-orthoesters.

Reactions of electronically and sterically different various N,N'-bis(trimethyl-silyl)-1,2-diamines with aldehyde or ketones gave corresponding imidazolidine derivatives in excellent yields.

$$\begin{array}{c} R \\ | \\ -N\text{-SiMe}_3 \\ \\ -N\text{-SiMe}_3 \\ | \\ R \end{array} \quad + \quad 0=C\underset{R''}{\overset{R'}{\diagup}} \quad \longrightarrow \quad \begin{array}{c} R \\ | \\ N \\ \diagdown \\ N \\ | \\ R \end{array}\underset{R''}{\overset{R'}{\diagup\!\!\!\diagdown}} \quad + \quad (Me_3Si)_2O$$

Hexamethyldisiloxane generated as a sole by-product could be removed completely by evaporation *in vacuo* at room temperature. When dimethylformamide was used as a reactant with N,N'-bis(trimethylsilyl)ethylenediamine and -*o*-phenylenediamine, subsequent elimination of dimethylamine induced the generation of 2-imidazoline and 2-benzimidazole, respectively. Preparative results are summarized in Table 13.
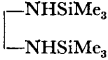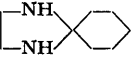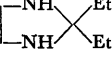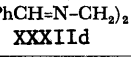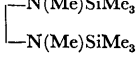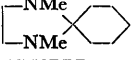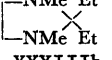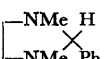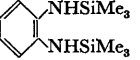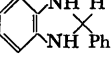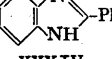
4-1   Reaction of N,N'-Bis(trimethylsilyl)ethylenediamine

N,N'-Bis(trimethylsilyl)ethylenediamine (XXIX) reacted with diethyl ketone and cyclohexanone to give the expected imidazolidines XXXIIb and XXXIIa, which were readily purified by distillation. Analytical and spectral information is consistent with the depicted structures. Dimethylformamide reacted with XXIX at 120 °C to give imidazoline (XXXIIc) by way of further elimination of dimethylamine. Although 2-substituted imidazolines have been prepared by dehydration condensation under highly drastic conditions (200-220 °C), the parent skeleton of 2-imidazoline has not been obtained. This method is extremely useful to prepare simplest 2-imidazoline (XXXIIc). The mechanism of this reaction was discussed later. Benzaldehyde did not give expected imidazolidine by ω-elimination of hexamethyldisiloxane but afforded N,N-dibenzylideneethylenediamine (XXXIId), which was definitely identified by analysis, IR ($\nu_{C=N}$ 1640 cm^{-1}), and NMR [τ_{CH} 1.80 (2H,s), τ_{CH_2} 6.16 (4H,s)].

4-2   Reaction of N,N'-Bis(trimethylsilyl)-N,N'-dimethylethylenediamine

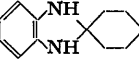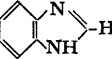Introduction of methyl groups on each nitrogen atom of XXIX increased both electron density and steric hindrance around the nitrogen atom. The reaction of N,N'-bis(trimethylsilyl)-N,N'-dimethylethylenediamine (XXX) with diethyl ketone, cyclohexanone, and even benzaldehyde, however, gave quantitatively the corresponding imidazolidines, XXXIIIb, XXXIIIa, and XXXIIIc, which were unambiguously identified by analytical and spectral information. Dimethylformamide did not react with XXX even at 120 °C for 6 hr indicative of the participation of steric effect to some extent.

Table 13. Cyclization Reaction of Bis(trimethylsilyl)diamines
with Carbonyl Compounds

Bis(TMS)-diamine	Carbonyl compound	Method[a]	Reaction conditions	Product	Bp (°C/mmHg) [mp] (°)	Yield[b] (%)
—NHSiMe₃ —NHSiMe₃ **XXIX**	⬡=O	A	20 °C/2 min	NH NH **XXXIIa**	41/0.2	59 (98)
	Et₂C=O	B	120 °C/1 hr	—NH Et —NH Et **XXXIIb**	31/2	59 (98)
	Me₂NCHO	B	120 °C/1 hr	—N —NH —H **XXXIIc**	50/1	87
	PhCHO	A	20 °C/2 min	(PhCH=N-CH₂)₂ **XXXIId**	152/0.8	98
—N(Me)SiMe₃ —N(Me)SiMe₃ **XXX**	⬡=O	A	20 °C/2 min	—NMe —NMe **XXXIIIa**	72/50	56 (100)
	Et₂C=O	B	180 °C/24 hr	—NMe Et —NMe Et **XXXIIIb**	40/7	33 (100)
	Me₂NCHO	B	120 °C/6 hr	No reaction		
	PhCHO	A	20 °C/2 min	—NMe H —NMe Ph **XXXIIIc**	63/1	93 (100)
NHSiMe₃ NHSiMe₃ **XXXI**	⬡=O	A	20 °C/2 min	NH NH **XXXIVa**	[131—133]	66 (100)
	Et₂C=O	B	180 °C/24 hr	No reaction		
	Me₂NCHO	B	120 °C/12 hr	N NH —H **XXXIVd**	[173—175]	97
	PhCHO	B	50 °C/3 hr	NH H NH Ph **XXXIVb**	[63—65]	91 (100)
	PhCHO	B	120 °C/12 hr	N NH —Ph **XXXIVc**	[298—300]	29

a) See experimental section. b) Yield is isolated yield and that in parentheses is determined by NMR.

Reaction of N,N'-Bis(trimethylsilyl)-*o*-phenylenediamine

    Benzimidazoline derivatives (XXXIVb and XXXIVa) were obtained successfully by
the reaction of N,N'-bis(trimethylsilyl)-*o*-phenylenediamine (XXXI) with benzaldehyde
or cyclohexanone in excellent yields, whereas diethyl ketone did not react with XXXI
even at 180 °C.   When XXXI reacted with benzaldehyde and with dimethylformamide
at elevated temperature (120 °C), 2-phenylbenzimidazole (29 %) and benzimidazole
(97 %) were generated respectively by way of the successive β-elimination of hydrogen
and dimethylamine.
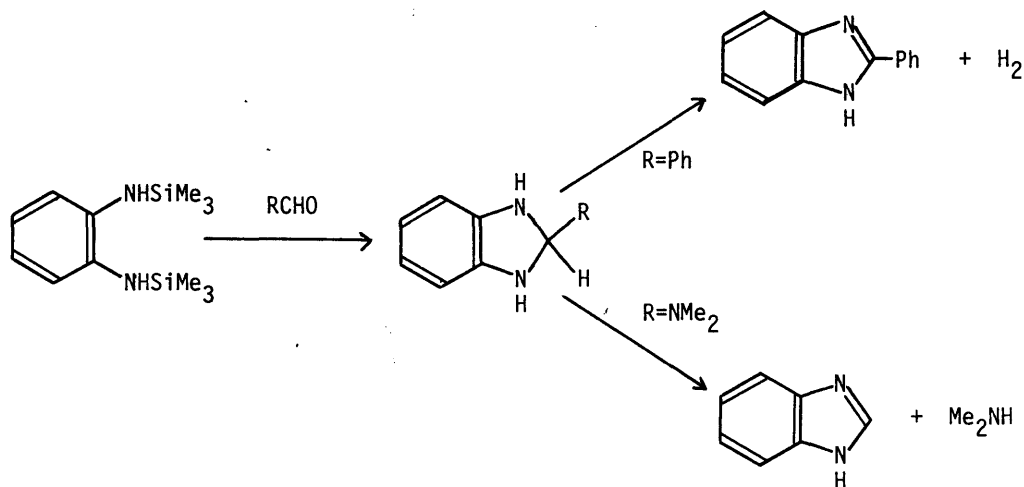
In fact, 2-phenylbenzimidazoline (XXXIVb), prepared from XXXI and benzaldehyde at
room temperature, caused smooth elimination reaction of hydrogen to aromatize to
benzimidazole at 120 °C.

4-4   Mechanism of the Formation of Imidazolidines

    Above-mentioned preparative reactions are reasonably explained by a β-addition-
ω-elimination reaction controlled by the affinity difference between labile Si-N and
stable Si-O bonds.   The primary step is the nucleophilic attack of either nitrogen
atom in N,N'-bis(trimethylsilyl)-1,2-diamines to the carbonyl carbon atom, followed
by the rapid migration of trimethylsilyl group to an oxyanion to give intermediate

insertion product [A]. The formation of extremely stable hexamethyldisiloxane is the driving force of the ω-elimination reaction to give imidazolidine [B] as cyclization product. The reaction between XXIX and benzaldehyde belongs to an exceptional case and facile β-elimination of trimethylsilanol is induced to give [C] which captures the second benzaldehyde at the another end to generate N,N'-dibenzylideneethylene-diamine [D].

[B]

ω-Elimination of
(Me$_3$Si)$_2$O

~SiMe$_3$

[A]

N$\overset{+}{\longrightarrow}O^-$

β-Elimination of
Me$_3$SiOH

[C]   [D]
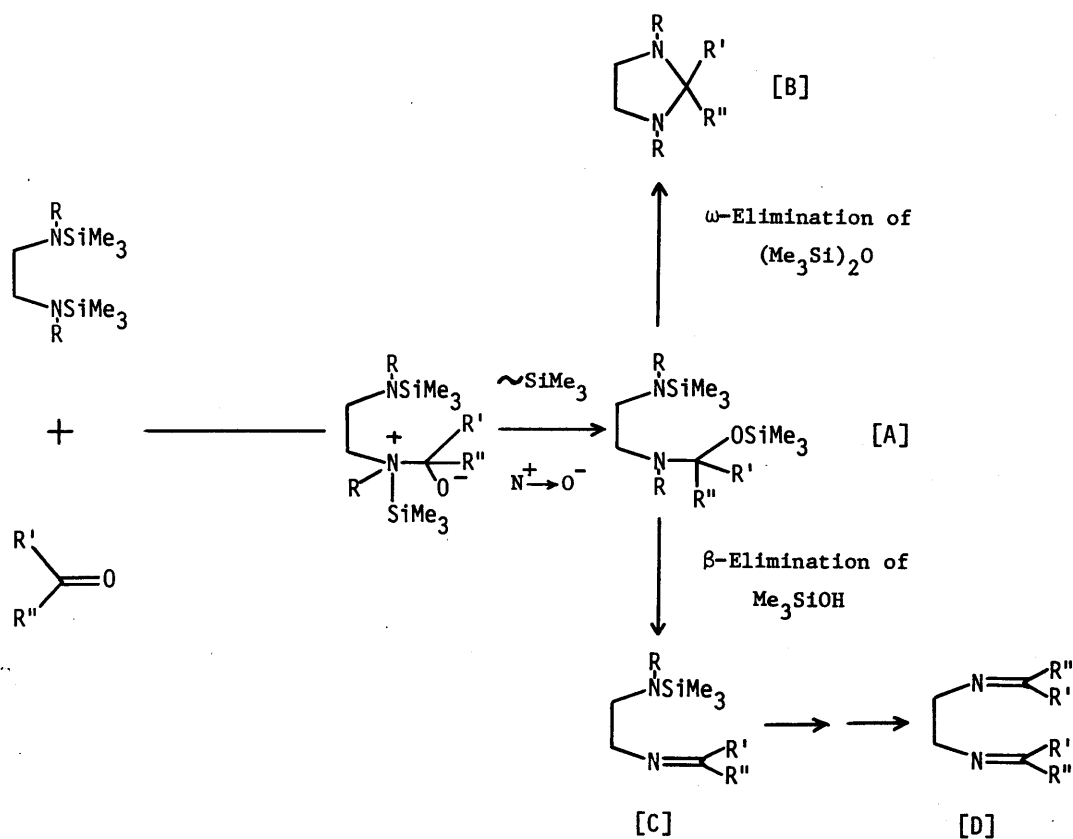
Experimental Section

General Procedure

All reactions were carried out under argon or nitrogen atmosphere. Melting points were determined in sealed capillaries filled with argon. Analyses were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany. IR spectra were recorded with a Japan Spectroscopic Co., Ltd. IR-S instrument. ^{1}H NMR spectra were measured with a Japan Electron Optics Lab. Co., Ltd. C-60HL instrument, with tetramethylsilane as an internal standard. UV spectra were determined with a Hitachi-124-spectrophotometer. Mass spectra were measured with Japan Electron Optics JMS-01SG or Hitachi RMS-4 instruments.

1   Stepwise Addition of Isocyanates and Isothiocyanates with N-Trimethylstannyl-(diphenylmethylene)amine

Starting Materials

N-Trimethylstannyl(diphenylmethylene)amine was prepared according to Chan and Rochow.[34]   Isocyanates and isothiocyanates were distilled before use

Reaction of N-*Trimethylstannyl(diphenylmethylene)amine with one Molar Equivalent of Benzoyl Isocyanate.*   A colorless solution was obtained by addition of benzoyl isocyanate (0.692 g, 4.71 mmol) to a solution of N-trimethylstannyl(diphenyl-methylene)amine (1.77 g, 5.15 mmol) in *ca.* 6 ml of benzene at 0 °C. The reaction was completed instantaneously. The 1/1 adduct (Ie) precipitated as white needles by the addition of *ca.* 4 ml of *n*-hexane was washed with *n*-hexane and dried *in vacuo* (2.19 g, 95 %). Mp 52.0-54.0 °C. Found: C, 58.78; H, 5.05 %. Calcd for $C_{24}H_{24}N_2O_2Sn$: C, 58.69; H, 4.92 %. IR (in C_6H_6): 1673 and 1626 cm^{-1}. ^{1}H NMR (in CDCl$_3$): τ9.68 (Me$_3$Sn, $J^{117/119}$Sn-C-H=55.0/58.0 Hz). Equimolar reactions of N-trimethylstannyl(diphenylmethylene)amine with other isocyanates or isothiocyanates were carried out under similar reaction conditions (at 0 °C under an atmosphere of nitrogen). The yields and results of elemental analyses of the 1/1 adducts are summarized in Tables 1 and 14, respectively.

Reaction of 1/1 Adduct (Ia) with Methyl Isocyanate. *Formation of 3,4-Dihydro-1,3-dimethyl-4,4-diphenyl-6-trimethylstannoxy-1,3,5-triazin-2(1H)-one* *(IIa)*:
To a solution of 0.81 g (2.02 mmol) of the 1/1 adduct of methyl isocyanate in 2 ml
of *n*-hexane was added 0.129 g (2.26 mmol) of methyl isocyanate at 0 °C under nitrogen.
White needles which separated out in a few minutes were washed with *n*-hexane and
recrystallized from a mixed solvent of *n*-hexane and benzene (1/1). This was iden-
tified as 1/2 adduct (IIa) (0.835 g, 77 %). Elemental analysis and ^{1}H NMR spectrum
identified the crystal as 3,4-dihydro-1,3-dimethyl-4,4-diphenyl-6-trimethylstannoxy-
1,3,5-triazin-2(1H)-one (IIa) containing 1 equivalent of benzene of crystallization.
Mp 149.0-152.0 °C. Found: C, 58.63; H, 5.80 %. Calcd for $C_{20}H_{25}N_3O_2Sn+C_6H_6$:
C, 58.24; H, 5.83 %. IR (in C_6H_6) 1688 and 1621 cm^{-1}. ^{1}H NMR (in $CDCl_3$): τ9.88
(Me_3Sn, $J^{117}/^{119}Sn$-C-H=54.0/56.0 Hz), 7.43 (Me-N), and 6.96 (Me-N). Preparation of
other 3,4-dihydro-4,4-diphenyl-1,3,5-triazin-2(1H)-ones; IIb (1-methyl-3-phenyl),
IIc (1-phenyl-3-methyl), and IId (1,3-diphenyl) was achieved similarly. Yields
and spectroscopic results are summarized in Table 2, and analytical data in Table 14.

Treatment of IIa with Ethanethiol. *Formation of Hexahydro-1,3-dimethyl-6,6-*
diphenyl-1,3,5-triazin-2,4-dione *(Va)*: Addition of ethanethiol to a benzene so-
lution of the 1/2 adduct (IIa) afforded the destannylated product (Va) as white
prisms. Mp 238.0-239.0 °C. IR (in KBr) 1723 and 1648 cm^{-1}. This compound was
identified as the triazindione (Va) which could be prepared independently by the
hydrolysis of the 1/2 adduct of N-trimethylsilyl(diphenylmehtylene)amine with methyl
isocyanate. Preparation of other *s*-triazindiones Vb, Vc, and Vd was achieved sim-
ilarly. Yields, mps, and IR data are given in Table 3, and elemental analysis data
in Table 14.

Reaction of 1/1 Adduct (Id) with One Equivalent of Phenyl Isocyanate.
To a solution of 0.910 g (2.65 mmol) of N-trimethylstannyl(diphenylmethylene)amine
in *ca.* 2 ml of benzene was added 0.350 g (2.59 mmol) of phenyl isothiocyanate at 0 °C
under the atmosphere of nitrogen. On addition of phenyl isothiocyanate the color of
the reaction mixture turned yellowish brown. The reaction mixture was left over-
night at room temperature. Its IR spectrum showed the formation of 1/1 adduct (Id).
A solution of 0.314 g (2.64 mmol) of phenyl isocyanate in *ca.* 4 ml of benzene was

then added at 0 °C.   The mixture was warmed up to room temperature and allowed to

stand for 15 hr.   White prisms of the 1/2 adduct (IVg) separated out quantitatively

were washed with benzene and recrystallized from a mixed solvent of n-hexane and

benzene (4/6).   Mp 164.5-166.0 °C.   Found: C, 60.05; H, 4.91 %.   Calcd for

$C_{30}H_{29}N_3OSSn$: C, 60.22; H, 4.89 %.   IR (in C_6H_6) 1698 and 1355 cm^{-1}. ^1H NMR

(in $CDCl_3$) τ9.72 (Me_3Sn, $J^{117/119}Sn-C-H=56.0/58.0$).

     Destannylation of IV.   Addition of ethanethiol to a benzene solution

of 1/2 adduct (IVg) gave the destannylated product (VIg) as white prisms.   Mp 252.0-

254.0 °C.   IR (in KBr) 1703 cm^{-1}. λ_{max}^{EtOH} 279 nm (logε=4.50).   Consecutive inser-

tion reactions of the isothiocyanate 1/1 adduct (Ib or Id) with another isocyanate or

isothiocyanate were performed under similar reaction conditions.   The yield and

the results of the elemental analysis are summarized in Tables 4, 5, and 14, respec-

tively.

Table 14.   Analytical data[a, b]

Compd.	C (%)	H (%)	N (%)	Calcd. for
Ia	54.08 (53.90)	5.63 (5.53)		$C_{18}H_{22}N_2OSn$
Ic	59.85 (59.65)	5.27 (5.22)		$C_{23}H_{24}N_2OSn$
Ie	58.78 (58.69)	5.05 (4.92)		$C_{24}H_{24}N_2O_2Sn$
IIa	58.63 (58.24)	5.80 (5.83)		$C_{20}H_{25}N_3O_2Sn+C_6H_6$
IVe	51.38 (51.18)	5.26 (5.27)		$C_{20}H_{25}N_3S_2Sn+(1/3)C_6H_6$
IVf	53.97 (53.82)	5.45 (5.50)		$C_{20}H_{25}N_3OSSn+(1/2)C_6H_6$
IVg	60.05 (60.22)	4.91 (4.89)		$C_{30}H_{29}N_3OSSn$
Vb	73.40 (73.93)	5.47 (5.36)	11.60 (11.76)	$C_{22}H_{19}N_3O_2$
Vc	74.09 (73.93)	5.50 (5.36)	11.60 (11.76)	$C_{22}H_{19}N_3O_2$
VIe	65.34 (65.54)	5.59 (5.50)	11.34 (11.46)	$C_{17}H_{17}N_3S_2+C_6H_6$
VIf	68.58 (68.54)	5.83 (5.75)	12.25 (11.99)	$C_{17}H_{17}N_3OS+(1/2)C_6H_6$
VIg	76.74 (77.16)	5.59 (5.30)	7.78 (8.18)	$C_{27}H_{21}N_3OS+C_6H_6$
VIh	67.07 (67.83)	5.00 (4.92)	10.56 (10.79)	$C_{22}H_{19}N_3S_2$

a) Calculated values in parentheses.   b) The demetallated products, Va and Vd,

were identified with the authentic samples.

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2   The Reaction of N-Trimethylsilyl- and -stannyl(diphenylmethylene)amine
     with Diketene

   Reaction of N-Trimethylstannyl(diphenylmethylene)amine with Diketene.
To a solution of 0.870 g (2.53 mmol) of N-trimethylstannyl(diphenylmethylene)amine
in *ca.* 3 ml of benzene was added 0.268 g (3.19 mmol) of diketene at 0 °C under
nitrogen.   The reaction proceeded exothermically.   The adduct was precipitated
as pale yellow crystals by the addition of *ca.* 4 ml of *n*-hexane after the completion
of the reaction.   This was identified as 1/1 adduct (XVII), after the purification
by reprecipitation from the mixed solvent of benzene and *n*-hexane (1/2) (1.044 g,
96 %).   Mp 130.0-133.0 °C.   Found: C, 56.29; H, 5.54 %.   Calcd for $C_{20}H_{23}NO_2Sn$:
C, 56.11; H, 5.41 %.   IR (in $CHCl_3$) 1673 and 1574 cm^{-1}. ^1H NMR (in $CDCl_3$) τ9.57
(Me_3Sn, $J^{117/119}Sn$-C-H=65.0/68.0 Hz), 7.05 (2H, m), 5.71 (1H, d, J=1.5 Hz), and
4.43 (1H, m).

   Destannylation of XVII.   Addition of ethanethiol (2 ml) to a benzene
solution (15 ml) of the 1/1 adduct (XVII) (0.900 g, 2.10 mmol) gave the destanny-
lated product (XXI) (0.513 g, 1.94 mmol) as white prisms in 93 % yield.   Mp 179.5-
181.5 °C.   Found: C, 77.17; H, 5.72; N, 5.20 %.   Calcd for $C_{17}H_{15}NO_2$: C, 76.96;
H, 5.69; N,5.27 %.   IR (in KBr) 3120, 1728, and 1661 cm^{-1}. ^1H NMR (in $CDCl_3$)
τ6.95 (2H, s), 6.68 (2H, s), 2.72 (10H), and 2.32 (NH, br. s).

   Reaction of N-Trimethylsilyl(diphenylmethylene)amine with Diketene.
The mixture of 1.916 g (7.58 mmol) of N-trimethylsilyl(diphenylmethylene)amine
and 0.819 g (9.75 mmol) of diketene was heated at 60 °C for 40 hr in a sealed tube.
The isomer ratio of XXII:XXIV:XXV was decided by the intensities of proton signals
of trimethylsilyl group in ^1H NMR spectrum of the reaction mixture.   The reaction
mixture was purified by vacuum distillation (bp 108.0-116.0 °C/0.02 mmHg) (1.85 g,
73 %).   Found: C, 71.22; H, 6.68 %.   Calcd for $C_{20}H_{23}NO_2Si$: C, 71.18; H, 6.78 %.
In the ^1H NMR spectrum (in CCl_4), the assignment of proton signals are as follows.
XXII: τ9.97 (Me_3Si, 9H, s), 6.91 (2H, s), 6.10 (1H, d, J=1.5 Hz), and 5.99 (1H, d,
J=1.5 Hz).   XXIV: τ9.85 (Me_3Si, 9H, s), 7.90 (3H, s), and 4.97 (1H, s).   XXV:
τ9.63 (Me_3Si, 9H, s), 8.11 (3H, d, J=0.8 Hz), and 5.04 (1H, q, J=0.8 Hz).
A mixture of XXII, XXIV, and XXV (2.55 g, 7.57 mmol) was desilylated by the treat-
ment with methanol (5 ml).   The desilylated product was isolated in 72 % yield
(1.45 g) and was identified to XVI by the comparison with the authentic sample.[14]

3   Modified Synthesis of Imidazolidines with N,N'-Bis(trimethylsilyl)-1,2-

diamines

N,N'-Bis(trimethylsilyl)-1,2-diamines were prepared according to Birkofer,
Kühlthau, and Ritter.[35)]

Synthesis of Imidazolidines.   To N,N'-bis(trimethylsilyl)-1,2-di-
amine (3.5—13.5 mmol) were added dropwise equimolar amounts of carbonyl compounds
under an atmosphere of nitrogen at 0 °C.   In *Method* A the reaction mixture was
warmed to room temperature.   In *Method* B the mixture was heated in a sealed tube.
In both methods, formed hexamethyldisiloxane was removed from the reaction mixture
to leave imidazolidine under reduced pressure (*ca.* 30 mmHg).   For the purpose of
elemental analysis, imidazolidines were distilled under reduced pressure.   The
elemental analyses, ^{1}H NMR spectra, IR spectra and other properties provided an
adequate support for the structure assigned.

Reaction of N,N'-*Bis(trimethylsilyl)ethylene diamine with Benzaldehyde.*
Synthesis of N,N'-*Dibenzylideneethylenediamine (XXXIId).*   To N,N'-bis(trimethyl-
silyl)ethylenediamine (2.75 g, 13.5 mmol) was added benzaldehyde (1.36 g, 12.8 mmol)
dropwise under nitrogen at -78 °C.   When the reaction mixture was warmed gradually
to room temperature, exothermic reaction occurred to give transparent liquid separated
into two layers.   The reaction mixture was then distilled under reduced pressure
(152 °C/0.8 mmHg) to yield colorless needles (1.48 g, 98 % yield based on benzaldehyde
used).   Mp 52.0-54.0 °C.   Found: C, 81.54; H, 7.06; N, 11.40 %.   Calcd for
$C_{16}H_{16}N_2$: C, 81.34; H, 6.83; N, 11.85 %.   IR (in KBr) 1640 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR
(in CCl$_4$) τ6.16 (4H, s), 2.25 (10H), and 1.80 (2H, s).

Conversion of 2-*Phenylbenzimidazoline (XXXIVb) to* 2-*Phenylbenzimidazole (XXXIVc).*
By the heating of a benzene solution of 2-phenylbenzimidazoline (1.00 g,5.11 mmol)
in sealed tube at 120 °C for 12 hr, colorless precipitates sparingly soluble in
benzene separated out.   Upon recrystallization from acetone 2-phenylbenzimidazole
precipitated as colorless prisms (0.291 g) in a 29 % yield.   The mp and spectroscopic
data of the product were in good agreement with those of the authentic sample.
Analytical and spectroscopic results are shown in Table 15.

Table 15. Analytical and spectroscopic results of products

	Analysis (Calcd)	^{1}H NMR (τ)	IR (cm^{-1})
XXXIIa	C 68.91 (68.54) H 11.71 (11.50) N 19.38 (19.98)	7.18 (4H, s)[a] 8.55 (10H, m) 8.82 (2H, s)	3250[a] (ν_{NH})
XXXIIb	C 65.30 (65.59) H 12.41 (12.58) N 22.29 (21.85)	7.20 (4H, s)[a] 8.40-9.34 (12H, over- lapping of NH, CH$_2$, and CH$_3$)	3260[a] (ν_{NH})
XXXIIc	C 52.05 (51.41) H 9.05 (8.62) N 38.89 (39.96)	3.01 (1H, m)[b] 5.89 (1H, m) 6.49 (4H, m)	3420[c] (ν_{NH})
XXXIId	C 81.54 (81.34) H 7.06 (6.83) N 11.40 (11.85)	1.80 (2H, s)[a] 2.55 (10H, m) 6.16 (4H, s)	1640[a] ($\nu_{C=N}$)
XXXIIIa	C 72.04 (71.36) H 11.98 (11.91) N 16.05 (16.64)	7.35 (4H, s)[a] 7.89 (6H, s) 8.60 (10H, m)	
XXXIIIb	C 69.47 (69.16) H 13.10 (12.90) N 17.43 (17.92)	7.27 (4H, s)[a] 7.75 (6H, s) 8.79 (4H, q, J=7 Hz) 9.33 (6H, t, J=7 Hz)	
XXXIIIc	C 75.27 (74.96) H 9.30 (9.15) N 15.43 (15.89)	2.75 (5H, m)[a] 6.89 (1H, s) 7.20 (4H, AA'BB') 7.97 (6H, s)	
XXXIVa	C 76.94 (76.53) H 8.57 (8.57) N 14.48 (14.88)	3.55 (4H, m)[a] 6.54 (2H, s) 8.38 (10H, m)	3320, 3230[d] (ν_{NH})
XXXIVb	C 79.31 (79.56) H 5.89 (6.16) N 14.00 (14.27)	1.60 (1H, s)[a] 2.42 (5H, m) 3.27 (4H, m) 6.00 (2H, s)	3470, 3370[d] (ν_{NH})
XXXIVc	C 80.25 (80.39) H 5.08 (5.19) N 14.31 (14.42)	sparingly soluble	mass m/e 194 (M$^+$)
XXXIVd	C 70.60 (71.19) H 5.28 (5.12) N 23.92 (23.72)	1.85 (1H, s)[e] 2.63 (4H, m)	mass m/e 118 (M$^+$)

a) in CCl$_4$, b) in CDCl$_3$, c) in CHCl$_3$, d) in KBr, e) in (CD$_3$)$_2$CO

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REACTION OF TRANSITION METAL COMPLEXES

WITH *N*-HALOAMINE AND -AMIDES

In this chapter, the interaction of the transition metal complexes with the Nitrogen-Halogen bonds is discussed.   In particular, the transition metal-assisted generation of nitrene and its stabilization on transition metals are focussed.

Despite of the large volume of information available on nitrenes,[1] studies pertaining to the generation and the stabilization of nitrenes by transition metal complexes have only appeared recently.   Dekker and Knox[2] reported that diiron nonacarbonyl decomposed phenyl azide at room temperature to give the low yield of the nitrene product, azobenzene, as well as interesting tricarbonyl complexes, possibly derived from nitrene intermediates.   The main product was the complex I, which decomposed spontaneously in solution to the urea complex II.
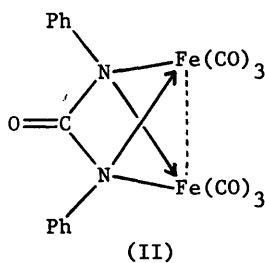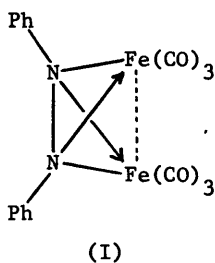

A similar complex was obtained from 2-azidobiphenyl, together with the urea and nitrene-derived products.[3]   The decomposition of excess methane-, benzene-, and *p*-toluene-sulfonyl azide with diiron nonacarbonyl at room temperature or iron pentacarbonyl at 60–65 °C gave a complex, $[Fe(RSO_2N)_2CO \cdot H_2O]_n$, involving the coordination of a sulfonyl oxygen to the metal.[4]   Basolo and Pearson[5] postulated a parent nitrene complex of ruthenium as an unstable intermediate in the conversion of $[(H_3N)_5RuN_3]^{2+}$ into $[(H_3N)_5RuN_2Ru(NH_3)_5]^{4+}$ by acid, while the reaction of organic azide with $(Ph_3P)_2Ir(CO)Cl$ afforded the dinitrogen complex, $(Ph_3P)_2Ir(N_2)Cl$, rather than "nitrene complex".[6]   Similarly, it was shown by the kinetic study that the acid decomposition of $[(H_3N)_5IrN_3]^{2+}$ salt occurs by a mechanism involving an intermediate complex of the coordinated parent nitrene, $[(H_3N)_5IrNH]^{3+}$.[7]   The complexation of fluoroalkyl-nitrene are known in several Group VIII transition metals.   The particular iridium
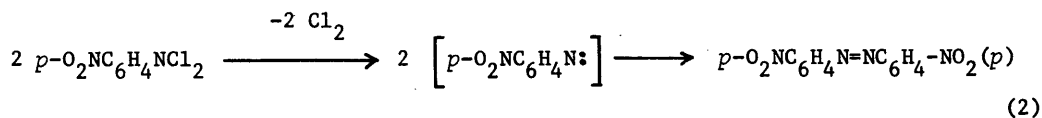
complex (III) is an example reported by Stone *et al..*[8]

$$(Ph_3P)_2Ir(N_2)Cl \xrightarrow{\text{2H-hexafluoropropyl azide}} (Ph_3P)_2Ir(NCF_2CHFCF_3)Cl$$

(III)
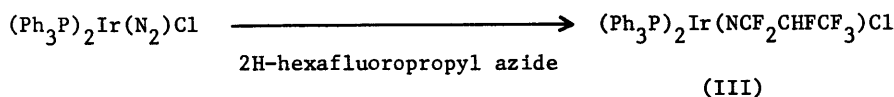
Simple alkylnitrenes coordinate to some rhenium complexes such as IV,[9] of which structure was determined by X-ray.[10]

$$[(R_3P)_2ReOCl_3] \xrightarrow[\text{(PR}_3\text{=PEtPh}_2)]{\text{MeNHNHMe·2HCl}}$$

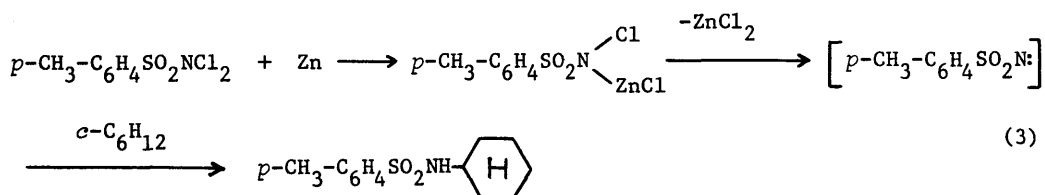∠ReNMe=173.4°

Re—N=1.685Å

(IV)
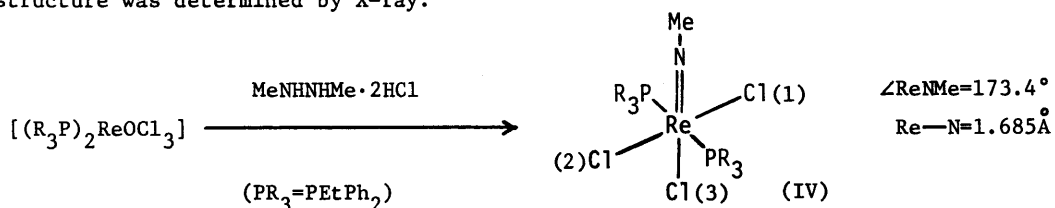
Symmetrical azo compounds are known to be prepared by coupling two moles of N,N-dichloramine *via* nitrene intermediate. For instance, symmetrical azo compound with the general formula NCRR'CN=NCR'RCN, in which R and R' are short alkyl or cyclo-alkyl groups, have been prepared by coupling two moles of N,N-dichloramine (eq 1).[11]

(1)
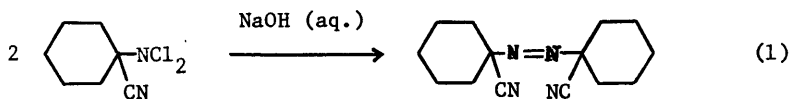
A nitrene intermediate was suggested in order to rationalize the formation of 4,4'-dinitroazobenzene from thermal decomposition of N,N-dichloro-*p*-nitroaniline (eq 2).[12]

$$2\ p\text{-}O_2NC_6H_4NCl_2 \xrightarrow{-2\ Cl_2} 2\ \left[p\text{-}O_2NC_6H_4N\colon\right] \longrightarrow p\text{-}O_2NC_6H_4N=NC_6H_4\text{-}NO_2(p)$$

(2)

Breslow and Sloan   reported that heating a solution of Dichloramine-T in cyclo-hexane with zinc yielded *p*-toluenesulfonylnitrene, which inserted into a C-H bond of the solvent.(eq 3).[13]

$$p\text{-}CH_3\text{-}C_6H_4SO_2NCl_2 \quad + \quad Zn \quad \longrightarrow \quad p\text{-}CH_3\text{-}C_6H_4SO_2N\begin{array}{c}{\scriptstyle Cl}\\{\scriptstyle ZnCl}\end{array} \quad \xrightarrow{-ZnCl_2} \quad \left[p\text{-}CH_3\text{-}C_6H_4SO_2\ddot{N}\!: \right]$$

$$\xrightarrow{c\text{-}C_6H_{12}} \quad p\text{-}CH_3\text{-}C_6H_4SO_2NH\text{-}\langle H \rangle \tag{3}$$
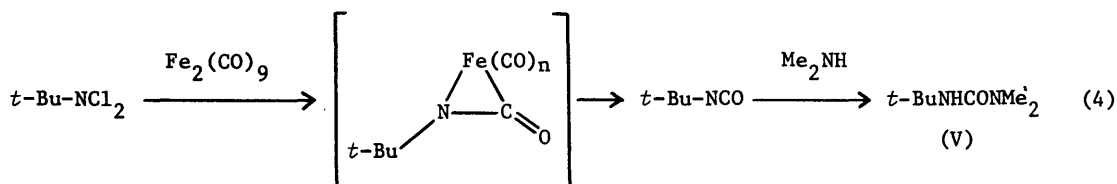
N,N-Dichloramine or -amide is, therefore, expected to generate nitrene in the reaction with low valent transition metal complexes which oxidatively form corresponding metal dichlorides, L_nMCl_2, in a similar manner to *gem*-dihaloalkanes for which some studies were achieved.[14, 15]

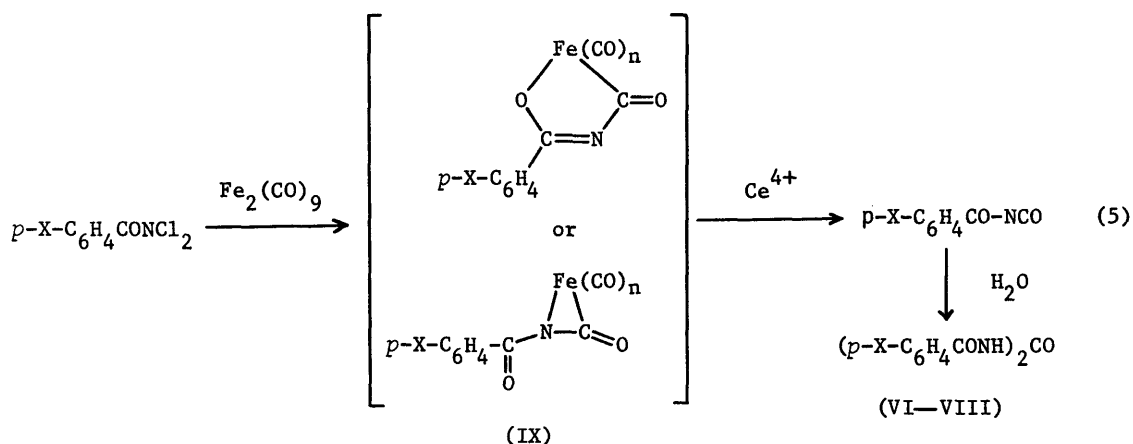1   Reactions of Iron Carbonyl Complexes with N,N-Dichloramine or -amides

1-1   Reactions of N,N-Dichloramine or -amides with Diiron Enneacarbonyl

In the presence of equimolar amounts of olefinic or acetylenic acceptor (cyclo-hexene, norbornadiene, benzene, dimethyl maleate, dimethyl acetylenedicarboxylate, diphenylacetylene, *etc.*) a dilute solution of N,N-dichloro-*t*-butylamine (0.170 g, 1.20 mmol, in 2 ml of benzene) was added to the diiron enneacarbonyl (0.408 g, 1.12 mmol, suspended in 8 ml of benzene) at 0 °C under an atmosphere of argon.   A detailed analysis of reaction mixture indicates no sign of nitrene adduct formation with the above-mentioned acceptors at all.   Infrared spectrum of the reaction mixture showed a sharp and strong absorption band due to isocyanate skeleton at 2240 cm^{-1}. Addition of dimethylamine to this mixture gave N,N-dimethyl-N'-*t*-butylurea (V) in 31 % yield.   This information suggests that the product is *t*-butyl isocyanate, which is given by the carbonylation of first generated *t*-butylnitrene or -nitrenoid as shown in Eq. 4.

$$t\text{-}Bu\text{-}NCl_2 \quad \xrightarrow{Fe_2(CO)_9} \quad \left[\begin{array}{c} \overset{\displaystyle Fe(CO)_n}{\diagup \quad \diagdown} \\ \underset{\displaystyle t\text{-}Bu}{N}\!\!-\!\!\underset{\displaystyle}{C}\!\!=\!\!O \end{array}\right] \longrightarrow t\text{-}Bu\text{-}NCO \quad \xrightarrow{Me_2NH} \quad t\text{-}BuNHCONMe_2 \quad \tag{4}$$
$$\text{(V)}$$

In spite of the presence of acceptor molecule, no nitrene adduct was also ob-tained by the reaction of diiron enneacarbonyl with N,N-dichloro-*p*-toluamide, N,N-dichloro-*p*-chlorobenzamide, or N,N-dichloro-*p*-nitrobenzamide under similar conditions. However, diaroylureas (VI-VIII) were obtained in good yields as sole isolated products, when the reactions of diiron enneacarbonyl with those dichloramides in benzene were

carried out at room temperature, followed by the treatment with ceric ammonium nitrate in 10 % aqueous methanol solution. Mps and spectroscopic data of the ureas (VI-VIII) fitted in those of authentic samples derived from hydrolyses of corresponding isocyanates. Similar to the former case, this urea-formation is explained by the intermediacy of corresponding carbonylnitrenes or -nitrenoids followed by carbonylation as shown in Eq. 5.
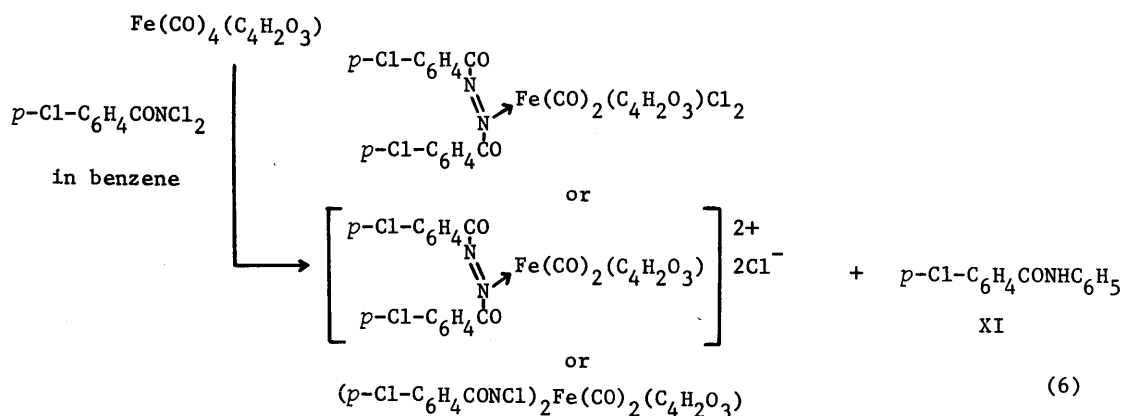
$$
p\text{-}X\text{-}C_6H_4CONCl_2 \xrightarrow{Fe_2(CO)_9}
\left[
\begin{array}{c}
\underset{\displaystyle p\text{-}X\text{-}C_6H_4}{\overset{\displaystyle Fe(CO)_n}{\underset{}{}}} \\
\text{(IX)}
\end{array}
\right]
\xrightarrow{Ce^{4+}}
p\text{-}X\text{-}C_6H_4CO\text{-}NCO \qquad (5)
$$

$$\downarrow H_2O$$

$$(p\text{-}X\text{-}C_6H_4CONH)_2CO$$

$$\text{(VI—VIII)}$$

At first step, nitrene or nitrenoid is formed by metal-assisted dehalogenation of N,N-dichloramide followed by complexation with iron to give IX.[16] Aroyl isocyanates liberate by oxidative demetallation with Ce^{4+}, and rapidly react with water to yield diaroylureas. Whole results on the reaction of N,N-dichloramine or -amides with diiron enneacarbonyl are summarized in Table 1.

Table 1. Reaction of N,N-Dichloramine and -amides with Diiron Enneacarbonyl in Benzene

Reactant	Product	Yield (isolated) (%)
$t\text{-}Bu\text{-}NCl_2$	$t\text{-}BuNHCONMe_2$ (V)	31
$p\text{-}CH_3\text{-}C_6H_4CO\text{-}NCl_2$	$(p\text{-}CH_3\text{-}C_6H_4CONH)_2CO$ (VI)	94
$p\text{-}Cl\text{-}C_6H_4CO\text{-}NCl_2$	$(p\text{-}Cl\text{-}C_6H_4CONH)_2CO$ (VII)	100
$p\text{-}NO_2\text{-}C_6H_4CO\text{-}NCl_2$	$(p\text{-}NO_2\text{-}C_6H_4CONH)_2CO$ (VIII)	50

1-2   Reaction of N,N-Dichloro-*p*-chlorobenzamide with Maleic Anhydride

       Iron Tetracarbonyl

    The reaction of N,N-dichloro-*p*-chlorobenzamide (0.137 g, 0.612 mmol) with maleic
anhydride iron tetracarbonyl (0.159 g, 0.598 mmol) proceeded in benzene (20 ml) at
room temperature with the evolution of about two moles of carbon monoxide.   By column
chromatographic separation on silica gel with acetone as solvent, white powder of dia-
magnetic complex (X) (decomp. 124.0-126.0 °C, 80 % yield) and N-phenyl-*p*-chlorobenz-
amide (XI) (mp 197.0-198.0 °C, 14 % yield) were obtained.   The latter compound indi-
cates the nitrene generation, because its formation is explained in terms of the
insertion of an intermediate *p*-chlorobenzoylnitrene into C-H bond of solvent benzene.
The yield of X increased to 95 % when *n*-hexane was used as the reaction solvent.
The elevation of the yield of X suggests that the amide formation and the complexation
are competitive processes *via* common reaction intermediate, *i. e.* nitrene intermediate.
Elemental analysis of complex X indicated the composition $C_{20}H_{10}N_2O_7Cl_4Fe$, which was
consistent with the formula of $(p\text{-}Cl\text{-}C_6H_4CON)_2Fe(CO)_2$(maleic anhydride)$Cl_2$.   In solid
state infrared spectrum, X showed five characteristic absorption bands at 2050, 2020,
1820, 1746, and 1655 cm^{-1}.   First two bands are attributed to the terminal $\nu_{c\equiv o}$ bond-
ing to iron, and carbonyl stretching vibrations of coordinating maleic anhydride appear
at 1820 and 1746 cm^{-1}. The last one (1655 cm^{-1}) is reasonably assigned to amide
carbonyl.   The ^{1}H NMR spectrum of X in $CDCl_3$ showed sharp singlet of olefinic protons
(2H) of maleic anhydride at τ6.07 and the phenyl ring protons (8H) with AA'BB' coupling
pattern centered at τ2.50.   Surprisingly, complex X was quite stable toward boiling
methanol and oxidation with ceric ammonium nitrate.   This indicates that X is in a
higher oxidation state.   As shown in Eq. 6, three probable structures of X might be
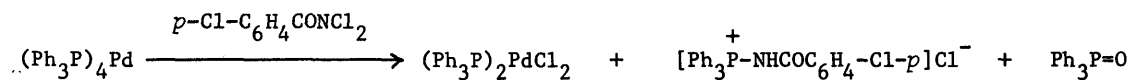formulated.

$Fe(CO)_4(C_4H_2O_3)$

$p\text{-}Cl\text{-}C_6H_4CONCl_2$

   in benzene

$$
\begin{array}{c}
p\text{-}Cl\text{-}C_6H_4\overset{O}{\underset{N}{C}} \\
\parallel \\
\nearrow Fe(CO)_2(C_4H_2O_3)Cl_2 \\
p\text{-}Cl\text{-}C_6H_4\overset{O}{\underset{N}{C}}
\end{array}
$$

                           or

$$
\left[\begin{array}{c}
p\text{-}Cl\text{-}C_6H_4\overset{O}{\underset{N}{C}} \\
\parallel \\
\nearrow Fe(CO)_2(C_4H_2O_3) \\
p\text{-}Cl\text{-}C_6H_4\overset{O}{\underset{N}{C}}
\end{array}\right]^{2+} 2Cl^- \quad + \quad p\text{-}Cl\text{-}C_6H_4CONHC_6H_5
$$

                                                    XI

                           or

                $(p\text{-}Cl\text{-}C_6H_4CONCl)_2Fe(CO)_2(C_4H_2O_3)$ (6)

                           X

2-1   Reaction of Tetrakis(triphenylphosphine)palladium with N,N-Dichloramine
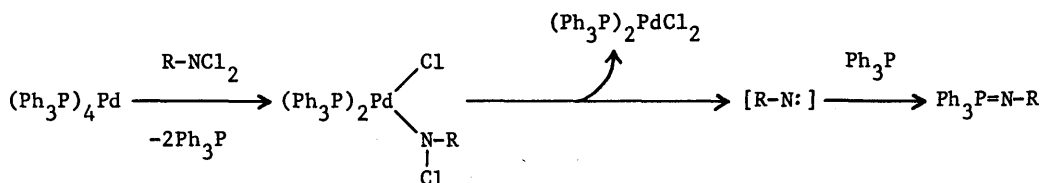   and -amides

     The generation of triphenylphosphinimines from triphenylphosphine and nitrenes
is well recognized as a typical reaction.[17, 18]   The reaction of tetrakis(triphenyl-
phosphine)palladium with N,N-dichloramide was, therefore, carried out to confirm the
formation of the nitrene intermediate.   Treatment of $(Ph_3P)_4Pd$ with equimolar amounts
of N,N-dichlorobenzenesulfonamide in benzene at room temperature yielded dichlorobis-
(triphenylphosphine)palladium together with (N-benzenesulfonyl)triphenylphosphinimine
in quantitative and 20 % yields, respectively.

$$(Ph_3P)_4Pd \xrightarrow{\quad C_6H_5SO_2NCl_2 \quad} (Ph_3P)_2PdCl_2 \quad + \quad Ph_3P=NSO_2C_6H_5$$
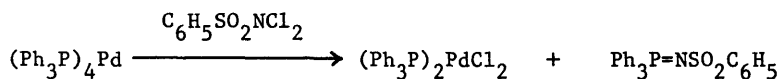
Similarly, N,N-dichloro-p-chlorobenzamide reacted with tetrakis(triphenylphosphine)-
palladium to give dichlorobis(triphenylphosphine)palladium and p-chlorobenzoylamino-
triphenylphosphonium chloride, which was the quaternary phosphonium salt derived from
the corresponding phosphinimine with hydrogen chloride, in 89 and 57 % yields, respec-
tively.

$$(Ph_3P)_4Pd \xrightarrow{\quad p\text{-}Cl\text{-}C_6H_4CONCl_2 \quad} (Ph_3P)_2PdCl_2 \quad + \quad [Ph_3\overset{+}{P}\text{-}NHCOC_6H_4\text{-}Cl\text{-}p]Cl^- \quad + \quad Ph_3P=O$$

The formation of the phosphinimines suggested the generation of the nitrene inter-
mediates.   A plausible mechanism of the formation of phosphinimine from dichloramide
and tetrakis(triphenylphosphine)palladium was depicted as follows:

$$(Ph_3P)_4Pd \xrightarrow[\text{-2}Ph_3P]{\quad R\text{-}NCl_2 \quad} (Ph_3P)_2Pd \overset{\displaystyle Cl}{\underset{\displaystyle \underset{\displaystyle Cl}{\overset{|}{N\text{-}R}}}{\big\langle}} \xrightarrow{\quad (Ph_3P)_2PdCl_2 \quad} [R\text{-}N\!:\,] \xrightarrow{\quad Ph_3P \quad} Ph_3P=N\text{-}R$$

The first step of the reaction involved the oxidative addition of N,N-dichloramides to a zerovalent palladium to liberate two molecules of triphenylphosphine with the simultaneous formation of palladium dichloride and a nitrene intermediate, which then reacted with liberated triphenylphosphine to give corresponding phosphinimines.

2-2   Reactions of Palladiacyclopentadiene Complexes with N,N-Dichloramine
   and -amides

2-2-1   Reaction of Bipyridinepalladiacyclopentadiene with N,N-Dichloramine
          and -amides

An early attempt[19] to obtain a pyrrole derivative from ferracyclopentadiene complex and N,N-dichloro-p-toluenesulfonamide (dichloramine T) was not fruitful, however, some products indicated a possibility of a nitrene intermediate.
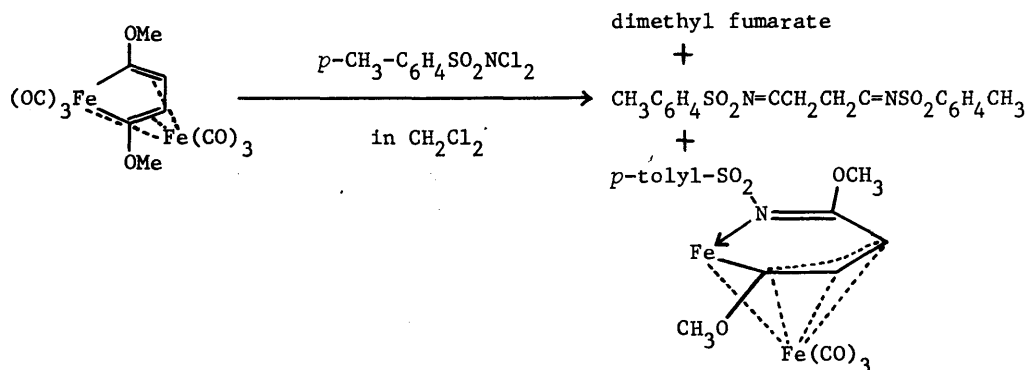
In order to examine the possibility of a palladium-assisted nitrene generation and of its coupling with a σ-diene ligand to yield pyrroles, bipyridinetetrakis(meth-oxycarbonyl)palladiacyclopentadiene[20] (XII) was treated with four N,N-dichloramine and -amides as a model system.

An equimolar mixture of palladiacyclopentadiene complex (XII) and N,N-dichloro-t-butylamine or N,N-dichloro-p-tolu-amide in benzene was kept at room temperature, under an atmosphere of nitrogen.   After 10 hr stirring σ-4-chloro-1,2,3,4-tetrakis(methoxycarbonyl)buta-1,3-dienylpalladium complex (XIII) precipitated, which was recrystallized from the mixed solvent of acetone and ethyl ether (6/5) as yellow crys-tals in a 64 % yield.


(R=COOCH$_3$)

(XII)
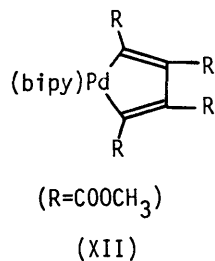
The reaction of XII with N,N-dichlorobenzenesulfonamide and that with N,N-dichloro-p-chlorobenzamide under similar conditions gave XIV and XV in 84 and 57 % yields, respectively. In both cases, any nitrene adduct with the ligand, $C_4(COOCH_3)_4$, was not isolated. The mp, ir, and nmr data of XIII, XIV, and XV are summarized in Table 2.

Table 2. The mp, ir, and nmr data of XIII, XIV, and XV.

Complex	Yield (%)	mp (°C)	$\nu_{C=O}$	$\nu_{Pd-Cl}(cm^{-1})$	$\tau COOCH_3$
XIII	64[a)] 73[b)]	168.0–170.0	1722	323	6.57 (3H), 6.36 (6H) 6.30 (3H)
XIV	84	185.0–186.0	1722		6.92 (3H), 6.29 (3H) 6.20 (3H), 6.16 (3H)
XV	57	115.5–117.5	1737 1720 1689		6.36 (3H), 6.34 (3H) 6.30 (3H), 6.18 (3H)

a), b); N,N-Dichloro-t-butylamine and N,N-dichloro-p-toluamide were used as reagents, respectively.

Three resonance peaks at τ6.57 (3H), 6.36 (6H), and 6.30 (3H) due to the methoxy-carbonyl group appeared in the ^{1}H NMR spectrum of XIII in CD_3COCD_3, whereas the original palladiacyclopentadiene complex (XII) showed only one resonance peak at τ6.25 in $CDCl_3$ or two peaks at τ6.34 and τ6.32 in CD_2Cl_2.[20] Similarly XIV and XV showed four resonance peaks in the methoxycarbonyl region. This NMR result strongly suggests that XIII, XIV, and XV have the linear (σ-1,3-butadienyl) structures by the cleavage of one Pd-C bond of the five-membered metallocycles. In ir spectra, XIII had an absorption band of the Pd-Cl stretching vibration at 323 cm^{-1}, while no absorption appeared around this region in those of XIV and XV. In addition, XV showed three absorptions at 1737, 1720, and 1689 cm^{-1} due to carbonyl stretching vibrations. The absorption at 1737 cm^{-1} could be assigned to the carbonyl stretching frequency of p-Cl-$C_6H_4CONCl_2$ ligand. The absorptions at 1720 and 1689 cm^{-1} were ascribed to ester carbonyl groups and carbonyl group of monochloramide coordinated in σ-manner, respectively. Proposed structure of the products; XIII, XIV, and XV, are shown below.


46
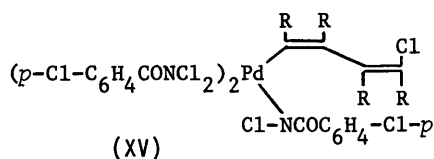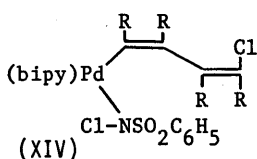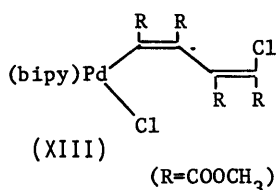
Maitlis et $al.$[21] reported on the cleavage of one Pd-C bond of the palladiacyclo-
pentadiene with HX.   Their results are shown in following scheme, in which the halide
anion selectively attacked the palladium atom.
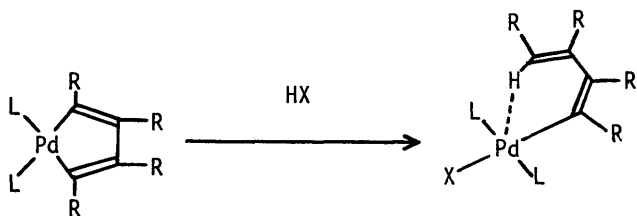
This is contrary to the ring-opening process with the N-Cl bonds, namely, the present
products, XIV and XV involves the formation of the Pd-N bond, and the chlorine atom
attacks diene skeleton.   It is consequently concluded that the ring-opening process
by the cleavage of the Pd-C bond in palladiacyclopentadiene moiety did not proceed
by an ionic mechanism, but by concerted or radical mechanism.   The possible reaction
sequence to give XIII, XIV, and XV is depicted in Scheme 1.

Scheme 1
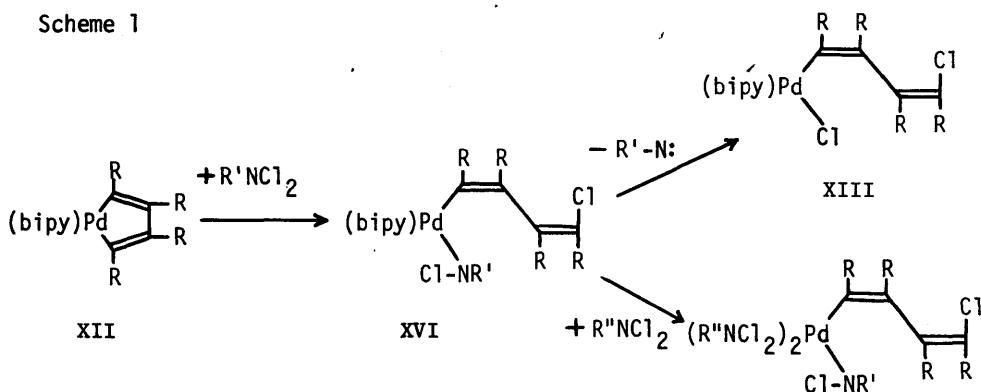
The formation of XVI is explained in terms of the Pd-Cl bond cleavage of XII by the
attack of the N-Cl bond.   The stability of the Pd-N bond in XVI mainly depends on
the electronic character of the substituents on the nitrogen atom.   It is indicated
that the delocalization of lone pair electrons by electron-withdrawing carbonyl or
sulfonyl group on the nitrogen atom increased the stability of the Pd-N σ-bond in
XIV and XV.

The stabilization of the Pd-N bond is insufficient, when the substituent on the
nitrogen atom is *t*-butyl or *p*-tolyl.   Consequently, XIII is formed with the elim-
ination of nitrene from XVI.

2-2-2   Reaction of Coordinatively Unsaturated Palladiacyclopentadiene with
          N,N-Dichloro-*t*-butylamine

     No nitrene adducts were obtained in the reaction of N,N-dichloramine or -amides
with (bipy)Pd[C_4(COOCH$_3$)].   N,N-Dichloramine or -amide skeletons must split up into
three fragments, that is, nitrene and two chlorine atoms to generate nitrene.
Coodinatively unsaturated and low valent complexes are, therefore, required to
obtain nitrene complexes from N,N-dichloramine.

     2,3,4,5-Tetrakis(methoxycarbonyl)palladiacyclopentadiene (XVII), formed by the
oxidative addition of two equivalents dimethyl acetylenedicarboxylate to tris(di-
benzylideneacetone)dipalladium,[20] is regarded as a coordinatively unsaturated complex.
There are two Pd-C σ-bonds and two weak intermolecular coordinate bonds in XVII.
The latter are easily displaced by entering ligands.

     N,N-Dichloro-*t*-butylamine (0.847 mmol) was added dropwise to the suspension of
XVII (0.398 mmol) in 5 ml of dry benzene, and the reaction mixture immediately
turned to orange.   After 10 hr stirring at room temperature under nitrogen, yellow
solid was precipitated by the addition of ethyl ether.   Recrystallization from the
mixed solvent (benzene-ethyl ether) yielded yellow prisms (XVIII) (decomp. 142.0-
143.0 °C) in 57 % yield.   The analysis of this complex is consistent with the formula,
$C_{15}H_{20}O_8Cl_2Pd$.   Found: C, 36.88; H, 4.29; N, 0.00; Cl, 14.57 %.   Calcd: C, 35.63;
H, 3.99; N, 0.00; Cl, 14.02 %.   There are four resonance peaks at τ8.81 (3H, d, J=6
Hz), 8.31 (3H, d, J=6 Hz), 7.58 (1H, sept, J=6 Hz), and 3.61 (1H, olefinic) besides
two ester signals at τ6.30 and 6.22 (each 6H) in the ^{1}H NMR spectrum in CDCl$_3$.
A set of peaks at τ8.81, 8.31, and 7.58 are ascribed to isopropyl group whose two
methyl groups are magnetically non-equivalent.   Treatment of XVIII with 2 equiv of
triphenylphosphine in benzene at room temperature gave dichlorobis(triphenylphosphine)-
palladium; (Ph$_3$P)$_2$PdCl$_2$, as yellow needles in 84 % yield and 1,2,3,4-tetrakis(methoxy-
carbonyl)-5-methyl-1,3-hexadiene (XIX) as yellow oily liquid in 53 % yield, which
showed resonance peaks at τ9.03 (6H, d, J=6 Hz), 7.90 (1H, sept, J=6 Hz), 6.36 (3H,
s), 6.31 (3H, s), 6.25 (3H, s),6.19 (3H, s), and 3.33 (1H, olefinic) in ^{1}H NMR in

CCl_4. The results of the ligand exchange reaction with triphenylphosphine indicates that 1,3-hexadiene (XIX) is coordinated to palladium as a bidentate ligand in the π-manner. Whereas the resonance absorption of methyl protons of isopropyl group of XIX appeared in doublet (τ9.03, J=6 Hz), those of XVIII in doublet of doublets (τ8.81 and 8.31, J=6 Hz). This non-equivalency of two methyl groups in ^{1}H NMR would be induced by the hindered rotation of isopropyl group. Therefore, it would be concluded that isopropyl group is directed to inside (*cis* to C(2)-C(3) bond) as shown in Fig. 1.

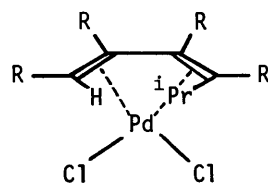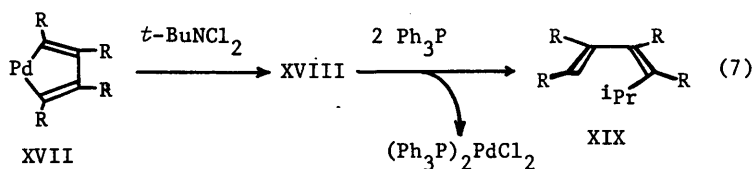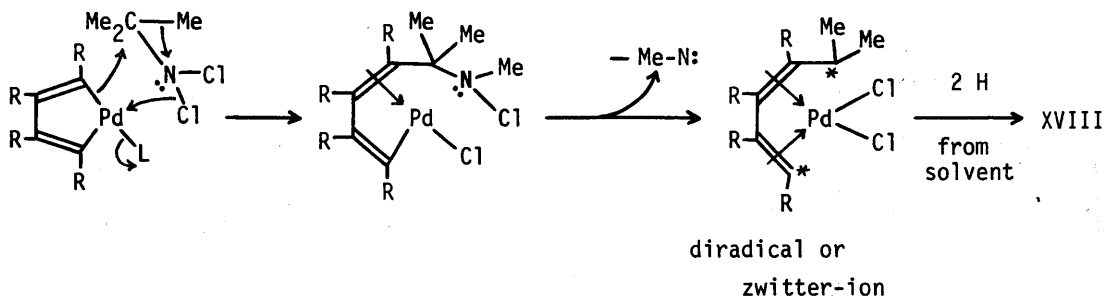And the reaction sequence is shown in Eq. 7.

Fig. 1 Structure of XVIII

The exclusive formation of XVIII (*cis*-isopropyl group to C(2)-C(3) bond) would suggest that the ring cleavage of XVII with N,N-dichloro-*t*-butylamine proceeds *via* a four-centered transition state with simultaneous methyl migration from carbon to nitrogen atom (Scheme 2).

Scheme 2

diradical or
zwitter-ion

2-2-3   Reaction of Coordinatively Unsaturated Palladiacyclopentadiene with
         N,N-Dichlorocyclohexylamine

     In order to avoid the methyl migration to nitrogen atom and the liberation of
methylnitrene, N,N-dichlorocyclohexylamine was used as a nitrene precursor.

     N,N-Dichlorocyclohexylamine (4.04 mmol) was added dropwise to the benzene
solution of 2,3,4,5-tetrakis(methoxycarbonyl)palladiacyclopentadiene (XVII) (1.01 mmol),
and reaction mixture was allowed to stand at room temperature under nitrogen for 15 hr.
Several unidentified products were isolated by the addition of ether to the reaction
mixture.   Finally, yellow powder was precipitated by the addition of methanol to the
filtrate.   Recrystallization from mixed solvent (CH_2Cl_2-CH_3OH, 1/1) yielded a
yellowish-orange crystals (XX)(mp 159.5-160.0 °C) in 17 % yield (based on used Pd).
surprisingly, XX is too stable to be decomposed by the standing for almost one year
without special care.   Infrared spectrum of XX in KBr showed an absorption at 338
cm^{-1} ascribed to terminal ν_{Pd-Cl}, but no absorption around ester region.   The analysis
of these crystals is consistent with the formula, $(c\text{-}C_6H_{11}N)_4PdCl_2$.   Found: C, 51.05;
H, 7.89; N, 9.74 %.   Calcd: C, 50.94; H, 7.84; N, 9.90 %.   Mass spectrum of XX
showed M^+, $(M^+\text{-}Cl)$, and $(M^+\text{-}2Cl)$ fragments.   The number of fragment peaks and their
relative intensity agreed well with theoretical values calculated from natural abun-
dance of isotopes of Pd and Cl (Table 3).

Table 3.

    MASS SPECTRUM OF $(c\text{-}C_6H_{11}N)_4PdCl_2$: RELATIVE INTENSITIES

$(c\text{-}C_6H_{11}N)_4PdCl_2$	m/e	562	563	564	565	566	567	568	569
	Obsd.	0.35	0.47	0.74	0.42	1.00	0.00	0.70	0.00
	Calcd.	(0.25)	(0.49)	(0.76)	(0.32)	(1.00)	(0.00)	(0.70)	(0.00)
$(c\text{-}C_6H_{11}N)_4PdCl$	m/e	527	528	529	530	531	532	533	
	Obsd.	0.26	0.58	0.90	0.00	1.00	0.00	0.45	
	Calcd.	(0.32)	(0.62)	(0.87)	(0.00)	(1.00)	(0.00)	(0.58)	
$(c\text{-}C_6H_{11}N)_4Pd$	m/e	492	493	494	495	496	497	498	
	Obsd.	0.44	0.81	1.00	0.00	0.90	0.00	0.47	
	Calcd.	(0.40)	(0.81)	(1.00)	(0.00)	(0.98)	(0.00)	(0.43)	

CCl_4. The results of the ligand exchange reaction with triphenylphosphine indicates
that 1,3-hexadiene (XIX) is coordinated to palladium as a bidentate ligand in the π-
manner. Whereas the resonance absorption of methyl protons of isopropyl group of
XIX appeared in doublet (τ9.03, J=6 Hz), those of XVIII in doublet of doublets
(τ8.81 and 8.31, J=6 Hz). This non-equivalency of two methyl groups in ^{1}H NMR
would be induced by the hindered rotation of isopropyl group. Therefore, it would
be concluded that isopropyl group is directed to inside (*cis* to C(2)-C(3) bond) as
shown in Fig. 1.
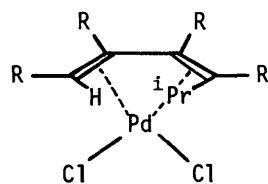
And the reaction sequence is shown in Eq. 7.
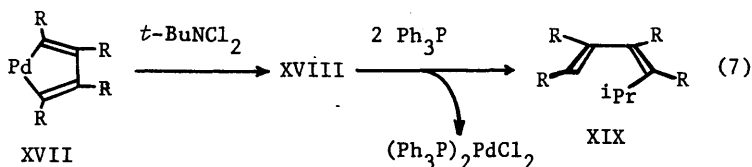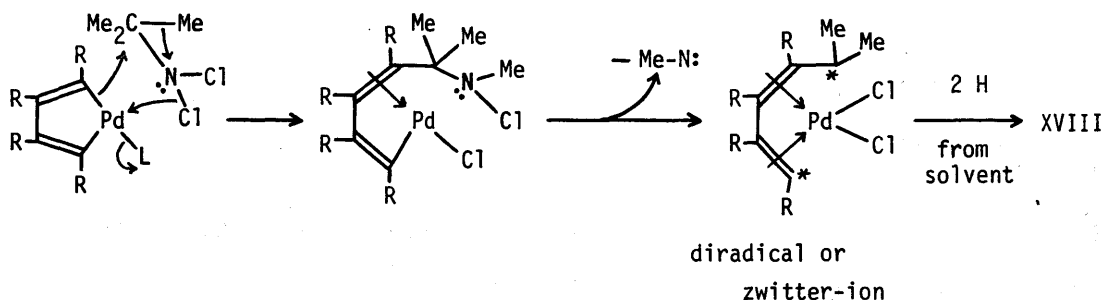

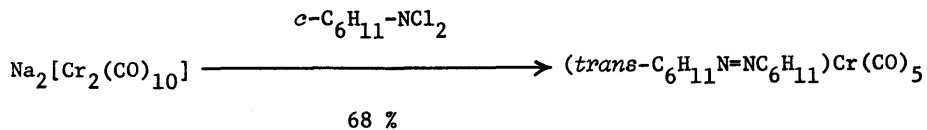Fig. 1   Structure of
         XVIII

The exclusive formation of XVIII (*cis*-isopropyl group to C(2)-C(3) bond) would
suggest that the ring cleavage of XVII with N,N-dichloro-*t*-butylamine proceeds *via*
a four-centered transition state with simultaneous methyl migration from carbon to
nitrogen atom (Scheme 2).

Scheme 2

diradical or
zwitter-ion

The X-ray diffraction showed that two types of nitrogen exist in XX. One of them positioned at N, and another oscillated between ^{1}N and ^{2}N.

Recently, Huttner et $al.$[22)] reported that azocyclohexane complex, ($trans$-$C_6H_{11}N=NC_6H_{11}$)Cr(CO)$_5$, was given in the reaction of same dichloramine with $Na_2[Cr_2(CO)_{10}]$.

$$Na_2[Cr_2(CO)_{10}] \xrightarrow[\textstyle 68\ \%]{\textstyle c\text{-}C_6H_{11}\text{-}NCl_2} (trans\text{-}C_6H_{11}N=NC_6H_{11})Cr(CO)_5$$

Comparing with their results, the structure of XX is quite unusual. Analysis of bonding mode by means of MO calculation is now in progress.

Experimental Section

1   Reactions of Iron Carbonyl Complexes with N,N-Dichloramine or -amides

   Reaction of Diiron Enneacarbonyl with N,N-*Dichloro*-t-*butylamine.*
To diiron enneacarbonyl (0.408 g, 1.12 mmol) suspended in 8 ml of dry benzene,
a dilute solution of N,N-dichloro-*t*-butylamine (0.170 g, 1.20 mmol, in 2 ml of dry
benzene) was added dropwise at 0 °C under an atmosphere of argon.   Reaction mixture
was gradually warmed up to room temperature.   Reaction proceeded with the evolution of
carbon monoxide, and yellowish brown powder was precipitated after stirring for 3 hr.
The reaction mixture was filtered,[*)] and excess dimethylamine (1 ml of 40 % aq. soln.)
was added to the filtrate.   After evaporation of reaction solvent and excess dimethyl-
amine, the reprecipitation (from benzene-methanol) of the obtained pale yellow powder
gave N,N-dimethyl-N'-*t*-butylurea (0.057 g, mp 87.0–89.0 °C) as white solid in 31 %
yield.   Mp, IR, NMR, and other properties of product are well agreed with those of the
authentic sample.

*)   The IR spectrum of filtrate showed a sharp and strong absorption band at 2240 cm^{-1}
    due to a heterocumulene skeleton.

   Reaction of Diiron Enneacarbonyl with N,N-*Dichloro*-p-*chlorobenzamide.*
Dilute benzene solution of N,N-dichloro-*p*-chlorobenzamide (0.302 g, 1.35 mmol, in 3 ml
of dry benzene) was added to diiron enneacarbonyl (4.61 g, 1.27 mmol, in 6 ml of dry
benzene) at 0 °C under an atmosphere of argon.   After the addition of chloramide,
the reaction mixture was warmed up to room temperature and stirred for 10 hr.
The reaction proceeds with the evolution of carbon monoxide, and dark brown powder
was finally precipitated.   To the reaction mixture, aqueous methanol solution of
excess ceric ammonium nitrate (1 g) was added dropwise.   Oxidation proceeded exo-
thermically with the evolution of carbon monoxide.   After the addition of water
(30 ml) to the reaction mixture, the aqueous mixture was extracted with chloroform.
From the organic phase, N,N'-bis(*p*-chlorobenzoyl)urea was obtained as white powder
(0.425 g, mp 218.0–220.0 °C) in quantitative yield.   Mp, IR, and other properties
of the product were well agreed with those of the authentic sample prepared by
hydrolysis of *p*-chlorobenzoyl isocyanate.
The reactions of diiron enneacarbonyl with other N,N-dichloramide under similar

condition yielded corresponding diaroylureas.

Reaction of Maleic Anhydride Iron Tetracarbonyl with N,N-*Dichloro*-p-*chloro-benzamide.* To a benzene solution of maleic anhydride iron tetracarbonyl (0.160 g, 0.598 mmol, in 20 ml of dry benzene) N,N-dichloro-p-chlorobenzamide (0.137 g, 0.612 mmol, in 3 ml of dry benzene) was added dropwise at room temperature under an atmosphere of argon, and stirred at room temperature. The reaction mixture changed from pale orange to brown. After stirring for about 50 hr, the evolution of carbon monoxide was reached *ca.* 1.8 equivalent, and brown solid was precipitated, which was purified by column chromatography on silica gel with acetone as solvent to give X as white powder in 80 % yield. Decomp. 124.0-126.0 °C. Found: C, 43.80; H, 2.69; N, 5.35 %. Calcd for $C_{20}H_{10}N_2O_7Cl_4Fe+2H_2O$: C, 43.60; H, 2.53; N, 5.07 %. IR (in KBr) 2050, 2020, 1820, 1746, and 1655 cm^{-1}. ^1H NMR (in $CDCl_3$) τ6.07 (2H, s), 2.50 (8H, aromatic, AA'BB'), and 8.31 (4H, s, exchangeable by D_2O).

Upon the evaporation of *n*-hexane from the filtrate, brown oily liquid was obtained, which was purified by column chromatography on silica gel with chloroform as eluting solvent to give N-phenyl-p-chlorobenzamide (XI) as colorless needles in 14 % yield. Mp 197.0-198.0 °C. N-phenyl-p-chlorobenzamide was identified from mp, IR, and mass spectrum by the comparison with those of the authentic sample.

When *n*-hexane was used as reaction solvent, X was obtained in 95 % yield.

2   Reactions of Palladium Complexes with N,N-Dichloramine and -amides

Reaction of Tetrakis(triphenylphosphine)palladium with N,N-*Dichloro*-p-*chloro-benzamide.* A benzene solution of N,N-dichloro-p-chlorobenzamide (0.036 g, 0.161 mmol, in 1 ml of dry benzene) was added dropwise to tetrakis(triphenylphosphine)-palladium (0.180 g, 0.154 mmol, in 2 ml of dry benzene) at room temperature under argon. After the addition of N,N-dichloro-p-chlorobenzamide, reaction mixture turned to greenish yellow solution, and then greenish yellow powder was precipitated. Reaction was completed by 2 hr stirring. To the reaction mixture ethyl ether (*ca.* 5 ml) was added, and precipitates were filtered. This greenish yellow powder was identified as dichlorobis(triphenylphosphine)palladium by the comparison of mp, IR, and other properties with those of the authentic sample. The yield of $(Ph_3P)_2PdCl_2$ is 89 %. *p*-Chlorobenzoylaminotriphenylphosphonium chloride was precipitated from

the pale yellow filtrate as colorless prisms after standing for a day. Mp 70.0-72.0 °C. Found: C, 66.60; H, 4.88; N, 2.61 %. Calcd for $C_{25}H_{20}NOCl_2P$: C, 66.39; H, 4.46; N, 3.10 %. IR (in KBr) 3450 (ν_{NH}), 3385, 1675, and 1588 cm^{-1}. ^1H NMR (in CDCl$_3$) NH overlapped phenyl protons.

Finally triphenylphosphinoxide was precipitated from the mother liquor as color-less prisms in 57 % yield, which was identified by the comparison with the authentic sample.

Reaction of Tetrakis(triphenylphosphine)palladium with N,N-*Dichlorobenzene-sulfonamide.* N,N-Dichlorobenzenesulfonamide (0.080 g, 0.354 mmol, in 3 ml of dry benzene) was added to the benzene solution of tetrakis(triphenylphosphine)-palladium (0.268 g, 0.230 mmol, in 6 ml of dry benzene) at room temperature under an atmosphere of nitrogen, and reaction mixture was stirred for 10 hr. Greenish yellow powder precipitated from the reaction mixture was separated by filtration. Recrystallization from the mixed solvent of dichloromethane and ethyl ether (1/1) gave dichlorobis(triphenylphosphine)palladium in quantitative yield. Pale yellow prisms (Mp 157.0-158.0 °C) were precipitated from the filtrate kept in a refrigerator, which were identified as N-benzenesulfonyltriphenylphosphinimine (20 % yield) by the comparison with the authentic sample.

Reaction of Bipyridinepalladiacyclopentadiene with N,N-*Dichloro-t-butylamine.* To bipyridinepalladiacyclopentadiene (0.698 g, 1.28 mmol) suspended in 5 ml of benzene N,N-dichloro-t-butylamine (0.182 g, 1.23 mmol) was added dropwise at 0 °C under an atmosphere of nitrogen. After stirring for 10 hr, pale yellow powder was precipitated. Filtration followed by recrystallization from the mixed solvent of acetone and ethyl ether (6/5) gave yellow crystals in a 64 % yield, which was identified σ-4-chloro-1, 2,3,4-tetrakis(methoxycarbonyl)buta-1,3-dienylpalladium (XIII) from the elemental anal-ysis and the spectroscopic data cited below. Mp 168.0-170.0 °C. Found: C, 43.29; H, 3.23; N, 4.55; Cl, 11.37 %. Calcd for $C_{22}H_{20}N_2O_8Cl_2Pd$: C, 42.73; H, 3.27; N, 4.53; Cl, 11.48 %. IR (in KBr) 1722, and 323 (ν_{Pd-Cl}) cm^{-1}. ^1H NMR (in CD$_3$COCD$_3$) τ6.57 (3H, s), 6.36 (6H, s), and 6.30 (3H, s).

Reaction of Bipyridinepalladiacyclopentadiene with N,N-*Dichloro*-p-*toluamide.*
N,N-Dichloro-*p*-toluamide (0.119 g, 0.583 mmol, in 5 ml of dry benzene) was added
dropwise to bipyridinepalladiacylopentadiene (0.213 g, 0.390 mmol) suspended in 20 ml
of dry benzene at 0 °C under nitrogen.   Immediately, reaction mixture turned yellowish
orange solution, and pale yellow powder was precipitated in several minutes.
Recrystallization from the mixed solvent of dichloromethane and *n*-hexane (1/1) gave
σ-4-chloro-1,2,3,4-tetrakis(methoxycarbonyl)buta-1,3-dienylpalladium (XIII) as yellow
crystals in 73 % yield.

Reaction of Bipyridinepalladiacyclopentadiene with N,N-*Dichlorobenzenesulfonamide.*
Equimolar amounts of N,N-dichlorobenzenesulfonamide was added to a stirred suspension
of bipyridinepalladiacyclopentadiene in benzene at room temperature.   From the
solution a pale yellow solid slowly precipitated.   This was filtered off and crys-
tallized from dichloromethane- ethyl ether to give yellow prisms of XIV in 84 % yield.
Mp 185.0-186.0 °C.   Found: C, 40.61; H, 3.17; N, 4.96 %.   Calcd for $C_{28}H_{25}N_3O_{10}Cl_2Pd$
+CH_2Cl_2 (solvent of crystallization): C, 40.61; H, 3.17; N, 4.90 %.   IR (in KBr)
1722 cm^{-1}. ^1H NMR (in $CDCl_3$) τ6.92 (3H, s), 6.29 (3H, s), 6.20 (3H, s), and 6.16
(3H, s).

Reaction of Bipyridinepalladiacyclopentadiene with N,N-*Dichloro*-p-*chloro-*
benzamide.   N,N-Dichloro-*p*-chlorobenzamide (0.073 g, 0.326 mmol) was added
to a stirred suspension of bipyridinepalladiacyclopentadiene (0.166 g, 0.304 mmol)
in 20 ml of dry benzene at room temperature under an atmosphere of argon.   Reaction
proceeded immediately and a pale yellow solid was precipitated after 3 min.
This was filtered off and crystallized from dichloromethane-*n*-hexane to give yellow
plates of XV in 57 % yield.   Mp 115.5-117.5 °C.   Found: C, 37.43; H, 2.49; N, 4.26;
Cl, 29.66 %.   Calcd for $C_{33}H_{24}N_3O_{11}Cl_9Pd$: C, 37.22; H, 2.27; N, 3.95; Cl, 29.96 %.
IR (in KBr) 1737, 1720, and 1689 cm^{-1}. ^1H NMR (in $CDCl_3$ at 90 °C) τ6.39 (3H, s),
6.34 (3H, s), 6.30 (3H, s), 6.18 (3H, s), and 1.90-2.70 (12H, m).   Mass (I.P. 70 eV)
m/e 223 (5) $[Cl-C_6H_4CONCl_2]^{\cdot+}$, 155 (33) $[^{37}Cl-C_6H_4-CON$ or $^{37}Cl-C_6H_4-NCO]^{\cdot+}$, 153 (100)
$[^{35}Cl-C_6H_4-CON$ or $^{35}Cl-C_6H_4-NCO]^{\cdot+}$, 127 (15) $[^{37}Cl-C_6H_4-N:]^{\cdot+}$, and 125 (45)
$[^{35}Cl-C_6H_4-N:]^{\cdot+}$.

Reaction of Palladiacyclopentadiene with N,N-*Dichloro*-t-*butylamine.*
To a suspension of palladiacyclopentadiene (0.155 g, 0.398 mmol) in 5 ml of dry
benzene was added N,N-dichloro-*t*-butylamine (0.120 g, 0.847 mmol, in 1 ml of dry

benzene) with stirring at room temperature. After stirring at room temperature
for 1 hr the solid was dissolved to give a clear orange solution, from which a brown
solid was slowly precipitated. This was removed by a filtration, and the filtrate
was evaporated *in vacuo*. To the remaining yellowish orange oily liquid was added
acetone and ethyl ether (3/2). From this solution brown solid was precipitated
after standing for 2 days, which was again removed by filtration. From the clear
yellow filtrate, solvent was evaporated under reduced pressure, and then acetone and
n-hexane was added to the remaining yellow oil. After standing for 1 day at 0 °C,
yellow solid was precipitated. Recrystallization from benzene and ethyl ether gave
dichloro[1,2,3,4-tetrakis(methoxycarbonyl)-5-methyl-1,3-hexadiene]palladium (XVIII)
as yellow prisms in 57 % yield. Decomp. 142.0–143.0 °C. Found: C, 36.88; H, 4.29;
Cl, 14.57 %. Calcd for $C_{15}H_{20}O_8Cl_2Pd$: C, 35.63; H, 3.99; Cl, 14.02 %. IR (in KBr)
1753, 1737, and 1729 cm^{-1}. ^{1}H NMR (in CDCl$_3$) τ8.81(3H, d, J=6 Hz), 8.31 (3H, d,
J=6 Hz), 7.58 (1H, sept, J=6 Hz), 6.30 (6H), 6.22 (6H), and 3.61 (1H, olefinic).

Reaction of XVIII with Triphenylphosphine.   Triphenylphosphine (0.044 g,
0.168 mmol) was added to a stirred solution of XVIII (0.041 g, 0.081 mmol) in 5 ml of
dichloromethane at room temperature under nitrogen.   From the solution a pale yellow
solid was immediately precipitated.   After stirring at room temperature for 3 hr,
this was filtered off and crystallized from the mixed solvent of benzene and ethyl
ether to give yellow needles of dichlorobis(triphenylphosphine)palladium in 84 % yield,
which were identified by the comparison with the authentic sample.   From the filtrate
the solvent removed by evaporation to give, after chromatography on silica gel in
benzene, 1,2,3,4-tetrakis(methoxycarbonyl)-5-methyl-1,3-hexadiene (XIX) as a viscous
yellow oil (0.014 g) in 53 % yield. ^{1}H NMR (in CCl$_4$) τ9.03 (6H, d, J=6 Hz), 7.90
(1H, sept, J=6 Hz), 6.36 (3H, s), 6.31 (3H, s), 6.25 (3H, s), 6.19 (3H, s), and 3.33
(1H, olefinic).

Reaction of Palladiacyclopentadiene with N,N-*Dichlorocyclohexylamine.*
To a stirred suspension of palladiacyclopentadiene (0.395 g, 1.01 mmol) in 10 ml of
dry benzene was added N,N-dichlorocyclohexylamine (0.678 g, 4.04 mmol, in 2 ml of
dry benzene) at room temperature under an atmosphere of argon.   After stirring at
room temperature for 15 hr, 5 ml of ethyl ether was added to the clear orange solution.
From the cooled (0 °C) reaction mixture, yellow crystalline product (decomp. 146.0 °C,
unidentified) was removed by filtration.   Ethyl ether and methanol (1/1) was added
to the filtrate partially evaporated *in vacuo*.   After standing for 1 day, yellow

solid was precipitated.   Recrystallization from the mixed solvent of dichloromethane and methanol gave XX as yellowish orange crystals in 17 % yield.   Decomp. 159.5–160.0 °C.   Found: C, 51.05; H, 7.89; N, 9.74 %.   Calcd for $C_{24}H_{44}N_4Cl_2Pd$: C, 50.94; H, 7.84; N, 9.90 %.   IR (in KBr) 2930, 2850, and 338(ν_{Pd-Cl}) cm^{-1}.

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CHAPTER III

A SELECTIVE PALLADIUM-CATALYZED CYCLOTRIMERIZATION

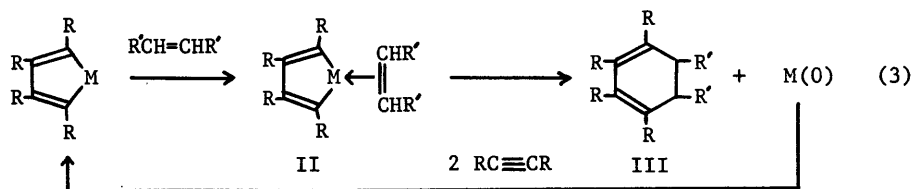OF DIMETHYL ACETYLENEDICARBOXYLATE WITH OLEFINS

The catalysis of the cyclotrimerization of acetylenes by transition metal complexes[1] has been extensively studied but few examples of the cyclotrimerization of acetylenes with olefins as in Eq. 1 has been noted.[2]

$$2 \ RC{\equiv}CR \ + \ R_2'C{=}CR_2' \longrightarrow \qquad (1)$$
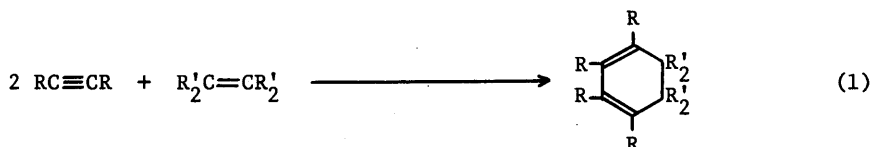
The cyclotrimerization of alkynes was suggested to proceed through the intermediary of metallocyclopentadiene, in fact, metallocyclopentadiene have been shown to react with acetylenes to give substituted benzene as in Eq. 2.[3]

$$[A] \ + \ RC{\equiv}CR \longrightarrow \qquad + \ M \qquad (2)$$
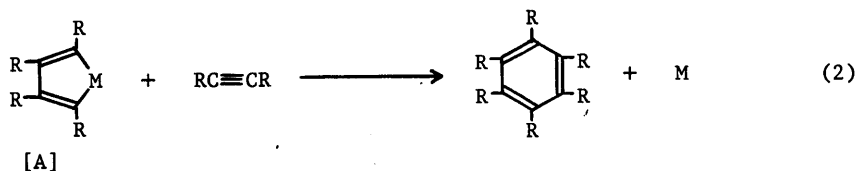
In the presence of an olefin it is expected to intercept [A] with a Diels-Alder reaction as in Eq. 3

$$\xrightarrow{\ R'CH=CHR'\ } \quad \text{II} \quad \xrightarrow{\ 2\ RC{\equiv}CR\ } \quad \text{III} \ + \ M(0) \qquad (3)$$

In this chapter, the cyclotrimerization of dimethy acetylenedicarboxylate (DMAD) and olefin catalyzed by tetrakis(methoxycarbonyl)palladiacyclopentadiene (I) is described.

The cycloaddition of DMAD (420 mg, 3.0 mmol) with norbornadiene (135 mg, 1.5 mmol) was achieved with I (39 mg, 0.1 mmol) in benzene (3 ml) at 45 °C for 4 days.   The isolated product was 1,2,3,4-tetrakis(methoxycarbonyl)benzene (IV) (35 % isolated yield) [Mp 127.0-128.0 °C.   Found: C, 53.77; H, 4.51.   Calcd: C, 54.20; H, 4.55 %.   NMR (in CDCl$_3$) τ6.19 and 6.18 (each 6H, s, COOCH$_3$),

τ2.12 (2H, s, aromatic CH)]. In this reaction, the formation of hexamethyl mellitate, the cyclic trimer of DMAD, was depressed completely. Moreover, dimethyl tetracyclo[3,2,1,1^{3,8},0^{2,4}]nonene-6-dicarboxylate which is the homo Diels–Alder adduct between DMAD and norbornadiene[4] was not obtained. The formation of IV is explained in terms of a cycloreversion[5] of the generated cycloadduct (V) according to the process shown in Scheme 1, and this mechanism is also supported by the presence of dicyclopentadiene and bis(methoxycarbonyl)norbornadiene in the reaction mixture.
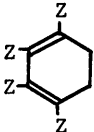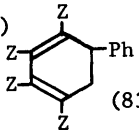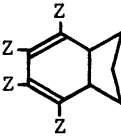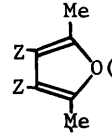
Scheme 1.

(Z=COOCH$_3$)
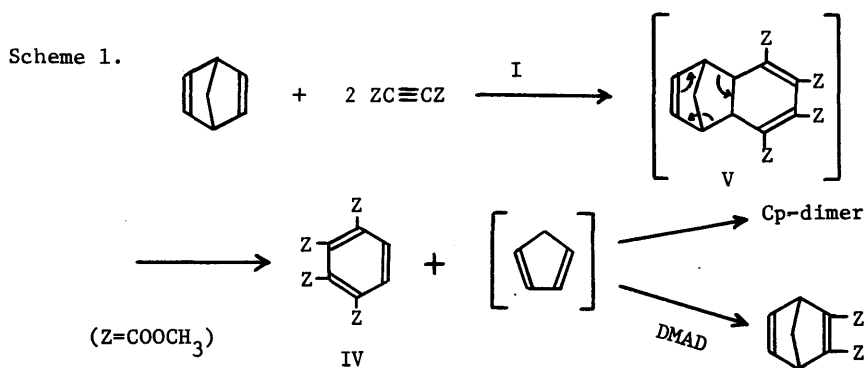
In order to avoid the cycloreversion process, the catalytic reaction between two DMADs and norbornene was undertaken. When a benzene solution of norbornene (3.30 mmol), DMAD (3.37 mmol), and I (0.05 mmol) was allowed to react at 45 °C for 20 hr. The expected cycloadduct (VI) was isolated in a 94 % yield based on DMAD. The cycloadduct (VI) [Mp 67.0–68.0 °C. Found: C, 60.44; H, 5.83 %. Calcd: C, 60.31; H, 5.86 %] is concluded to be the exo-adduct, because the chemical shift difference between Ha (τ8.61) and Hb (τ8.21) was sufficiently large and the coupling constant between Hd and He (J$_{de}$=0.8 Hz) was reasonably small. The formation of hexamethyl mellitate was also prohibited in the present case.

(Z=COOCH$_3$)
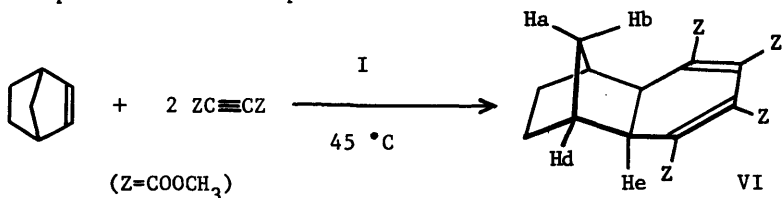
This catalytic process is also efficient for less strained olefins as, styrene, ethyl vinyl ether, or even ethylene. To cite one example, 1,2,3,4-tetrakis-

(methoxycarbonyl)-3-phenylcyclohexa-1,4-diene [Mp 105.0-107.0 °C.   Found: C, 61.77; H, 5.26 %.   Calcd for $C_{20}H_{20}O_8$: C, 61.84; H, 5.19 %.] was prepared in 83 % yield by the reaction of DMAD (4.23 mmol) with styrene (1.99 mmol), catalyzed by I (0.043 mmol) in benzene (3 ml) at 45 °C for 138 hr.   The results of cyclotrimerization are summarized in Table 1.

Table 1.

Olefin	Reaction Conditions[a]					Products (yield;%)
	Olefin (mmol)	DMAD (mmol)	Cat. (mmol)	Temp. (°C)	Time (hr)	
C_2H_4	2 atm[b]	3.15	0.044	50	150	(96) (TMCB)
$C_6H_5-CH=CH_2$	1.99	4.23	0.043	45	139	(83)
Norbornene	3.30	3.37	0.10	45	40	(94)
Norbornadiene	1.50	3.00	0.10	45	96	TMCB (35) + Cp-dimer
Et-O-CH=CH$_2$	1.00	4.67	0.037	45	45	TMCB (64) + EtOH
2,5-Dimethylfuran	1.36	3.11	0.031	45	48	TMCB (69) + (86)

a) in benzene (3∼4 ml).   b) in autoclave.

In the reaction with furan or 2,5-dimethylfuran, 1,2,3,4-tetrakis(methoxycarbonyl)-benzene is concluded to be formed *via* 7-oxa-norbornadiene which is Diels-Alder adduct of furan and DMAD, because 3,4-bis(methoxycarbonyl)furan was isolated as a by-product (Eq. 4).
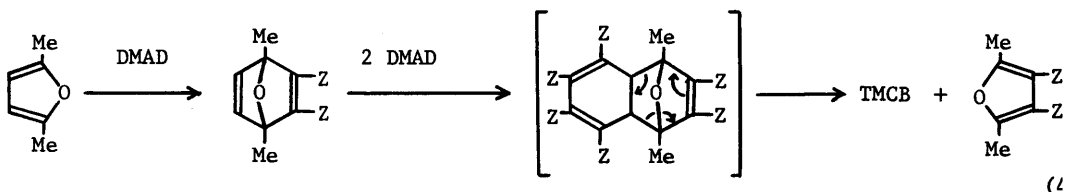
To prepare a model complex of the key intermediate (II) for the above-mentioned catalytic process, the reactions of (I) with cyclic diolefins were carried out. When norbornadiene (0.04 ml) was added to an acetone (7 ml) suspension of I (96 mg, 2.46 mmol) at room temperature, the reaction mixture became a greenish brown homogeneous solution which was concentrated to 0.5 ml under reduced pressure. Addition of ether (1 ml) and two drops of norbornadiene caused the precipitation of VII in 51 % yield as yellowish brown prisms after standing for two days at 0 °C [Mp 130.0-132.0 °C (dec.). Found: C, 47.32; H, 4.42 %. Calcd: C, 47.27; H, 4.18 %. ^{1}H NMR (in $CDCl_3$) $\tau7.97$ (2H, t, J=0.8 Hz, bridge CH_2), $\tau6.35$ and 6.33 (each 6H, s, OCH_3), $\tau5.93$ (2H, m, bridgehead CH) and $\tau3.51$ (2H, t, J=2 Hz, olefinic)]. When VII was treated with two molar amounts of DMAD in $CDCl_3$ at 50 °C for 2hr, IV was generated with the quantitative recovery of I. VII is an actual intermediate of the cyclotrimerization followed by cycloreversion process; I→VII→V→IV.

VII
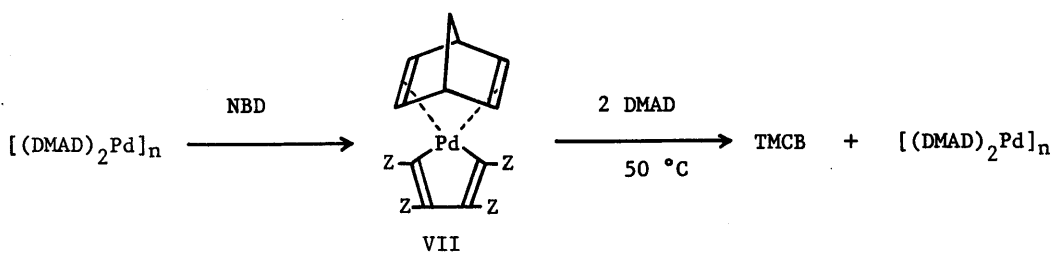
Experimental Section

The Cyclotrimerization of DMAD and Norbornadiene Catalyzed by [(DMAD)$_2$Pd]$_n$.
Benzene (3 ml) solution of norbornene (0.311 g, 3.30 mmol) and dimethyl acetylene-
dicarboxylate (0.478 g, 3.37 mmol) were warmed at 45 °C in a sealed tube filled with
argon in the presence of [(DMAD)$_2$Pd]$_n$ (0.020 g, 0.05 mmol) for 20 hr.
Reaction mixture turned to reddish brown solution.   The tube was cooled and opened,
and the solution was concentrated by evaporation *in vacuo* to give viscous oil.
Purification by a column chromatography on silica gel in benzene gave pale yellow
solid of VI with low melting point.   Mp 66.5-68.0 °C.   Found: C, 60.44; H, 5.83 %.
Calcd for C$_{19}$H$_{22}$O$_8$: C, 60.44; H, 5.86 %.   IR(neat) 2960, 1733, and 1720 cm^{-1}.
^{1}H NMR (in CDCl$_3$) τ8.61 (1H, m), 8.46 (4H, m), 8.25 (1H, m), 7.66 (2H, doublet of
triplets, J=0.75 and 1.5 Hz), 7.08 (2H, d, J=0.75 Hz), 6.32 (6H, s), and 6.29 (6H, s).

The catalytic cyclotrimerization of DMAD with other olefins were carried out
similarly.   Results of cyclotrimerization are summarized in Table 1.

The Cyclotrimerization of DMAD and Ethylene Catalyzed by [(DMAD)$_2$Pd]$_n$.
A solution of DMAD (0.291 g, 2.05 mmol) and [(DMAD)$_2$Pd]$_n$ (0.011 g, 0.028 mmol) in
40 ml of dry benzene was heated in a glass autoclave for 15 hr at 45 °C under 2 atm
of ethylene.   The ethylene was vented, and the solvent was removed under reduced
pressure yielding a brown oil , which was purified by column chromatography on silica
gel (11 g) in chloroform to give yellow crystals (0.308g, 96 %).   Recrystallization
from CCl$_4$-*n*-hexane gave 1,2,3,4-tetrakis(methoxycarbonyl)cyclohexa-1,3-diene as
colorless needles in 62 % yield.   Mp 94.5-95.0 °C.   Found: C, 53.58; H, 5.42 %.
Calcd: C, 53.86; H, 5.16 %.   IR (in KBr) 1729 and 1720 cm^{-1}. ^{1}H NMR (in CCl$_4$)
τ7.34 (4H, s) and 6.25 (12H, s).

Reaction of Palladiacyclopentadiene with Norbornadiene.   Palladiacyclo-
pentadiene (0.0356 g, 0.091 mmol) was suspended in 3 ml of acetone.   Norbornadiene
was added to the above suspension with stirring at room temperature until whole solid
disappear (nearly 0.060 g, 0.65 mmol was required) and the solution turned to
greenish brown.   Stirring was continued for 4 hr, and the solution was filtrated
in order to remove metallic palladium (very small amount).   The filtrate was care-
fully concentrated by rotary evaporator to result dark orange to brown solution.
After 1-2 drops of norbornadiene was added, twice volume of ethyl ether was carefully

added with swirling.   Crystallization started at the wall of the flask to yellow
prisms and became complete by setting the mixture into refrigerator.
Decomp. 130.0-132.0 °C.   Found: C, 47.32; H, 4.42 %.   Calcd for $C_{19}H_{20}O_8Pd$:
C, 47.27; H, 4.18 %.   IR (in KBr) 1713 and 1692 cm^{-1}. ^1H NMR (in $CDCl_3$) $\tau 7.97$
(2H, t, J=0.8 Hz, bridge CH_2), 6.35 (6H, s), 6.33 (6H, s), 5.93 (2H, m, bridgehead CH),
and 3.51 (2H, t, J=2 Hz, olefinic).

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LIST OF PUBLICATIONS

[1] Reactions of Group IV Organometallic Compounds. XXX.
Stepwise Addition of Isocyanates and Isothiocyanates with
N-Trimethylstannyl(diphenylmethylene)amine.
   H. Suzuki, K. Itoh, I. Matsuda, and Y. Ishii,
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[2] Reaction of Group IV Organometallic Compounds. XXXI.
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[3] Semi-empirical SCF-MO Studies on Cyclization of Silylimine
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[4] Reaction of Group IV Organometallic Compounds. XXXII
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Metal-assisted nitrene Generation.
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dicarboxylate with Olefins.
   H. Suzuki, K. Itoh, M. Ohashi, K. Hirai, and Y. Ishii, to be published.